YEAR 2

THE FATE AND TRANSPORT OF INORGANIC CONTAMINANTS IN NEW JERSEY SOILS

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Final Report

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ABSTRACT

A major problem in the remediation of contaminated sites is frequently the lack of appropriate standards for chemicals in soils. While a few standards exist for organic and inorganic materials for such exposure routes as direct ingestion of soil, there are no standards applicable to the prediction of the potential for groundwater contamination by inorganic materials. Lack of standards can result in subjective judgments regarding the extent of remediation needed. 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. Soil sorption behavior is the criterion upon which to establish a standard based on a maximum permissible concentration in groundwater. The maximum level of metal in soil for which the equilibrium soluble metal does not violate the drinking water standard has been computed from the measured partition coefficient for Cd(II) as a function of pH and metal concentration for another ten New Jersey soils. Clean-up of contaminated sites require a target such as that provided by standards based on this research.

The work accomplished in the second year includes soil characterization experiments, adsorption/desorption experiments, cycling experiments, and hexavalent chromium adsorption experiments.

INTRODUCTION

The aqueous concentration of an inorganic contaminant in contact with a soil can be predicted from appropriate thermodynamic measurements. At high concentrations, cationic metals will form insoluble hydroxide, carbonate, or sulfide precipitates (Stumm and Morgan 1981; Evans 1989; Sposito 1989). Their solubility can be easily calculated even in situations where the solution may contain complexing agents which result in solubility enhancement (Allen and Unger 1981).

Usually, trace elements, such as those studied in this project, are present at levels below those at which precipitation occurs. Their presence in the solid phase is a 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 Langmuir and Freundlich, 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

$$\Gamma = \frac{x}{m} = \frac{bK[Me]}{1 + K[Me]} \qquad (1)$$

where

$[Me]$ = the equilibrium concentration of metal

b = monolayer coverage

K = constant.

At low concentration of metal the equation simplifies to a linear adsorption isotherm

$$\Gamma = \frac{x}{m} = K_d[Me] \qquad (2)$$

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 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 MINTEQ (Brown and Allison 1987).

This pH dependence of adsorption of metals onto soils has been frequently reported (Kuo and Baker 1980; Harter 1983; Elliott et al. 1986). Christensen (1989) found that the K_d values for 63 samples of Danish agricultural soils correlated very well ($r^2 = 0.72$) with soil pH. For anions, such as chromate, a reverse trend, in which adsorption is maximum at low pH and decrease with increasing pH is found (Zachara et al. 1989).

The binding of metals by soluble complexing agents is similarly highly dependent on pH. Knowledge of the stability constant for metal reacting 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 solid phase reactions. It is also necessary that equilibrium constants of the reaction sites on the solid phase with protons be available. In the absence of such information, it would be necessary to measure the extent of adsorption at each pH of interest.

The high degree of adsorption dependency on pH results from the surface chemistry of soil materials. Soils have pH-dependent, or variable, charge associated with the reaction of protons with oxide and hydroxide minerals and with certain functional groups of humic substances (Evans 1989; Sposito 1984). A common surface group which reacts with protons is hydroxide. A surface hydroxide, $\equiv S\text{-OH}^0$, can undergo two protolysis reactions:

3

$$\equiv S\text{-}OH_2^+ \Leftrightarrow \equiv S\text{-}OH^0 + H^+ \qquad (3)$$

$$\equiv S\text{-}OH^0 \Leftrightarrow \equiv S\text{-}O^- + H^+ \qquad (4)$$

The corresponding conditional stability constants are

$$K_{cond,a1} = \frac{\left[\equiv S\text{-}OH^0\right]\left\{H^+\right\}}{\left[\equiv S\text{-}OH_2^+\right]} \qquad (5)$$

$$K_{cond,a2} = \frac{\left[\equiv S\text{-}O^-\right]\left\{H^+\right\}}{\left[\equiv S\text{-}OH^0\right]} \qquad (6)$$

where the brackets, [ ], indicate surface concentration and the braces, { }, indicate the buck phase concentration of the enclosed chemical species. Because adsorption is a surface phenomena, concentrations of bound metals or of surface sites are expressed on an area, rather than mass, basis to enable one to relate different materials. The surface area is most commonly determined by determining the volume of nitrogen which can be adsorbed. The BET equation enable the calculation of the area for a complete monolayer surface sorption (Hiemenz 1986).

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 necessary 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

$$K_{cond} = K_{int}\left[-\Psi_0 F / RT\right] \qquad (7)$$

where

ψ_0 = the electrical potential at the surface

F = the Faraday

R = the gas constant

4

T = the absolute temperature.

The surface potential can be calculated from the surface charge, s_0 (Sposito 1984; Hiemenz 1986; Schindler and Stumm 1987; Westall 1987; Singh and Uehara 1986):

$$\sigma_0 = k\psi_0 \qquad (8)$$

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 7 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). Experimental data fit the simpler model as well as the fit the more sophisticated models (Westall and Hohl 1980; Morel 1981).

It is now easy to understand the reason that metal sorption is so 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+}

$$\equiv S\text{-}OH + Me^{2+} \Leftrightarrow \equiv S\text{-}OMe^+ + H^+ \qquad (9)$$
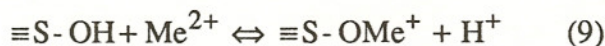
for which the conditional stability constant is

$$K_{cond} = \frac{\left[\equiv S\text{-}OMe^+\right]\left\{H^+\right\}}{\left[\equiv S\text{-}OH\right]\left\{Me^{2+}\right\}} \qquad (10)$$

This conditional constant is related to an intrinsic constant in a similar fashion to that in equation 7. An analogous reaction to equation 10 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, $MeOH^+$, to $\equiv S\text{-}O^-$ to give $\equiv S\text{-}OMeOH$ 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 that which there is direct experimentally measured data, it is essential to have the acid base equilibrium constants of equations 5 and 6.

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

$$\equiv S\text{-}OH + L^- \Leftrightarrow \equiv S\text{-}L + OH^- \tag{11}$$
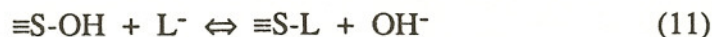
Again, the pH dependency of the reaction is predicted and accounted for by the conditional constants

$$K_{cond} = \frac{[\equiv S\text{-}L]\{OH^-\}}{[\equiv S\text{-}OH]\{L^-\}} \tag{12}$$

which can be converted to an intrinsic constant by equation 7.

While the above approach will adequately describe the binding of cations and anions by a soil, additional efforts have been undertaken in this and other laboratories to further describe adsorption by heterogeneous materials. These approaches are ultimately aimed at the ability to predict the adsorption properties from independent chemical measurements of the soil (Jenne et al. 1986). Such approaches aim at the *a priori* prediction of sorption from determination of the concentrations of chemically active surface components such as organic matter and reactive iron and manganese oxide. These approaches are not inconsistent with those described above. In general, they only require a different treatment of the data.

Within the past half-dozen years there have been significant advances in the description of a related problem, the binding of protons and metals by fulvic acids. Fulvic acids are important materials in affecting the transport and toxicity of metals in natural water (Saar and Weber 1982). These materials 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).

Another 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 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.

In addition to the the important topic of how best to describe the binding of a metal to a soil which has been discussed above, there is yet another important topic to discuss. All of the approaches commonly applied to the measurement of proton or metal binding involve either titrations or batch equilibration. In either case the equilibration is accomplished in a slurry. In the field, the soil column is stationary. The laboratory-derived constants must be the same as those applicable to the field situation for the results to be predictive of sorption/desorption behavior. Research is presently underway in this laboratory to relate the desorption of metals from soil columns to the sorptio-basebased partition coefficients.

MATERIAL AND METHODS

I. Soil Pretreatment:

The new ten new soil samples collected by the New Jersey Department of Environmental Control and Energy for this project extend the range of major soil types present in New Jersey available for use in this project. This permits the results to be easily applied to a great range of soils.

The new 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 1) so that results can 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.

II. Soil Sample Characterization Analysis:

1. Particle Size Distribution Sedimentation - Hydrometer (Sims and Heckendorn 1991a):

A. Procedure:

a) Take 50 grams of each soil with particle size less than 2 mm into a 600 mL dispersing cup. Determine the oven dry weight of the soil, on a separate subsample, by drying at least 10 g of soil for 24 hours at 105°C. Use the corrected (oven dry) weight in the calculations shown in next page.

b) Add 100 mL of 5% sodium hexametaphosphate and 400 mL double deionized water to the suspension. Transfer the suspension to the sedimentation cylinder and insert plunger and mix contents thoroughly.

c) About 15 seconds after mixing the suspension, lower the hydrometer into the suspension. After 40 seconds, read the scale at the top of the meniscus. Record the hydrometer value.

d) Record temperature of sample and blank at 40 seconds.

e) At 2 hours after suspending the soil in the cylinder, lower the hydrometer into the sedimentation cylinder and record the hydrometer value, then record the temperature of sample and blank at 2 hours.

B. Calculations:

Corrected Hydrometer Reading = (Hydrometer Reading - Blank) + (correction value)

Where: Correction value = 0.36 (Measured Temperature - 20°C)

Particle Size:

$$\% \text{ Sand} = 100 - \left[\frac{(\text{Corrected Hydrometer Reading at 40 Seconds})}{(\text{Corrected Weight of Soil})} \times 100 \right]$$

$$\% \text{ Clay} = \left[\frac{(\text{Corrected Hydrometer Reading at 2 Hours})}{(\text{Corrected Weight of Soil})} \times 100 \right]$$

$$\% \text{ Silt} = 100 - (\% \text{ Sand} + \% \text{ Clay})$$

Where:

$$\text{Corrected Weight of Soil} = \frac{(\text{Oven dry weight of subsample} \times 50g)}{(\text{Air} - \text{dried weight of subsample})}$$

C. Results

The percentage of sand, silt and clay for all soil sample studied is shown in Table 2.

2. Soil pH (Storer 1991)

A. Significance and Use:

This measurement determines the degree of acidity or alkalinity in soil materials suspended in water and 0.01 M calcium chloride solution. Measurements in both liquids are necessary to fully define the soil's pH.

9

B. Reagents:

    a) Purity of Water - Water should be distilled, deionized water, but not necessarily free of carbon dioxide.

    b) Calcium chloride stock solution (1.0 M) - Dissolve 14.7 g of $CaCl_2$-$2H_2O$ in water in a 100 mL volumetric flask. Dilute to volume with water.

    c) Calcium chloride stock solution (0.01 M) - Dilute 10.0 mL of stock 1.0 M $CaCl_2$ solution to 1 L with water.

C. Procedure:

    Both methods begin with an air dried soil that has been sieved through a 2 mm sieve to remove the coarse soil fraction. For both methods, weigh out approximately 10 g of soil and place the soil into 20 mL glass vial and add approximately 10 mL of distilled water and 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 2 buffer solutions, pH 4 and pH 7. Both pH-value buffer solutions are rechecked after each 5 measurements. If the measured value is 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.

D. Results:

    The soil pH value for all soil sample studied is shown in Table 2.

3. Soil Organic Matter (Walkley-Black Wet Combustion Method) (Sims and Heckendorn, 1991b)

A. Procedure:

    a) Weigh 1.50 ± 0.01 g of soil sample into a 250 mL Erlenmeyer flask and add 25 mL of 0.4 N $K_2Cr_2O_7$ to the soil. Then add 20 mL of concentrated H_2SO_4.

    b) Swirl gentle for one minute to thoroughly mix all reagents with soil.

    c) Prepare a blank and a reference soil sample for the standard calibration, and do the same procedures as a and b.

d) Using a graduated cylinder, add 100 mL distilled, deionized water and 5 drops of Ferroin indicator.

e) Titrate the solution with 0.4 N $FeSO_4\text{-}7H_2O$.

f) Record titration volume, and titrate blanks in the same manner.

B. Calculations:

% Organic Matter = (B-T) x (F)

Where: B = mL of $FeSO_4$ for blank titration.

T = mL of $FeSO_4$ for sample titration.

$$F = \frac{(0.74 \times N)}{W} \quad \text{and} \quad 0.74 = \frac{(3) \times (1.72) \times (100)}{(0.70) \times (1000)}$$

Where: 3 = mg carbon per milliequivalent of carbon

1.72 = Correction factor, based on assumption soil organic matter is 58% carbon.

0.70 = Correction factor for incomplete oxidation of soil carbon during acid digestion (i.e. only about 70% of the soil carbon is oxidized)

1000 = Conversion factor for mg to g

100 = Conversion factor to percentage (%)

W = Weight of soil sample (g)

N = Normality of $FeSO_4 \cdot 7H_2O$, calculated as follows:

$$N_1 V_1 = N_2 V_2$$

N_1 = Normality of $FeSO_4 \cdot 7H_2O$

V_1 = mL of $FeSO_4 \cdot 7H_2O$ to titrate blank

N_2 = Normality of $K_2Cr_2O_7$ = 0.4 meq/mL

V_2 = Volume of $K_2Cr_2O_7$ = 25 mL

C. Results

The soil organic matter for all soil sample studied is shown in Table 3.

4. Soil Effective Cation Exchange Capacity (Sims and Heckendorn 1991c):

Both exchangeable cations and acidity were determined at the soil's pH.

A. Procedure for Determination of Exchangeable Cations:

a) Weigh 10 g of soil sample into a 100 mL polyethylene cup and add 50 mL of 1 N NH_4OAc (for exchanging cations), pH 7.0 to the cup then shake for 30 min.

b) Filter the suspension into a 100 mL volumetric flask, using medium qualitative grade filter paper and add 25 mL of 1 N NH_4OAc to the soil, swirl by hand and pour onto soil on filter paper. Repeat this step.

c) Collect a total of 90 to 95 mL of ammonium acetate filtrate. Make the solution to volume with 1 N NH_4OAc and mix well.

d) Determine K, Ca, and Mg in the solution by atomic absorption spectrophotometry.

B. Calculations for Exchangeable Cations:

$$Exchangable\ Cations\ (meq\ /\ 100g) = \frac{(C) \times (df) \times (0.100\,L) \times (1\,meq) \times (100)}{(s\ wt) \times (meq\ wt)}$$

Where:

C = Concentration of Ca, Mg or K in diluted sample, mg/L

df = Dilution factor (Ca, Mg = 28; K=10)

0.100 L = volume of original NH_4OAc extract

s wt = Sample weight (10 g)

meq wt = Weight per milliequivalent (Ca = 20 mg; Mg = 12 mg; K = 39 mg)

C. Procedure for Determination of Exchangeable Acidity at the pH of the Soil:

   a) Weigh 10 g of soil sample into a 125 mL Erlenmeyer flask and add 25 mL of 1 N KCl (for acidity exchange) and swirl well for half hour, then add 25 mL KCl and repeat 4 times to obtain a total 150 mL KCl.

   b) Filter the suspension into a 300 mL Erlenmeyer flask.

   c) Add 4 drops of phenolphthalein indicator to the KCl solution.

   d) Titrate the KCl solution with the standard 0.01N NaOH.

D. Calculations for Determination of Exchangeable Acidity at the pH of the Soil:

$$\text{Exchangable Acidity (meq / 100g)} = \frac{(T-B) \times (N) \times \times (100)}{(W)}$$

Where:

T = mL of NaOH to titrate sample

B = mL of NaOH to titrate blank

N = Normality of NaOH (meq/mL)

W = Sample weight, g

E. Results

   The soil effective cation exchange capacity for all soil sample studied is shown in Table 3.

5. Soil Zeta Potential

   A. Procedure:

   a) Prepare 4L each of 0.1M, 0.01M, and 0.001M $NaNO_3$.

   b) Weigh out 0.50 g soil samples and add to each of 15 beakers. Add 200 mL of 0.001M $NaNO_3$ solution.

c) Stir solution about 2 minutes with the stirrer. Continue to stir while adjusting solution pH to the following values: 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5 9, 9.5, and 10. Wait for at least 1 hr.

d) Stir for 2 minutes and measure the solution pH before determining soil zeta potential.

e) Put the thermometer into solution. Read the temperature of solution.

f) Use the solution to rinse electrophoretic cell 2 or 3 times and fill the cells.

h) Turn D.C. voltage to 72. Set D.C. polarity to normal. Turn microamps 1000X, 100X, or 10X and read microamps from ammeter. This is specific conductivity.

i) Observe a particle which is on the 6.3x line from microscope. Turn on D.C. polarity to normal.

j) Use timer to track rate of particle migration. Time particle traversing standard divisions (large blocks 1/8, 1/4, 1/2, 1 or several blocks). Turn D.C. polarity off. Write down direction, number of divisions, and time of particle migration.

k) Turn D.C.polarity to reverse and repeat step j to track this particle.

l) Repeat step i - k to determine another 19 particles.

m) Repeat steps f - l for other pH solutions.

o) Repeat steps b - m for 0.01 M $NaNO_3$ and 0.001 M $NaNO_3$.

p) Use the chart provided, find the C_t from T (temperature of solution). Calculate electrophoretic mobility and calculate zeta potential from electrophoretic mobility value. Plot pH - zeta potential graph.

B. Calculation:

Electrophoretic Mobility = 160 microns x divisions / time x voltage

Zeta Potential = C_t x Electrophoretic Mobility

These data will be used in conjunction with those for the acid-base titration which will be conducted over the next several months.

14

C. Results:

Figures 1 - 15 show zeta potential as a function of pH for fifteen New Jersey soils in three different ionic strengths.

6. Soil Metal Oxides

The amount of amorphous Al, Fe, and Mn oxides in the soils was determined by three different extraction methods: (1) perchloric - nitric acid digestion (acid method), (2) sodium citrate - bicarbonate - dithionite extraction (CBD method), and (3) acid ammonium oxalate extraction (oxalate method).

(1). Perchloric - nitric acids digestion (Hesse, 1972)

A. Reagents

a) 69 % perchloric acid.

b) Nitric acid

c) Lithium chloride, 9000 mg Li per liter, 55.2 g/L LiCl

B. Standards

Fe: 0, 10, 20, 40, 60, 80, 100, 200, 300 mg/L Fe in the digestion solution

Al: 0, 10, 20, 40, 80, 100 and 200 mg/L Al in the digestion solution

Mn: 0, 2, 4, 6, 8, 10 mg/L Mn in the digestion solution

C. Procedure

a) Weigh 0.5 g air-dried, crushed soil into 125 mL beakers.

b) Add 20 mL of concentrated nitric acid. Cover beaker and cautiously heat to oxidize organic matter. Add 10 mL of 69% perchloric acid and digest the mixture until dense white acid fumes appear. Use a little extra perchloric acid to wash down the sides of the beaker as necessary. Dilute residue to 100 mL.

c) Take 0.50 mL of each sample and standard and add 9.5 mL distilled water from a bottle - top dispenser. Determine Fe in solution by atomic absorption spectrophotometry (AAS) using standard methods.

d) Pipet 1.0 mL of each sample and standard and add 9.0 mL distilled water from a bottle - top dispenser. Take 5 mL of each sample and standard into a 12 mL test tube and add 1.0 mL of 9000 mg/L Li solution to each tube. Determine Al on the AAS using standard methods.

e) Pipet 1.0 mL of each sample and standard and add 9.0 mL distilled water by a bottle - top dispenser. Determine Mn on the AAS using standard methods.

D. Calculations

% Fe = mg Fe (from calibration curve) x 100 x 100/(500 mg soils x 0.5 mL)

% Fe oxide (Fe_2O_3) = % Fe x 160/112

% Al (or Mn) = mg Al (or Mn) (from calibration curve) x 100 mL x 100/(500 mg soil x 1.0 mL)

% Al oxide (Al_2O_3) = % Al x 102/54

% Mn oxide (MnO_2) = % Mn x 87/55

E. Results:

Table 4 shows amorphous Fe, Al, and Mn oxides extracted by perchloric - nitric acids.

(2). Sodium citrate - bicarbonate - dithionite extraction (CBD) (Mehra and Jackson 1960)

A. Reagents

a) 1M sodium bicarbonate

b) Sodium citrate 0.3 M, pH 8.5.

c) Sodium dithionite

d) Lithium chloride, 9000 mg Li per liter, 55.2 g/L LiCl

B. Standards

Fe: 0, 10, 20, 40, 60, 80, 100, 200, 300 mg/L Fe in the extracting solution

Al: 0, 10, 20, 40, 80, 100 and 200 mg/L Al in the extracting solution

Mn: 0, 2, 4, 6, 8, 10 mg/L Mn in the extracting solution

C. Procedure

a) Weigh 1.0 g air dried, crushed soil into a centrifuge tube.

b) Add 20.0 mL of 0.3 M sodium citrate and 2.5 mL of 1 M sodium bicarbonate. The temperature is brought to 75 to 80°C in a water bath. Then 5 g of solid $Na_2S_2O_4$ is added from a spoon, and the mixture is stirred constantly for 15 minutes at 75 to 80°C. After cooling and centrifuging for 10 minutes at 1600 - 2200 rpm, the clear supernatant is decanted into a 250 mL volumetric flask.

c) Repeat step b twice. Transfer supernatant to the same flask. Using the saturated NaCl bring volume 250 mL.

d) Take 0.5 mL samples and standards and add 10 mL distilled water from a bottle - top dispenser. Determine Fe in solution on the atomic absorption spectrophotometer (AAS) using standard methods.

e) Pipet 5.0 mL of each sample and standard into a 12 mL test tube. Add 1.0 mL of 9000 mg/L Li solution to each tube. Determine Al on the AAS using standard methods.

f) Pipet 5.0 mL of each sample and standard into a 12 mL test tube. Determine Mn on the AAS using standard methods.

D. Calculations

% Fe = mg Fe (from calibration curve) x 250 mL x 100/(1000 mg soil x 0.5 mL)

% Fe oxide (Fe_2O_3) = % Fe x 160/112

% Al (or Mn) = mg Al (or Mn) (from calibration curve) x 250 mL x 100/(1000 mg soil x 5 mL)

% Al oxide (Al_2O_3) = % Al x 102/54

% Mn oxide (MnO_2) = % Mn x 87/55

E. Results:

Table 5 shows amorphous Fe, Al, and Mn oxides extracted by sodium dithionite - citrate - bicarbonate.

(3). Acid ammonium oxalate extraction (oxalate method) (Iyengar et al. 1981)

A. Reagents:

a) Ammonium oxalate extractant, 0.2 M, pH 3.0. Prepare 0.2 M ammonium oxalate (28.4 g/L) and 0.2 M oxalic acid (25.2 g/L). Mix small test batches (20 mL) in ratios 8 : 12, 9 : 11, 10 : 10, etc. and measure pH. Choose ratio that gives pH closest to 3.0, and mix a larger batch of the reagent (Generally, this is about 9 parts oxalic acid to 11 parts ammonium oxalate).

b) Lithium chloride, 9000 mg Li per liter (55.2 g/L)

B. Standards

Fe: 0, 10, 20, 50, 100 and 200 mg/L Fe in the extracting solution

Al: 0, 10, 20, 50, 100 and 200 mg/L Al in the extracting solution

Mn: 0, 2, 4, 6, 8, 10 mg/L Mn in the extracting solution

C. Procedure

a) Weigh 0.50 g air - dried, crushed soil into centrifuge tube. Add 20.0 mL extracting solution and stopper (seal tightly).

b) Shake horizontally in darkness for 4 hours at $25^\circ C$.

c) Centrifuge at 2500 rpm for 15 minutes. Decant supernatant and retain for analysis.

d) Take 0.5 mL samples and standards and add 10.0 mL distilled water from a bottle-top dispenser. Determine Fe in solution on the atomic absorption spectrophotometer (AAS) using standard methods.

e) Pipet 5.0 mL of each sample and standard into a 12 mL test tube. Add 1.0 mL of 9000 mg/L Li solution to each tube. Determine Al on the AAS using standard methods.

f) Pipet 5.0 mL of each sample and standard into a 12 mL test tube. Determine Mn on the AAS using standard methods.

D. Calculations

% Fe = mg Fe (from calibration curve) x 20 mL x 100/(500 mg soil x 0.5 mL)

% Fe oxide (Fe_2O_3) = % Fe x 160/112

% Al (or Mn) = mg Al (or Mn) (from calibration curve) x 20 mL x 100/(500 mg soil x 5 mL)

% Al oxide (Al_2O_3) = % Al x 102/54

% Mn oxide (MnO_2) = % Mn x 87/55

E. Results:

Table 6 shows amorphous Fe, Al, and Mn oxides extracted by ammonium oxalate.

III. Cadmium and Hexavalent Chromium Adsorption

Batch equilibration studies have been conducted for cadmium(II) and chromium(VI) for the fifteen New Jersey soils. 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 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 the 24 hours shaking. These values were taken to be the reaction values. The samples were then filtered through 25 mm diameter, 0.45 μm membrane filters.

The cadmium concentration in the filtered solution was determined by atomic absorption spectrophotometry using a Perkin-Elmer Model 5000 atomic absorption spectrophotometer.

The procedures for the 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 $Cr_2O_7^{-2}$ can be detected by this method. Total chromium was determined by oxidizing the chromium with permanganate followed by analysis of hexavalent chromium. The procedures for oxidizing chromium with permanganate are: (1) Put 20 mL filtered sample solutions to 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 1-5 minutes until the color disappear, (5) Cool down for analyzing of hexavalent chromium.

The instruments were calibrated with a calibration curve prior to sample analysis. Samples were analyzed in groups of 16, representing a single initial cadmium concentration. The sixteen samples were the 15 which had been equilibrated at different pH values and the initial cadmium 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.

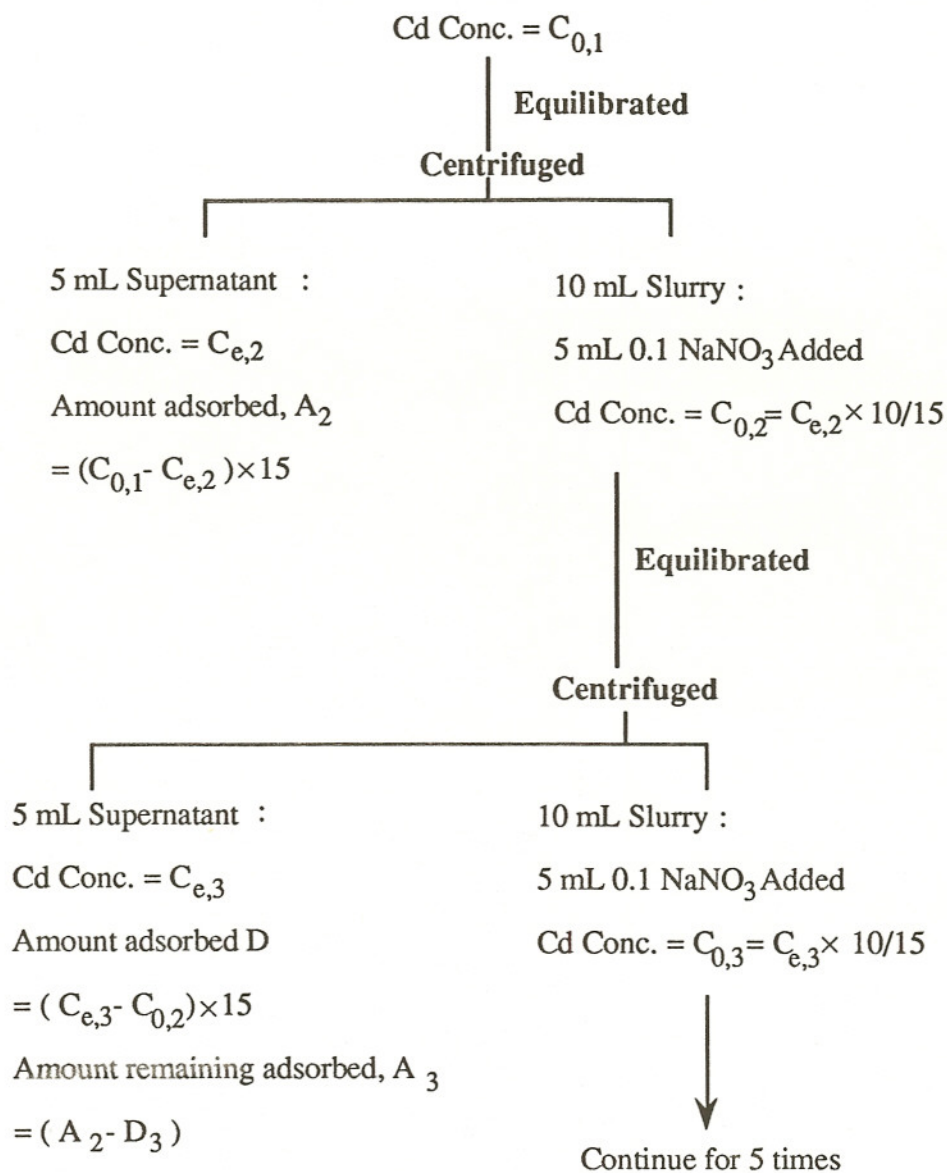## IV. Adsorption-Desorption Equilibria And K_d Determination

The Cd adsorption-desorption experiments were conducted with size fractionated soil samples taken from the Lake Wood sand, Rockaway Stony loam, and Washington loam in New Jersey. The soil samples were air-dried, sieved, and homogenized. All of particles with diameter more than 2 mm were removed from the sample by sieving. The Cd solution on the range of 0.00008M to 0.15M for a series of adsorption-desorption experiments were prepared from Cd nitrate in 0.1 N sodium nitrate solution and determined using a Perkin-Elmer 5000 atomic absorption spectrophotometer.

For studying the desorption, batch equilibration was followed by replacing the supernatant with 0.1 M $NaNO_3$. Adsorption was initially carried out on 15 g soil in 15 mL of a series of solutions containing 11.24 to 1686 mg/L of Cd. On an attainment of equilibrium adsorption, the suspensions were contained in seven centrifuge tubes and shaken for 48 hours at 25 ± 0.5 °C. Then the slurries were centrifuged at 1500 rpm for 20 minutes. 5 mL of the supernatant was withdrawn and the Cd concentration of the supernatant was measured by atomic absorption

20

spectrophotometer. The volume of the remaining slurry was made up by adding 5 mL of 0.1 N NaNO$_3$ solution, equilibrated again and centrifuged. The process of withdrawing 5 mL supernatant, measuring it's Cd concentration and replacing it by adding 5 mL 0.1 M NaNO$_3$ solution was repeated daily for five days. The amount of Cd desorbed and the amount of Cd remaining in soil were calculated according to the flow chart of desorption experiment shown on next page. In the flow chart, the initial concentration of Cd at each step of the desorption process is denoted as C$_0$. Moreover, at each of the desorption process the Cd concentration in aqueous phase is denoted as C$_e$; the amount of Cd remained in soil is denoted as A; and the amount of Cd desorbed is denoted as D. Both adsorption and desorption isotherms were drawn by employing the Langmuir equation and the Freundlich equation. The partition coefficients (K$_d$) were determined from the slope of linear plots of Cd sorbed concentration vs. Cd concentration in the aqueous phase.

15 g Soil + 15 ml Cd (11.24 - 1680 µg/mL in 0.1M $NaNO_3$)

Cd Conc. = $C_{0,1}$

| Equilibrated

Centrifuged

5 mL Supernatant :

Cd Conc. = $C_{e,2}$

Amount adsorbed, A_2

$= (C_{0,1} - C_{e,2}) \times 15$

10 mL Slurry :

5 mL 0.1 $NaNO_3$ Added

Cd Conc. = $C_{0,2} = C_{e,2} \times 10/15$

Equilibrated

Centrifuged

5 mL Supernatant :

Cd Conc. = $C_{e,3}$

Amount adsorbed D

$= (C_{e,3} - C_{0,2}) \times 15$

Amount remaining adsorbed, A_3

$= (A_2 - D_3)$

10 mL Slurry :

5 mL 0.1 $NaNO_3$ Added

Cd Conc. = $C_{0,3} = C_{e,3} \times 10/15$

Continue for 5 times

Flow chart of desorption experiment evaluated in laboratory batch studies in conjunction with adsorption isotherm studies.

V. Wet-Dry Cycle Study

A wet-dry cycle design of Cd desorption was employed to simulate the field condition. A batch technique was employed to study the equilibrium of Cd desorption on soils and to find the difference of Cd desorption on soils treated by various numbers of wet-dry cycles. With the exception of soil employed in the 0 cycle, the soil samples were rewetted by adding distilled water to give a soil:water ratio of 10:7 (wet process) and air dried for four days (dry process). The process of soil wetting then drying is defined as a wet-dry cycle. In this experiment, soil samples were treated by wet-dry cycle for zero to five times after attaining equilibrium adsorption, denoted as 0 cycle to 5 cycles. 1 Kg soil sample and 1 liter of 8×10^{-5} M Cd solution were placed into a 2000 mL beaker, and the pH of the suspension was adjusted to 5.00 ± 0.05. Then the suspension was stirred at 300 rpm for 48 hours using a mixer to ensure the sorbent was equilibrated with Cd. After attaining adsorption equilibrium, the suspension was kept for one day, and then centrifuged at 1500 rpm for 20 minutes to separate liquid and solid phases. The Cd concentration of the supernatant was analyzed by Perkin-Elmer 5000 atomic absorption spectrophotometry to determine the amount of Cd adsorbed. The separated solid was air-dried for 4 days, and then used in desorption experiments, denoted as 0 cycle. For the subsequent desorption experiments, ten samples of 15 g soil and 15 mL 0.1 N sodium nitrate solution were placed into 30 mL polystyrene centrifuge tubes. The centrifuge tubes were shaken using a reciprocating shaker at 150 rpm and the temperature was maintained at $25 \pm 0.5°$C. After shaking for 5 min, the pH of each suspension was adjusted to 5.00 ± 0.05. Then the centrifuge tubes were continuously shaken and they were sampled at the following times: 1, 3, 6, 12, 24, 36, 48, 60, 72, and 84 hours. The suspension sampled at each time was centrifuged for 20 min to obtain a clear supernatant. The Cd concentration of supernatants were analyzed by using atomic absorption spectrophotometer to determine the amount of Cd desorbed. The processes of adding soil and 0.1 N sodium nitrate solution to centrifuge tubes, adjusting pH, shaking, sampling, and centrifuging to separate liquid and solid were repeated for five wet-dry cycles.

23

| Adsorption experiment | ← | Equilibriate sorbent with 8×10^{-5} M cadmium solution and calculate the amount of cadmium adsorbed |

↓

| Wet-dry process | ← | Soil sample wet by adding distilled water then air dried for zero to five times to simulate the field condition of varying soil moisture |

↓

| Desorption experiment | ← | Study the equilibrium desorption of Cd affected by each wet-dry cycle treatment using batch equilibration |

Flow chart of wet-dry cycle study.

QUALITY CONTROL-QUALITY ASSURANCE PROCEDURES

1. Data Quality Objectives:

The QA/QC objective level will be "Level 4". The results of this research will be used to establish environmental standards which could be used to establish clean-up levels. Such actions on the part of a regulatory agency are frequently subjected to litigation.

2. Monitoring Network Design and Rationale:

The field samples were collected by NJDEP at five sites which had been chosen to represent a distribution of the major soil types present in New Jersey.

3. Sampling Procedure:

The surfacial soil layer, as well as the vegetation, was removed with a spade. The B horizon was collected with the spade. The soil was placed in a 10-gallon opaque plastic container.

4. Sample Custody Procedures:

The soil samples were placed in the 10-gallon opaque plastic containers. These were labeled prior to the soil being placed in them. The soil was kept in the same container during transportation and storage prior to use.

5. Monitoring Sites and Frequency of Sample Collection:

The fifteen soils were collected in June and July 1990 by NJDEP personnel. One sample of each soil was collected. The soils collected for use in this study are Sassafras sandy loam, Lakewood sand, Penn silt loam, Whippany silty clay loam, and Washington loam.

6. Data Quality Requirements:

Parameter	Sample Matrix	Detection Limit	Quantitation Limit	Precision	Accuracy
pH	wastewater	±0.01	1.00-14.00	±1 %	99 %
Cd	wastewater	Details in Standard Methods			
Cr(III)	wastewater	Details in Standard Methods			
Cr(VI)	wastewater	0.01 mg/L	0.5 mg/L	±5 %	99 %
Pb	wastewater	Details in Standard Methods			
Soil pH	soil-wastewater	±0.01	1.00-14.00	±1 %	99 %
Organic Matter	soil	0.1 %	100 %	±10 %	95 %
inorganic Carbon	soil	0.1 %	10 %	±10 %	95 %
Extractable Fe, Al, Mn, Si	soil	Details in Standard Methods for metal analysis			
Surface Area	soil	0.1 m^2/g	-----	±5 %	99 %
CEC	soil	0.1 meq/kg	5 meq/kg	±5 %	95 %
Particle Size	soil	38 μm	25 mm	±5 %	95 %
pH$_{zpc}$	soil	0.1 mV	100 mV	±5 %	95 %

Note: Method detection limit, quantitation limit, precision, and accuracy are calculated by the methods in ASTM D1687-86 p. 366, 1990.

The most pertinent data to the project are pH and the concentrations of the four metals. The criteria by which the data for these parameters will be judged are described in Section 8. Calibration Standards and Preventive Maintenance.

7. Data Quality Assessments:

Only data which fall in the stated precision range and accuracy limit will be selected to represent that characteristic of the population.

8. Calibration Standards and Preventive Maintenance:

Commercially prepared and certified metal and pH standards are routinely utilized in the laboratory. Instruments are calibrated each time they are used.

For pH, meters are calibrated using 2 buffer solutions. Depending on the pH of the samples to be measured, the buffers are pH 4 and pH 7 or pH 7 and pH 10. The higher pH-value buffer solution is rechecked after each 15 measurements. If the measured value is not within ±0.1 pH units of the accepted value, the data for the previously measured samples are rejected. If the measured value of the buffer solution is within ±0.1 pH units of the accepted value, the data for the previously measured samples are accepted. Following the quality check, the pH meter is restandardized using the two buffer solutions.

For the metal analyses, a calibration curve which covers the entire working range of the method is prepared. At least five concentrations are prepared for the curve. One of these is near the upper limit (quantitation limit) and the remainder are approximately evenly distributed. For atomic absorption analyses, a blank is run after each sample. Analyses for adsorption experiments are run in groups of 18 samples. These 18 represent one initial metal concentration. Fifteen of the the samples are the fifteen different pH values used in the experiment. A mid-pH sample is run in duplicate to assess precision. Another portion of that sample is spiked by the method of standard additions to test recovery. The last sample of the 18 in the group is the initial solution used in the adsorption test. This analysis is for the purpose of ascertaining the exact metal concentration used in the experiment. For both atomic absorption and colorimetric analyses, a standard is run after each group of 18 samples. If the value of this standard differs from its stated value by more than ±10%, the data for the previous set of 18 samples is rejected and the samples are reanalyzed. If the standard does not differ from its stated value by more than ±10%, the data are accepted. If the analysis is by flame atomic absorption, the instrument is also restandardized using this standard. If the analysis is by electrothermal atomization atomic absorption or by colorimetric analysis, the value of the slope of the calibration curve used for the subsequent 18 samples is assumed to have changed by the same amount as for the standard.

Instruments are maintained and calibrated according to manufacturers recommendations. Balances are calibrated on an annual basis.

9. Quality Control Checks:

Spiked samples and replicates are an important part of our quality control procedures. These have been discussed in the preceding section.

10. Documentation, Data Reduction, and Reporting:

Depending on the type of data, results are recorded on data sheets or in permanent notebooks. Data are also stored in a computer file and are graphed and subjected to statistical analyses. Data will be reported to NJDEP by quarterly reports.

11. Performance and System Audits:

The data for samples and for quality control samples are regularly checked by the Project Quality Assurance Officer.

12. Project Operations and Responsibility:

Sampling operations	P.F. Sanders and H.E. Allen
Sampling QC	P.F. Sanders
Laboratory analysis	J. Lee, C.P. Huang
Laboratory QC	J. Lee, C.P. Huang
Data processing activities	J. Lee, C.P. Huang
Data processing QC	J. Lee, C.P. Huang
Data quality review	H.E. Allen, C.P. Huang, D.L. Sparks
Performance evaluation/auditing	H.E. Allen, C.P. Huang, D.L. Sparks
Overall QA	H.E. Allen
Principal investigators	H.E. Allen, C.P. Huang, D.L. Sparks

RESULTS AND DISCUSSION

The basic physical and chemical properties of the New Jersey soils are listed in Table 1-Table 6. Data for all fifteen soils are included, some of these results had previously been reported in the final report for the first year of the project.

Table 1. The fraction of material larger than 2 mm

Soil Name	< 2 mm (g)	> 2 mm (g)	percentage > 2 mm (%)
Birdsboro silt loam	20203.0	10555.5	34.32
Boonton Bergen County	16571.0	3745.5	18.44
Boonton 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 material dredged from Del. River	38273.5	770.0	1.97
Freehold sandy loam (surface)	32294.5	2518.0	7.23
Freehold sandy loam (subsurface)	29394.5	2242.0	7.09
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

Table 2. Analysis of particle size distribution, and soil pH

Soil Type	Particle Size Distribution			pH*	
	Sand Clay %	Silt %	*Sand* % *Clay*	In water	In CaCl$_2$
Birdsboro silt loam	50	32	18	5.69	5.24
Boonton Bergen County	60	27	13	5.12	4.31
Boonton 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 material dredged from Del. River	85	5	10	4.77	4.09
Freehold sandy loam (subsurface)	37	42	21	6.44	5.72
Freehold sandy loam (surface)	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	57	6.17	5.72

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

Table 3. Analysis of cation exchange capacity, and soil organic matter

Soil Type	K	Mg	Ca	ECEC	Organic Matter
		(meq/100g)		meq/100g	%
Birdsboro silt loam	0.47	1.37	3.30	5.30	2.2
Boonton Bergen County	0.017	0.60	2.59	4.20	8.6
Boonton Union County	0.19	0.42	1.58	4.20	5.3
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 material dredged from Del. River	0.21	0.43	1.10	2.30	1.2
Freehold sandy loam (surface)	0.07	0.21	0.46	0.80	0.2
Freehold sandy loam (subsurface)	0.33	0.91	2.84	4.30	2.4
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 4. Amorphous Fe, Al, and Mn Oxides Extracted by Perchloric - Nitric Acids

	Fe_2O_3	Al_2O_3	MnO_2
Soil Type		(%)	
Birdsboro silt loam	4.723	3.697	0.077
Boonton Bergen County	3.859	4.541	0.057
Boonton 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 national dredged from Del. River	2.065	1.165	0.042
Freehold sandy loam (surface)	1.553	2.009	0.028
Freehold sandy loam (subsurface)	3.538	3.697	0.037
Lakewood sand	0.657	0.321	0.008
Hazen gravelly loam	4.307	4.372	0.116
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 5. Amorphous Fe, Al, and Mn Oxides Extracted by Sodium Dithionite - Citrate - Bicarbonate

Soil Type	Fe_2O_3	Al_2O_3	MnO_2
		(%)	
Birdsboro silt loam	1.600	0.744	0.119
Boonton Bergen County	2.080	0.661	0.076
Boonton 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 material dredged from Del. River	2.559	0.118	0.077
Freehold sandy loam (surface)	1.281	0.053	0.017
Freehold sandy loam (subsurface)	1.813	0.382	0.053
Lakewood sand	1.600	0.201	0.016
Hazen gravelly loam	1.493	0.958	0.189
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 6. Amorphous Fe, Al, and Mn Oxides Extracted by Ammonium Oxalate

Soil Type	Fe_2O_3	Al_2O_3	MnO_2
		(%)	
Birdsboro silt loam	1.035	0.714	0.025
Boonton Bergen County	1.563	1.321	0.013
Boonton 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 national dredged from Del. River	0.578	0.105	0.012
Freehold sandy loam (surface)	0.178	0.052	0.001
Freehold sandy loam (subsurface)	0.519	0.442	0.009
Lakewood sand	0.344	0.096	0.0002
Hazen gravelly loam	1.117	0.574	0.034
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

Soil Sample Characterization Analysis:

1. Particle size distribution

Particle size distribution is one of the most stable soil characteristics. 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.

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 pH of a soil measured in 0.01 M $CaCl_2$ is independent of dilution over a wide soil-solution ratio range and soil suspensions are flocculated in 0.01 M $CaCl_2$, the errors resulting from the

liquid junction potential can be minimized by placing the calomel electrode in the clear supernatant liquid. 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 2). Apparently, the released aluminum ions undergo hydrolysis. As a result, protons are generated. Therefore, both measurements are required to fully define the character of the soil's pH. 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 indicate the presence of alkaline material in the soil that might have a stronger buffering capacity (Foth, 1984a).

3. Soil Organic Matter

Almost all soil properties, including adsorption and soil structure stabilities are dependent upon organic matter for energy and nutrients (Foth 1984b). The soil organic matter is one of the main substances onto which metals bond. 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). We employed the later method (the Walkley - Black method) for determining the soil organic matter. The organic matter content ranged from 0.2 to 8.6 percent in our soil samples (Table 3).

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 which 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 our soil samples (Table 3). These data can be used to predict adsorption abilities of soils. The soils with higher effective cation exchange capacity might indicate the soil has higher adsorption ability undergoing a nonspecific (outer sphere) adsorption.

5. Zeta potential

The electrophoretic mobility of each soil was determined at 15 pH values over the range of 3 to 10. This was determined at ionic strengths of 0.1, 0.01, and 0.001 M. These data are still being evaluated and will be used in conjunction with those for the acid-base titration.

6. Metal oxides

Metal oxides provide surfaces 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 (Barrow, 1985).

The amount of Al, Fe, and Mn oxides in the soils was determined by three different extraction procedures: (1) perchloric - nitric acid digestion (acid method), (2) sodium citrate - bicarbonate - dithionite extraction (CBD) (3) acid ammonium oxalate extraction (oxalate method).

Cadmium and Hexavalent Chromium Adsorption

Batch equilibration studies have been conducted for cadmium(II) and chromium(VI). The adsorption of cadmium and hexavalent chromium have been conducted at the concentrations of 1×10^{-4} and 1×10^{-5} M at 15 values of pH, covering the range 3 to 10, for the fifteen New Jersey soils. The most important factor in controlling the partitioning of a metal to soil is the solution pH (Allen and Huang, 1990). Figures 16 and 19 show data for the adsorption of cadmium by New Jersey soils. At higher pH, virtually all the added cadmium was adsorbed. As the pH decreases, the concentration of soluble cadmium increased.

As has been done before, the cadmium sorption data were evaluated to provide maximum soil contamination levels that will not exceed drinking water standards. Different soils exhibit different absorption ability, as is shown in Figures 16 and 19 which compare the adsorption of cadmium by Birdsboro silt loam, Boonton Bergen County soil, Boonton Union County soil, Downer loamy sand, Dunellen sandy loam, fill material dredged from Delaware River, Freehold sandy loam (surface), Freehold sandy loam (subsurface), Hazen gravelly loam, and Rockaway stony loam. The soils vary in their strength and capacity for metal binding. Metal adsorption was highly pH dependent. The Hazen gravelly loam displayed a greater extent of adsorption for cadmium than did the other soils . Freehold sandy loam (surface) had the poorest adsorption capacity. The percent of metal adsorbed increased with rising pH.

36

We also have transformed these percentage cadmium adsorbed data into sorption coefficients (K_d) which are a function of pH (Figures 17 and 20). The partition coefficient is determined from the experimental data by the following equation:

$$K_d = \frac{C_s}{C_w}$$

where

K_d = adsorption coefficient

C_s = metal concentration in soil ($\mu g/g$)

C_w = metal concentration in water ($\mu g/mL$)

The higher the K_d value, the higher the ratio of metal bound by soil to that remaining in solution.

To apply such data in the decision making process, it is necessary to use the K_d and appropriate conditions of soil/groundwater in the environment. We used adsorption/desorption relationships in the form of a mathematical model and computed the maximum level of metal in soil for which the equilibrium soluble metal will not exceed the drinking water standards:

$$\text{Maximum allowed soil concentration} = C_w \left\{ K_d + \frac{n \times p}{D_s \times (1-n)} \right\}$$

where

C_w = drinking water standard

K_d = adsorption coefficient

n = soil porosity

p = degree of water saturation of the soil, and

D_s = soil density, usually 2.65 g/mL.

The calculation determines the maximum concentration of cadmium which will not violate the water quality standards. These maximum permissible metal concentrations can be used as soil

clean-up criteria which can be used to protect groundwater quality and to predict the effect of metal addition to soil.

The maximum permissible level of cadmium in soil increases dramatically with increasing pH values (Figures 18 and 21). The effect of pH on the sorption of cadmium is a consequence of the acid-base characteristics of the soils. Different soils have very different metal adsorption abilities. For example, at the same pH, the Hazen gravelly loam could have the highest cadmium concentration, whereas Freehold sandy loam (surface) could have the lowest cadmium concentration, without causing a violation of the Drinking Water Standard (Figures 18 and 21).

Chromium exists almost exclusively in the Cr(III) oxidation state or in the Cr(VI) oxidation state (Udy 1956). In the environment Cr(III) is basically not a problem because of its relatively immobile in the aqueous environment due to its strong adsorption onto soils and it typically precipitates as the hydroxide in alkaline soil solution. In contrast, Cr(VI) is relatively mobile in the aqueous environment because Cr(VI) is not as strongly absorbed by soil as Cr(III) (Amacher and Baker 1982). Hexavalent chromium is a strong oxidizer and therefore is harmful in biological systems.

Redox reaction is a very important metal transformation process in soils. Reduction of hexavalent chromium to trivalent chromium can occur in the presence of reductive solids, such as Fe(II) (Eary and Rai 1988; Eary and Rai 1989) and organic materials (Mayer and Shick 1981; Bartlett and Kimble 1976), especially under acidic conditions.

For hexavalent chromium, a reverse trend of adsorption relative to that for cadmium is found. Adsorption of hexavalent chromium is maximum at low pH and decreases with increasing pH (Figures 22 to 36). The Boonton Union County soil displayed largest extent of adsorption. It adsorbed hexavalent chromium much more than did the other fourteen soils. Fill material from Delaware River had the poorest adsorption capacity. Also, we find that for the same soil at the same pH, a lower concentration of added hexavalent chromium has a higher percentage adsorbed than does a higher concentration (Figures 22 to 36). We have not yet been able to compute the sorption coefficients (K_d) and maximum level of hexavalent chromium in soil for which the equilibrium soluble metal will not exceed the drinking water standards. For this computation we need to know how much of each the hexavalent chromium and trivalent chromium is adsorbed by soil. This will be available after the adsorption measurements of trivalent chromium have been conducted. The experimental data of hexavalent chromium can be directly utilized to predict solution hexavalent chromium concentrations as a function of the soil hexavalent chromium concentration and the solution pH.

Two methods were used to determine hexavalent chromium: (A) Direct determination of hexavalent chromium by the colorimetric method and (B) Addition of potassium permanganate to oxidize trivalent chromium to hexavalent chromium, then determination of total chromium by the colorimetric method. The difference of the absorbance value between (A) and (B) was taken as the trivalent chromium, which had been formed by reduction of hexavalent chromium by soil reductants. The absorbance value obtained from (B) should be no less than that obtained from (A). In the oxidation of trivalent chromium to hexavalent chromium by potassium permanganate, the potassium permanganate will be reduced to both Mn^{2+} and MnO_2. However, MnO_2 is undesirable because it is a colloid and will adsorb both trivalent and hexavalent chromium. We decreased the solution pH to about 1.45 to avoid forming MnO_2 before adding the potassium permanganate to the filtered soil sample. When the solution pH increased, MnO_2 became the predominant species and this adsorbed hexavalent chromium. This then resulted in the amount of total chromium which was obtained from procedure (B) being less than that obtained from procedure (A) (Figure 37).

Control of the pH is important in total chromium determination. As mentioned above, a low pH (about 1.45) is required to avoid MnO_2 formation. The other important step is to add excess potassium permanganate in the oxidation of trivalent chromium. Permanganate solution is added until a purple color was detected in the samples held in the 85 °C water bath. A sample with a purple color indicates that all trivalent chromium and soil reductants have been oxidized. If enough potassium permanganate was not added, the potassium permanganate will be consumed by soil reductants. Thus, there will not be sufficient potassium permanganate available for oxidation of trivalent chromium to hexavalent chromium. The reaction of Mn(VI) → Mn(II) has a higher reduction potential (E^O) than that of Cr(VI) → Cr(III) and Soil oxidized organics → Soil organics, whereas the reaction of Soil oxidized organics → Soil organics has the lowest reduction potential (E^O), so soil reductants will reduce haxavalent chromium to trivalent chromium, especially for a higher organic content soil.

All metal sorption data have a strong pH dependency in which there is a transition over a pH range of approximately 2-pH units in which the sorption changes from nearly zero to nearly complete. What is very important to note is that, in the case of the New Jersey soils, this transition zone corresponds to the pH of the soil. This indicates that in any soil sampling program undertaken to assess metal contamination, the need for remediation, or to evaluate the effectiveness of remedial actions, it is essential that the soil pH be determined. Without the pH, it is not possible to make satisfactory predictions, or to compare results among sites.

Wet-Dry Cycle Study

The results of the adsorption study and the wet-dry cycle effect on Cd desorption from the three soils studied are shown in Figures 38-45.

It can be seen in Figure 38 and Figure 39 that the extent of cadmium adsorption on the three soils is in the following order: Washington loam > Rockaway Stony loam > Lakewood sand. The ECEC and contents of amorphous oxides and clay in these soils are in the same order (Table 2-6). These indicate that adsorption should be easier for Cd when the soil has a high level of ECEC and amorphous oxides. The influence of organic matter on Cd adsorption has been studied by a number of people. However, no general conclusion has been obtained. Many investigators found that the organic matter has strong influence on Cd adsorption (Getties and Driel, 1984). Nevertheless, some studies postulated that the organic matter only slightly contributes on Cd adsorption (King, 1988). In this study, the organic matter level of the Rockaway Stony loam is greater than that of the Washington loam (Table 3). This implies that the organic matter effect on Cd adsorption is not significant. Figures 40, 42, and 44 show that the extent of Cd desorption (desorption percentage) of the Lakewood sand, Rockaway Stony loam, and Washington loam are in the following order 0 cycle > 1 cycle ≥ 3 cycle ≥ 2 cycle > 4 cycle > 5 cycle, 0 cycle >5 cycle ≥ 4 cycle ≥ 3 cycle ≥ 2 cycle ≥ 1 cycle, and 5 cycle > 4 cycle ≥ 3 cycle > 2 cycle > 1 cycle ≥ 0 cycle, respectively. It is expected that the greater the number of wet-dry cycles, the further the Cd would be transported into the pores. Therefore, desorption should be more difficult for Cd when more adsorption wet-dry cycles are applied. We found that the cycling effect is not the only factor strongly governing the release of Cd when soil is predominatly sand. Dissolution may be another important factor in the release of Cd when sand is the predominant soil component. For sandy soil, more Cd^{2+} are concentrated in pore water and then form surface complexes with organic matter or amorphous oxides. These cadmium complexes are likely to release Cd^{2+} during the desorption process. Figures 40 and 42 show that the zero cycle has the highest desorption percentage after 84 hours because most Cd complexes are likely to be on the soil surface and be released to the aqueous phase in the zero cycle. Another explanation for the order of desorption of the Lakewood sand is the two sites theory (Griffin and Burau, 1974). Adsorption sites have a distribution of affinities for adsorbing Cd and the most favorable sites are filled first. At high equilibrium sorbed concentrations the less favorable sites are also utilized. The high affinity sites will be dominant when the surface coverage is low; whereas, at high sorption levels (high equilibrium sorbed concentration) both the high and low affinity sites will be occupied by Cd and desorption occurs at low affinity sites first. Cd may jump to high affinity sites from low affinity sites to attain more stable state when more wet-dry cycles are applied. Therefore, the desorption should be more difficult when more wet-dry cycles are applied.

Adsorption-Desorption Equilibria and K_d Determination

Figure 46 shows the relationship between sorbed concentration of Cd and equilibrium concentration of Cd after attaining equilibrium adsorption for both the Lakewood sand loam and the Rockaway Stony loam. It shows that the extent of sorbed Cd is higher in the Rockaway Stony loam than in the Lakewood sand after attaining equilibrium adsorption. The log-log plot of sorbed concentration vs. equilibrium concentration in aqueous phase is shown in Figure 47. Figure 47 shows that the linear isotherm of log-log plot have a good fit for Cd adsorption on the Lakewood sand. It is also seen in Figure 47 that log transformed data of Cd adsorption on the Rockaway Stony loam has two linear segments of different slopes. This may imply that there are two different adsorption sites in the Rockaway Stony loam. The desorption isotherms for five subsequent desorption experiments are shown in Figure 48 and Figure 49. To illustrate the "hysteresis" of adsorption-desorption, and the relationship between sorbed concentration of Cd and equilibrium concentration of Cd in the aqueous phase, the results of both adsorption and desorption isotherms for the two soils (the Lakewood sand and the Rockaway Stony loam) are plotted in the Figure 50 and Figure 51. Each isotherm is seen to be curvilinear. It can be seen in Figure 50 and 51 (plots of linear isotherm) that there is apparent hysteresis of desorption. The desorption data should fall on the adsorption isotherm if there is no hysteresis of desorption. In an attempt to find a better fit for both adsorption and desorption results, the Freundlich and Langmuir linear isotherms were employed and are plotted in Figure 52-58.

The Freundlich equation used to describe the adsorption-desorption is:

$$q = K_F \cdot C_e^N$$

where

K_F = Freundlich partition coefficient $(\mu g g^{-1}/(mgL^{-1})^{1/n}$

N = Freundlich exponent coefficient

The Langmuir equation employed to describe the adsorption-desorption is:

$$\frac{x}{m} = \frac{bK_L[M^{2+}]}{1 + K_L[M^{2+}]}$$

where

x/m = sorbed phase concentration when at equilibrium with aqueous phase($\mu g/g$)

41

$[M^{2+}]$ = the metal ion equilibrium concentration in solution (mg/L)

b = maximum adsorption capacity (μg/g)

K_L = Langmuir intensity coefficient (μg g^{-1}/mg L^{-1})

All the isotherm parameters and the partition coefficient (K_d) are given in Table 7. The partition coefficient was determined from the slope of linear plots of Cd sorbed concentration vs. Cd concentration in the aqueous phase. The Freundlich isotherm parameter (K_F) was determined from the slope of linear plots of log Cd sorbed concentration vs. log Cd concentration in aqueous phase. The results of cumulative Cd adsorption and desorption percentage are given in Table 8 and Table 9.

Table 7 Cd adsorption-desorption isotherm parameters

Sample	N^*	Linear isotherm		Freundlich isotherm[c]			Langmuir isotherm[d]		
		$K_d{}^a$	r^2	K_F	$1/n$	r^2	b	bK_L	r^2
Lakewood sand									
Adsorption (1-2 days)	7	0.47	0.95	1.11	0.90	0.99	1229.79	0.81	0.84
Desorption 1 (3 day)	7	0.68	0.97	1.73	0.88	0.97	1153.34	1.19	0.63
Desorption 2 (4 day)	7	1.01	0.91	3.30	0.83	0.98	933.10	2.07	0.69
Desorption 3 (5 day)	7	1.79	0.90	3.14	0.88	0.99	1635.16	2.19	0.28
Rockaway Stony loam									
Adsorption (1-2 days)	7	4.87	0.84	58.00	0.61	0.95	1432.19	38.32	0.93
Desorption 1 (3 day)	7	11.62	0.89	59.71	0.66	0.96	1332.80	53.27	0.81
Desorption 2 (4 day)	7	9.81	0.88	77.79	0.62	0.95	1453.02	65.23	0.91
Desorption 3 (5 day)	7	10.84	0.85	95.68	0.60	0.95	1408.67	85.96	0.93
Desorpiton 4 (6 day)	7	14.68	0.88	107.62	0.60	0.96	1421.14	105.00	0.93
Desorption 5 (7 day)	7	18.42	0.88	127.12	0.60	0.96	1422.31	138.34	0.95

* N, number of samples.

a. Partition coefficient measured from the slope of linear plot of sorbed concentration vs. equilibrium concentration in aqueous phase ($\mu g\ g^{-1}/mg\ L^{-1}$)

c. Freundlich isotherm expressed in the linear plot of log-log linear form.

d. Langmuir isotherm expressed in the linear plot of $[Cd]_{soln}/[Cd]_{sorb}$ vs. $[Cd]_{soln}$.

Table 8 Cumulative adsorption of Cd after equilibrium adsorption

Initial concentration of Cd M	Cd adsorption percentage in two days	
	Lakewood sand	Rockaway Stony loam
(1) 1.5×10^{-4} M	42.10	98.00
(2) 1.0×10^{-3} M	48.60	98.90
(3) 1.4×10^{-3} M	39.70	97.70
(4) 5.0×10^{-3} M	39.50	95.00
(5) 8.0×10^{-3} M	39.60	87.80
(6) 1.0×10^{-2} M	36.00	91.80
(7) 1.5×10^{-2} M	31.20	83.73

Table 9 Cumulative desorption of Cd

| Initial concentration of Cd | Cd desorption percentage in five days | |
M	Lakewood sand	Rockaway Stony loam
(1) 1.5×10^{-4} M	13.90	0.43
(2) 1.0×10^{-3} M	15.33	0.48
(3) 1.4×10^{-3} M	17.40	1.21
(4) 5.0×10^{-3} M	19.40	1.48
(5) 8.0×10^{-3} M	37.80	3.60
(6) 1.0×10^{-2} M	35.70	3.45
(7) 1.5×10^{-2} M	45.60	4.10

Figures 53 and 55 show the hysteresis of desorption in log-log Freundlich isotherm for the Lakewood sand and the Rockaway Stony loam. According to the log-log Freundlich isotherm of Cd adsorption-desorption on Lakewood sand, it is seen in Figure 53 and Figure 57 that there is apparent hysteresis of desorption between adsorption and desorption 1 (the first day of desorption after attaining the equilibrium adsorption for 2 days). However, there is no apparent hysteresis of desorption between equilibrium adsorption and desorption 1 on Rockaway Stony loam (Figure 55 and Figure 58). This may be due to the fact that it is harder to get equilibrium desorption on Rockaway Stony loam than on Lakewood sand. On the other hand, it is harder to release Cd from the Rockaway Stony loam than from the Lakewood sand. According to Figure 52-55, the Freundlich isotherm describes the adsorption-desorption processes well and has good fit for all data. Generally speaking, the correlation coefficient (r) is a useful tool for quantifying the relationship between two variables. The closer | r | is to 1, the more closely related the variables are. On the other hand, one variable can be predicted exactly from the other when | r | = 1. The Cd cumulative adsorption percentage on Rockaway stony loam is much higher than on the Lakewood sand (Table 7). Conversely, the cumulative Cd desorption percentage on Rockaway Stony loam is much less than on the Lakewood sand (Table 8). These may be due to the fact that the ECEC value, content of organic matter, and contents of Fe, Al, and Mn oxides on the Rockaway Stony loam are much greater than on the Lakewood sand.

CONCLUSIONS AND RECOMMANDATION

The Cd adsorption-desorption on the soil is complex and depends strongly on the soil components present. The wet-dry cycle treatment changes the desorption percentage of Cd on the two soils (the Rockaway Stony loam and the Lakewood sand). There is an associated increase of desorption percentage on the Lakewood sand, whereas a decrease in desorption percentage on the Rockaway Stony loam is observed.

The adsorption reaction is much faster than desorption reaction. More than 95 percent of Cd adsorption takes place within 1 hour and equilibrium adsorption of Cd is attained in one day; however, there is on an average of 85 percent of Cd to be desorbed after three days. The soil factors most responsible for Cd adsorption-desorption are pH, percent organic matter, ECEC, and metal oxides. Hysteresis is apparent in both the Rockaway Stony loam and the Lakewood sand. The desorption hysteresis is greater in the Rockaway Stony loam than in the Lakewood sand.

The sorption of Cd(II), Pb(II), and Cr(VI) as a function of soil characteristics and solution pH have been studied. The soils vary in their strength and capacity for metal binding. Different soils exhibit different absorption ability. Metal adsorption was highly pH dependent. The percent of Cd(II) and Pb(II) adsorbed increased with rising pH, whereas the adsorption of Cr(VI) decreased with rising pH. Based on these data, we have predicted the maximum concentration of metal which would be expected to be in a solution that was in contact with a soil having a given metal concentration and pH. It is possible that this predicted concentration is greater than that which would actually be observed. The overprediction could result from such phenomena as slow desorption. In that case, the overprediction would provide a measure of insurance when used as a soil standard. However, this insurance would be at the cost of greater levels of soil remediation or lower levels of introduction of metals. It is important to ascertain the magnitude of the difference between the sorption and desorption values. We have been determining desorption in both batch systems and in column studies so that the results can be easily applied to field conditions.

45

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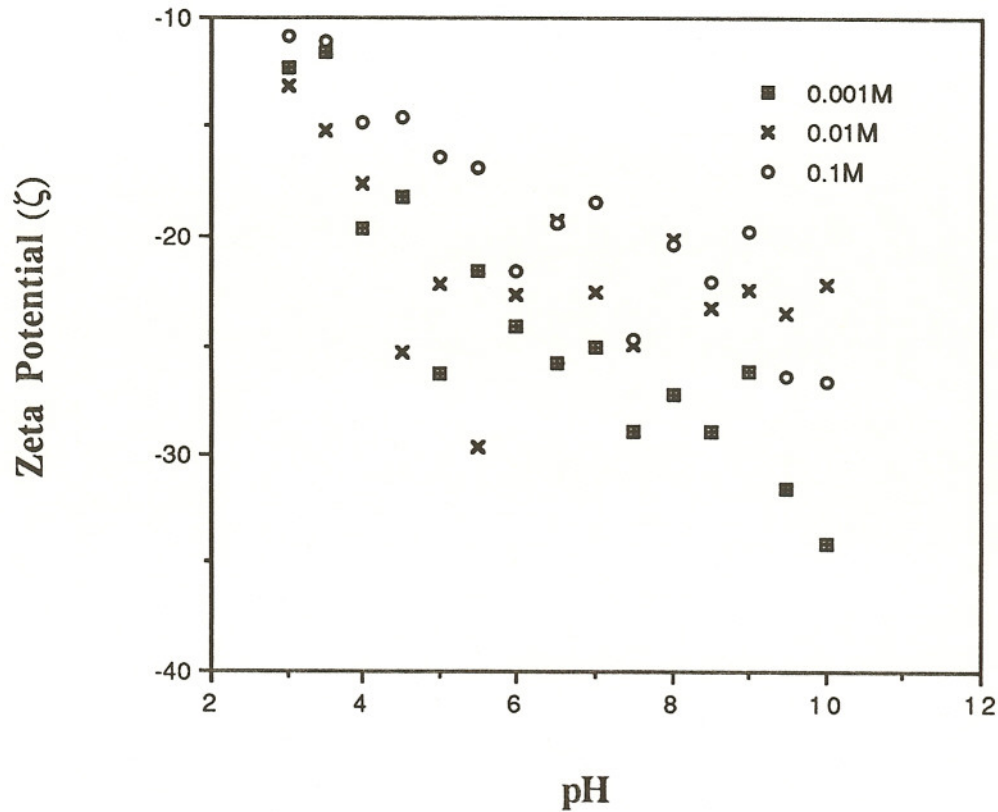
Figure 1. Zeta potential for Birdsboro silty loam in 0.1, 0.01, and 0.001 M NaNO₃.
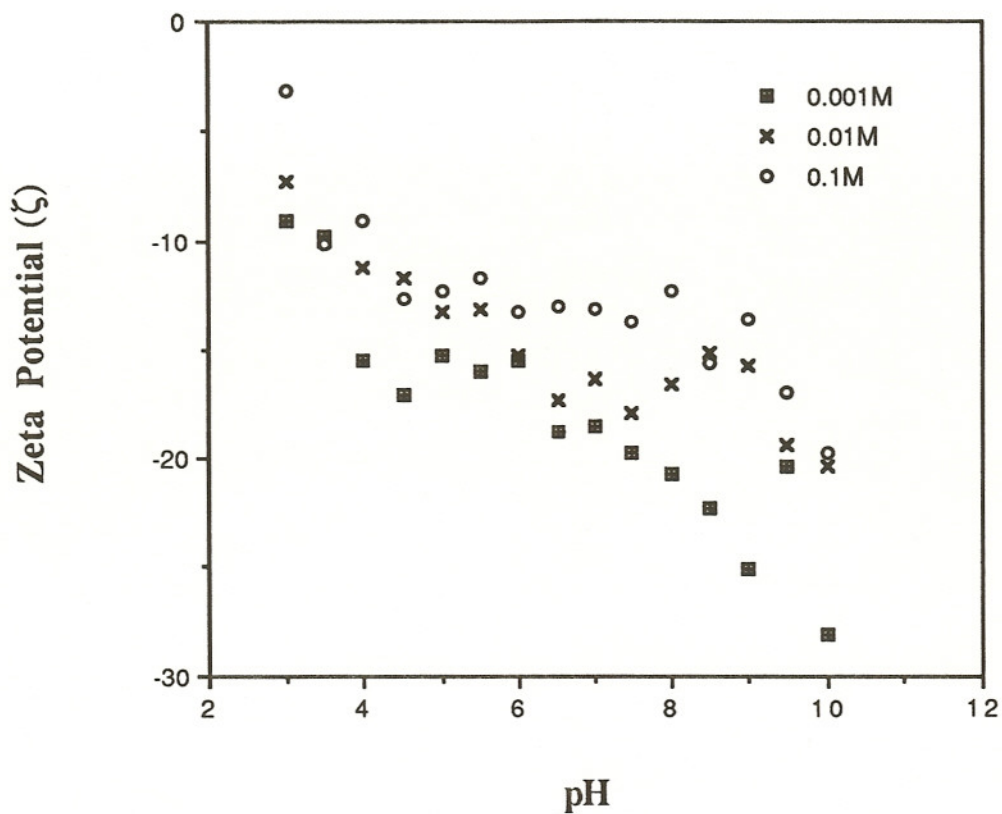
Figure 2. Zeta potential for Boonton Bergen County soil in 0.1, 0.01, and 0.00
M NaNO₃.
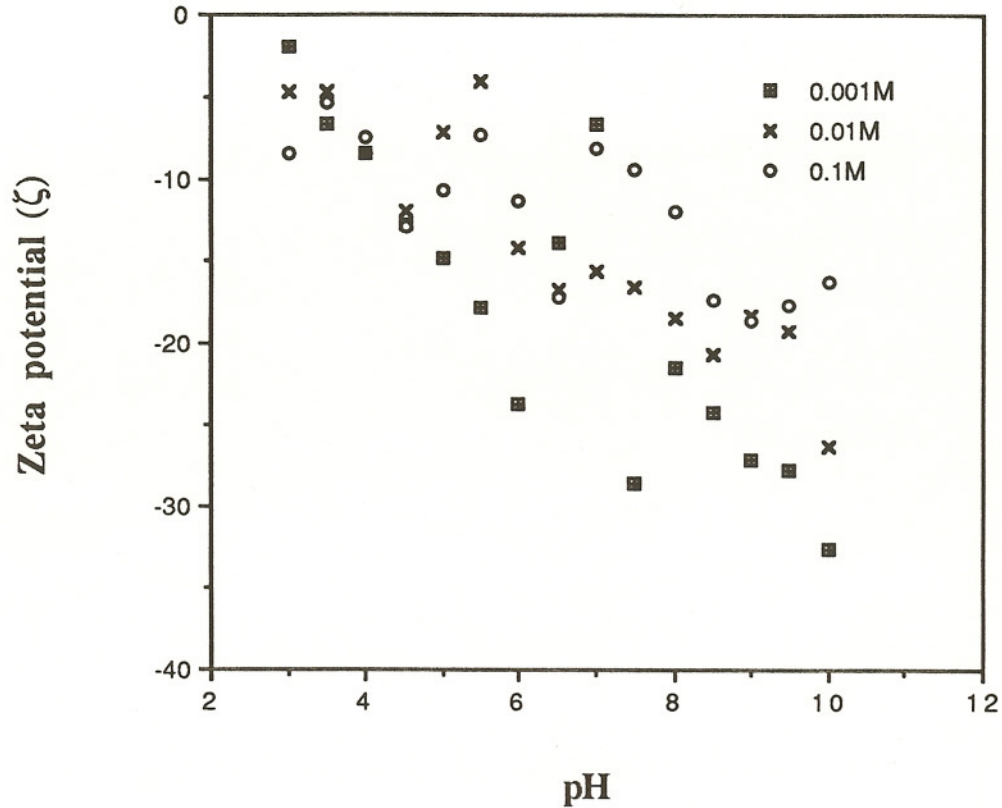
Figure 3. Zeta potential for Boonton Union County soil in 0.1, 0.01, and 0.00
M NaNO₃.
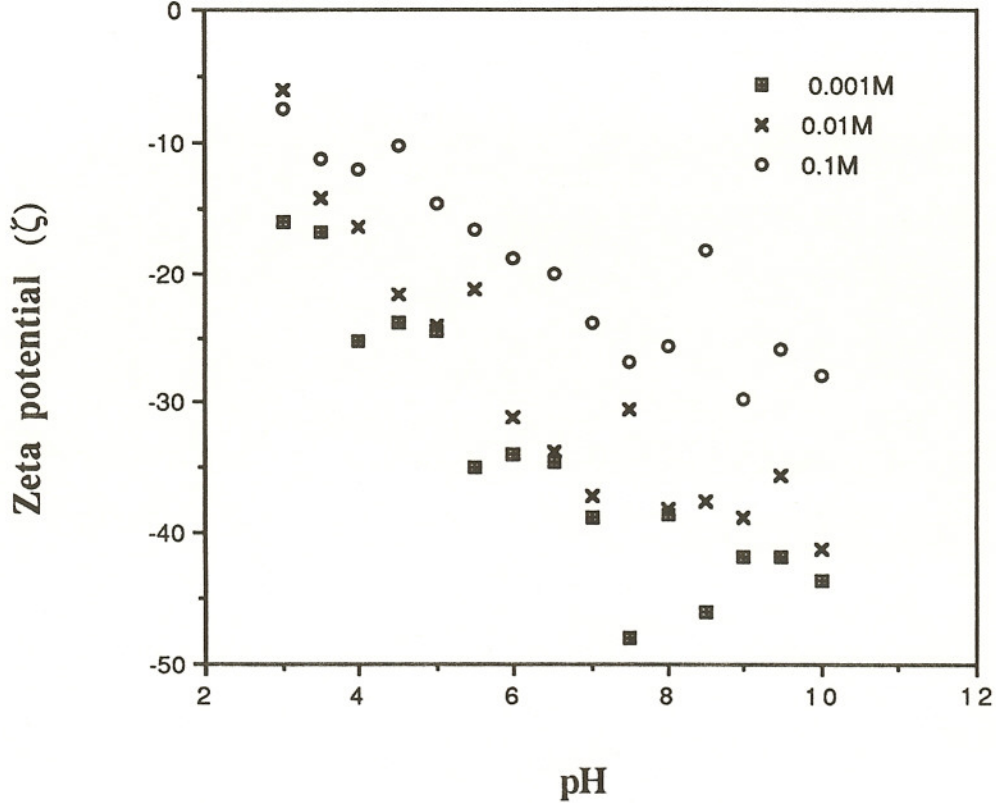
Figure 4. Zeta potential for Downer loamy sand in 0.1, 0.01, and 0.001 M NaNO$_3$.
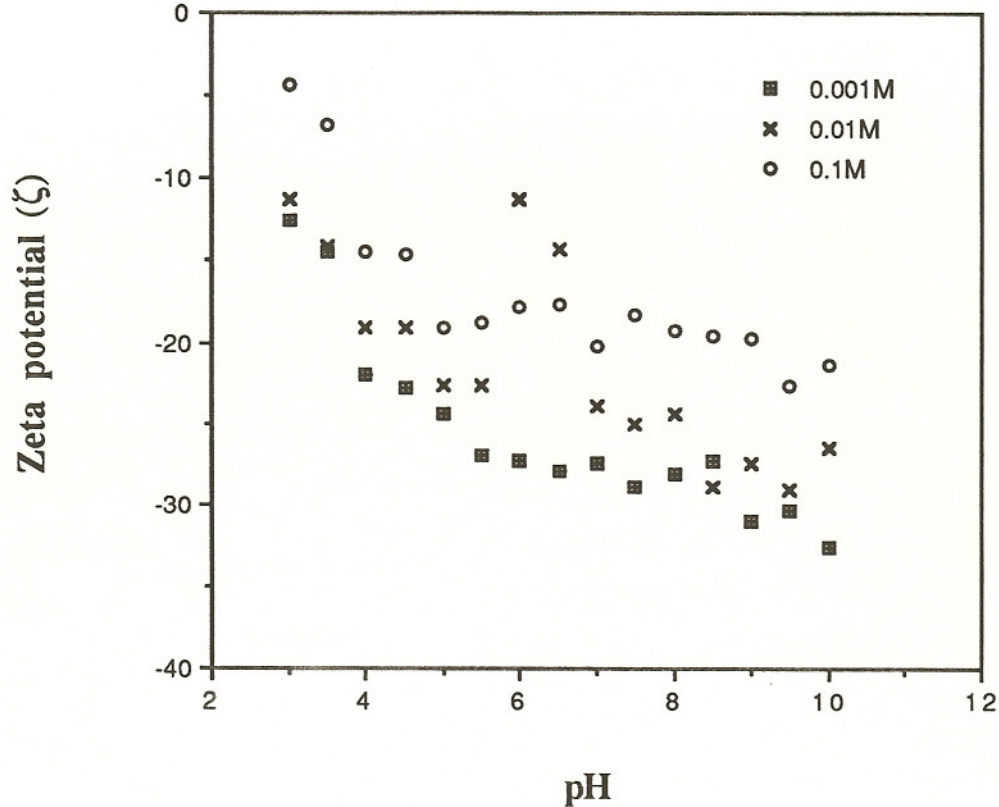
Figure 5. Zeta potential for Dunellen sandy loam in 0.1, 0.01, and 0.001 M NaNO$_3$.
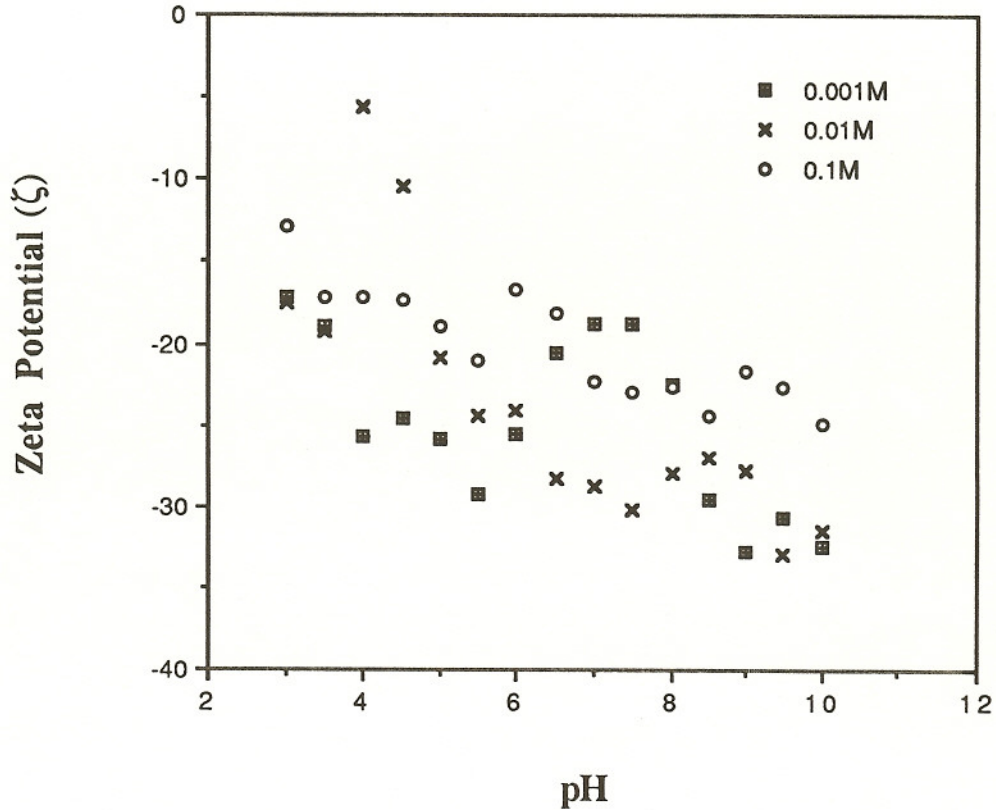
Figure 6. Zeta potential for fill material dredged from Delaware River in 0.1, 0.01, and 0.001 M NaNO₃.
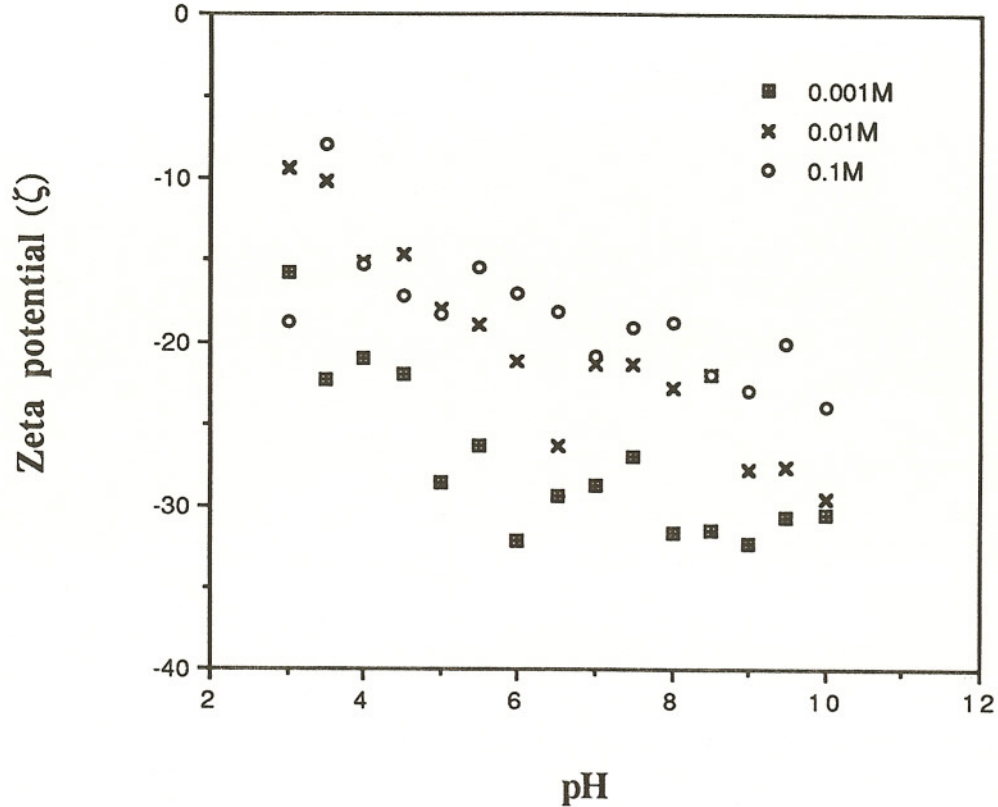
Figure 7. Zeta potential for Freehold sandy loam (surface) in 0.1, 0.01, and 0.001 M NaNO$_3$.
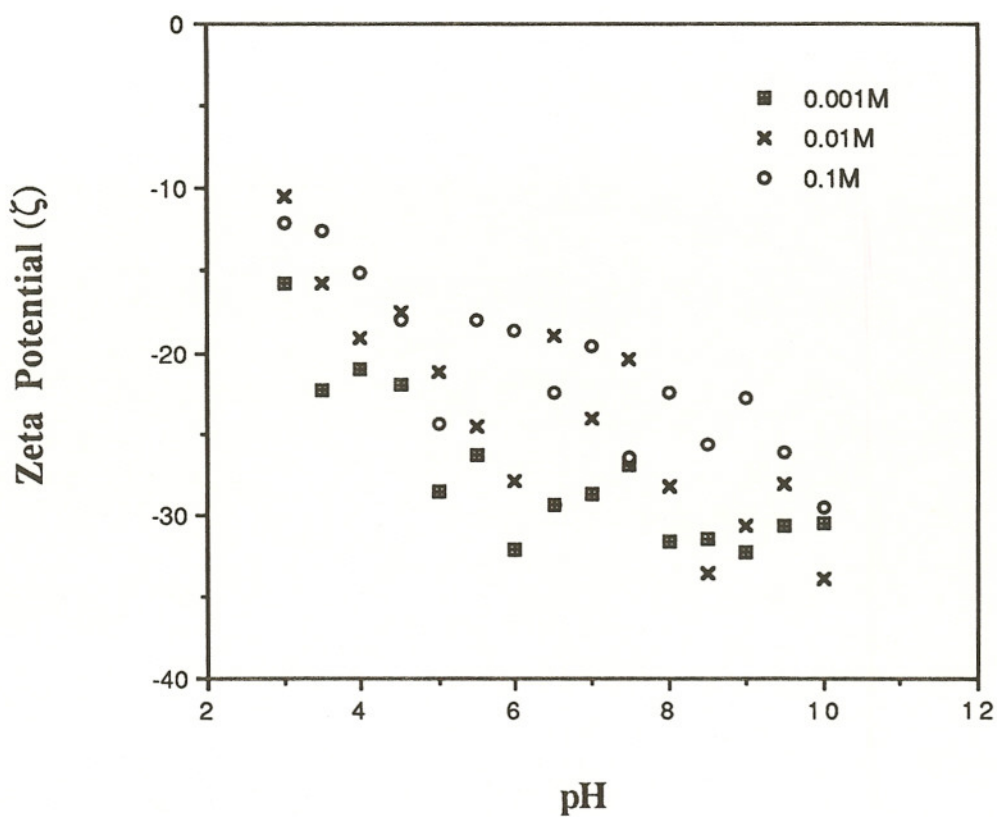
Figure 8. Zeta potential for Freehold sandy loam (subsurface) in 0.1, 0.01, and 0.001 M NaNO$_3$.
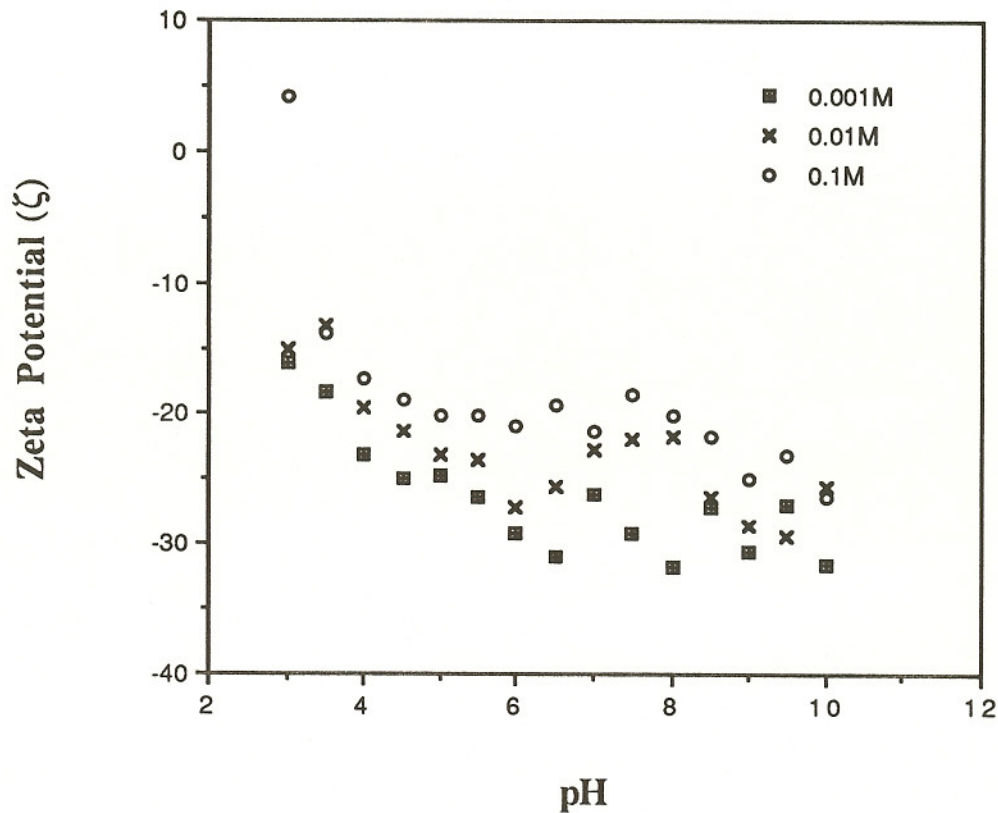
Figure 9. Zeta potential for Hazen gravelly loam in 0.1, 0.01, and 0.001 M NaNO$_3$.
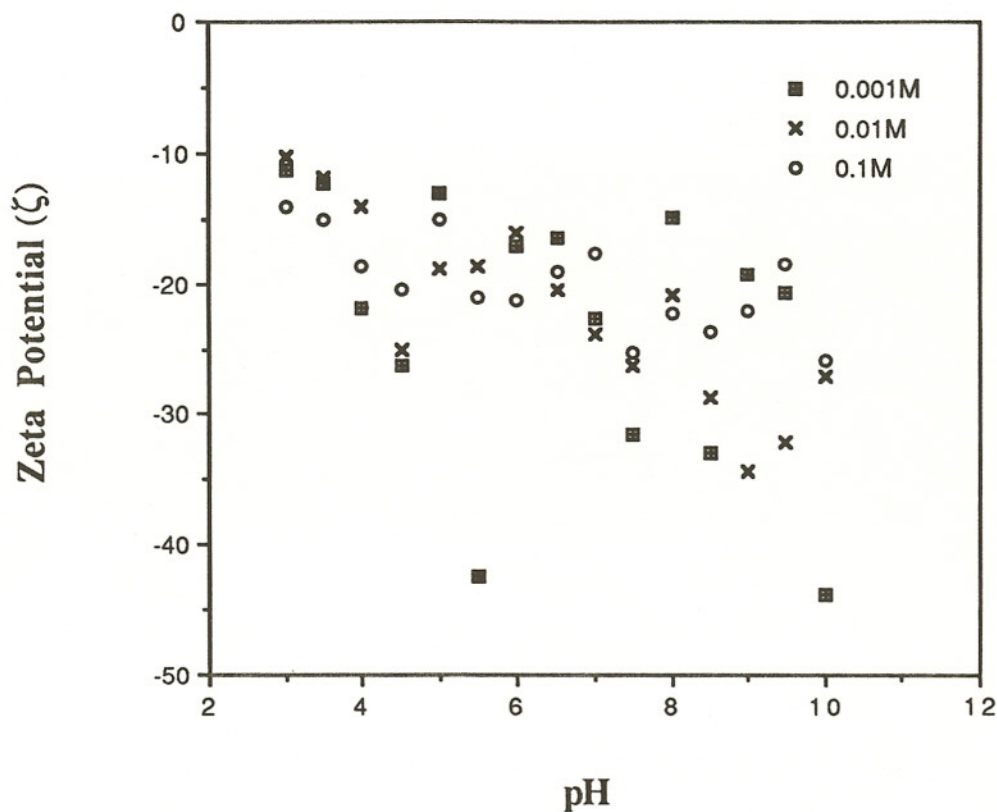
Figure 10. Zeta potential for Lakewood sand in 0.1, 0.01, and 0.001 M NaNO$_3$.
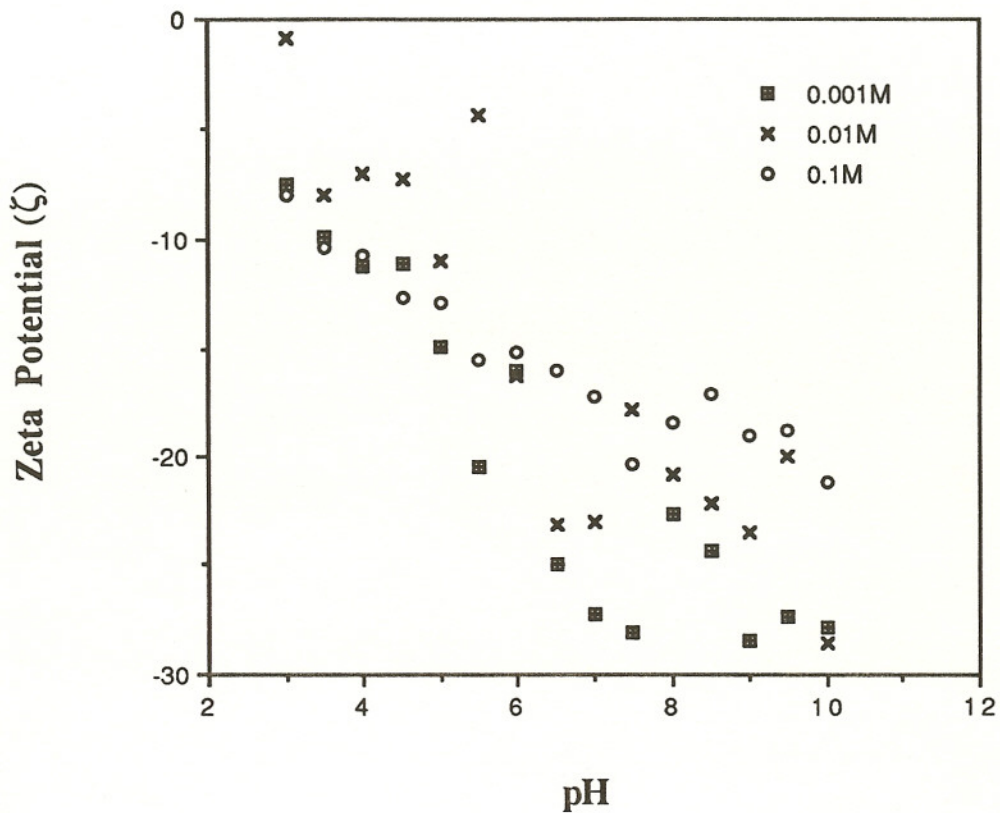
Figure 11. Zeta potential for Rockaway stony loam in 0.1, 0.01, and 0.001 M NaNO$_3$.
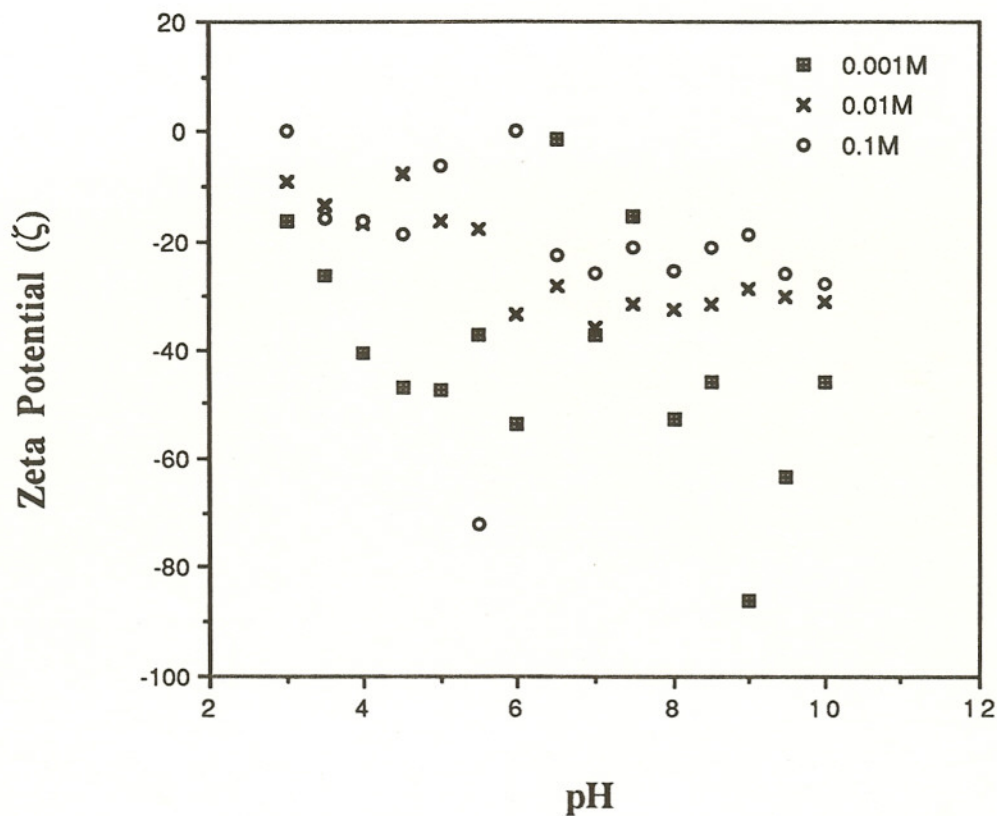
Figure 12. Zeta potential for Sassafras sandy loam in 0.1, 0.01, and 0.001 M
NaNO₃.
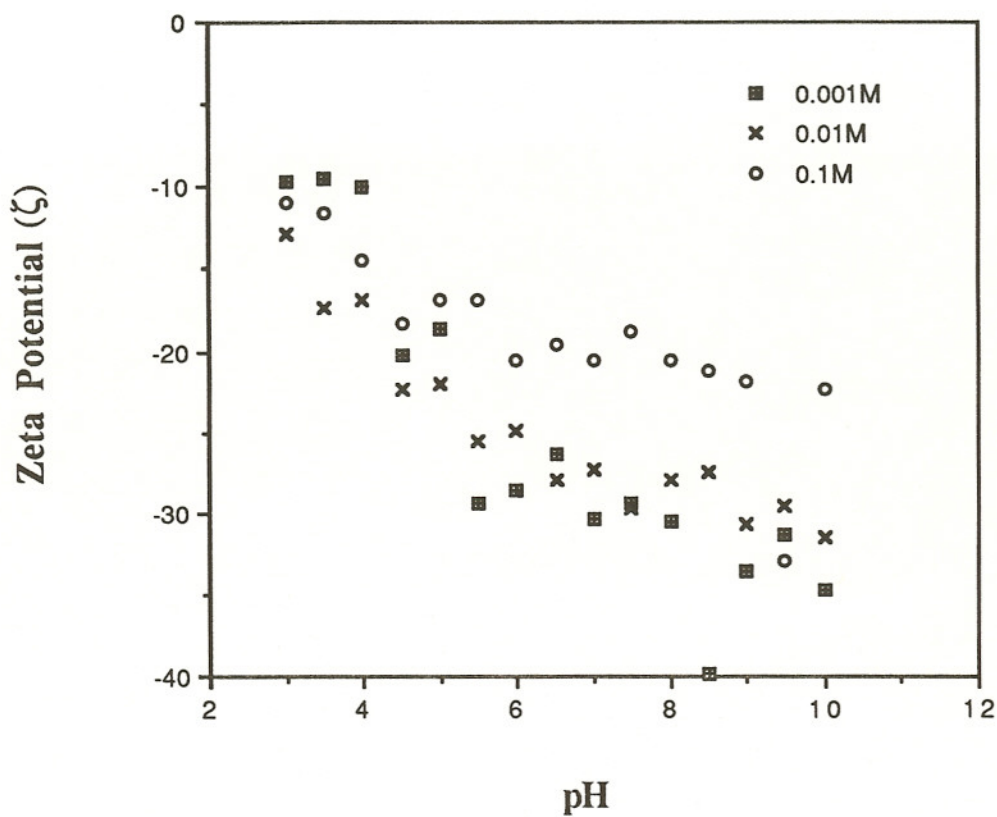
Figure 13. Zeta potential for Penn silt loam in 0.1, 0.01, and 0.001 M NaNO$_3$
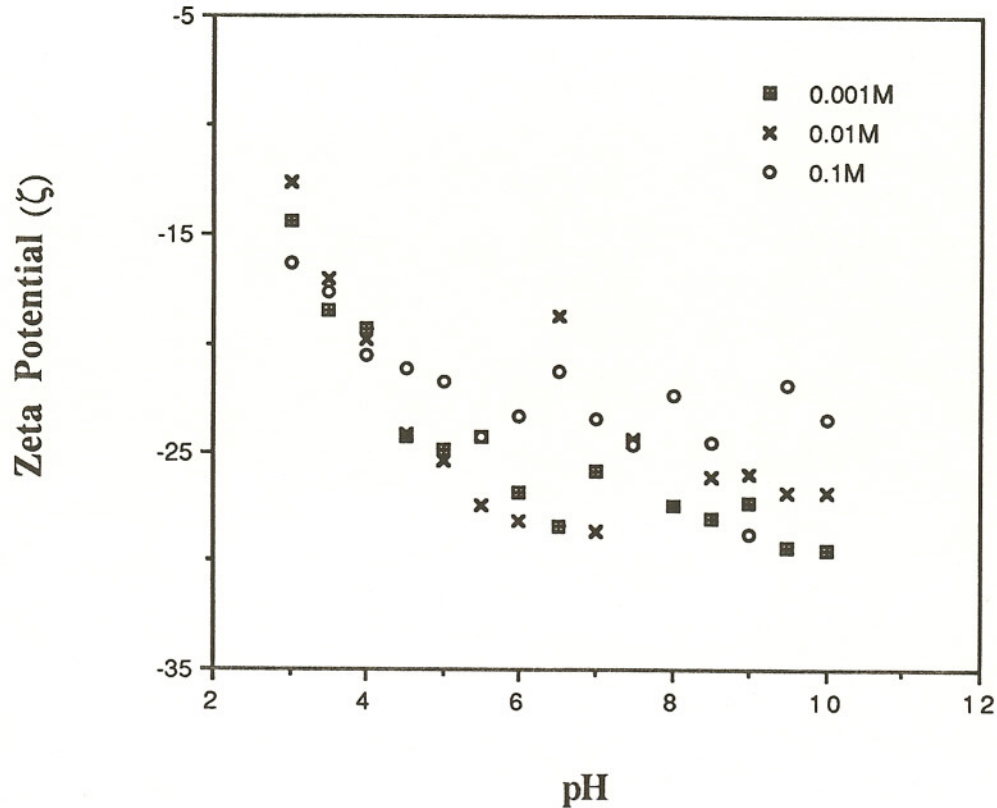
Figure 14. Zeta potential for Washington loam in 0.1, 0.01, and 0.001 M NaNO$_3$.
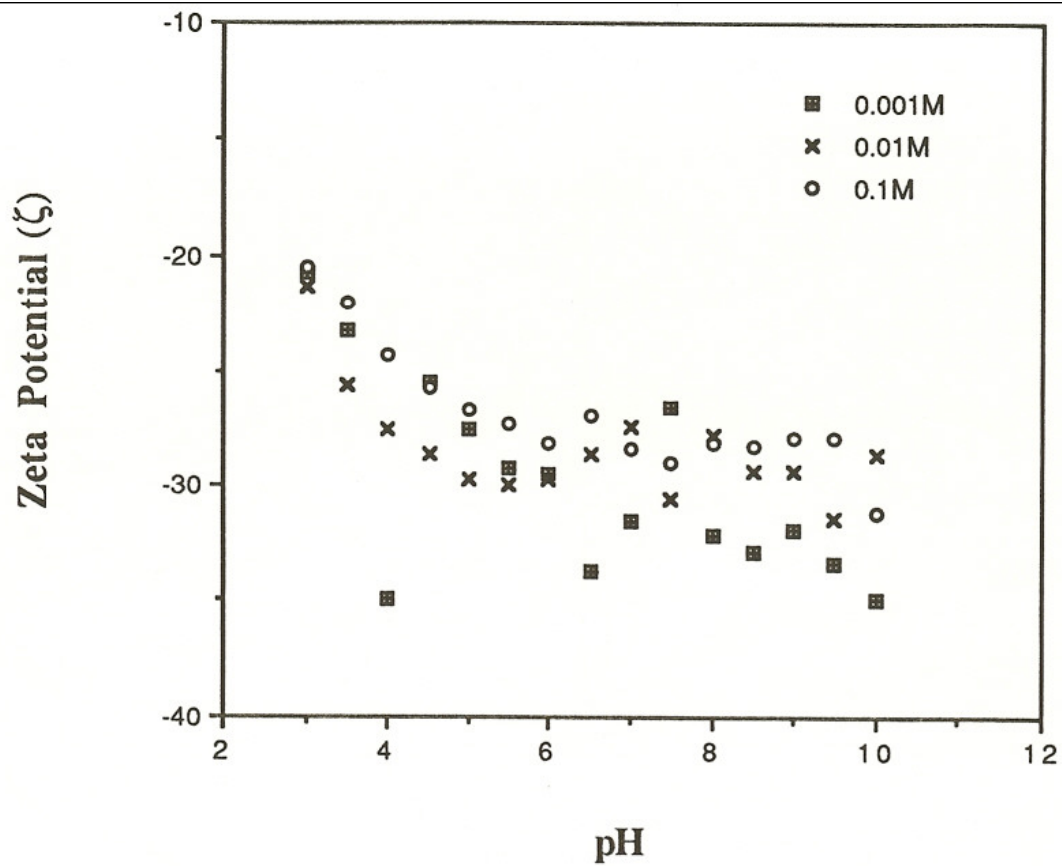
Figure 15. Zeta potential for Whippany silty clay loam in 0.1, 0.01, and 0.001 M NaNO$_3$.
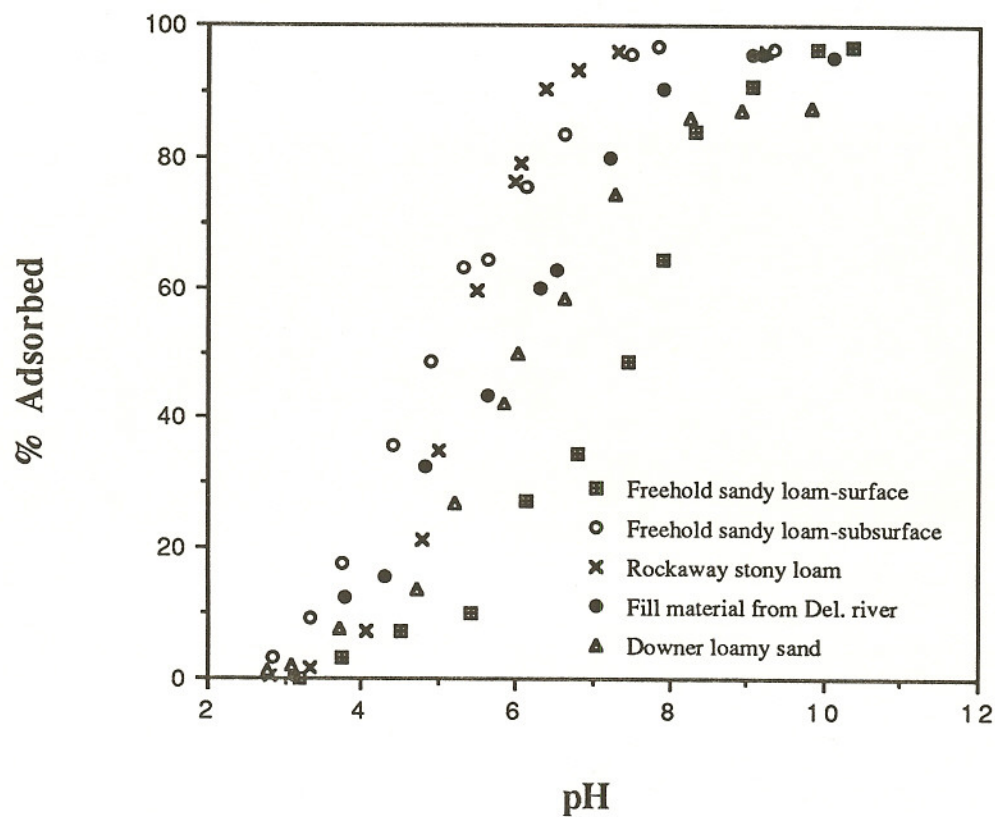
Figure 16. Adsorption of 1 x 10⁻⁴ M cadmium onto Freehold sandy loam (surface), Freehold sandy loam (subsurface), Rockaway stony loam, Fill material dredged from Delaware River, and Downer loamy sand. Soil:water = 1g/100mL; I = 0.01 M NaNO₃; T = 25°C.

Figure 17. Adsorption coefficient (Kd) for the adsorption of 1 x 10^{-4} M cadmium onto Freehold sandy loam (surface), Freehold sandy loam (subsurface), Rockaway stony loam, Fill material dredged from Delaware River, and Downer loamy sand. Soil:water = 1g/100mL; I = 0.01 M $NaNO_3$; T = 25°C.

Figure 18. The maximum permissible level of cadmium for Freehold   sandy loam
(surface), Freehold sandy loam (subsurface),   Rockaway stony loam,
Fill material dredged from   Delaware River, and Downer loamy sand
for 1×10^{-4} M   cadmium.
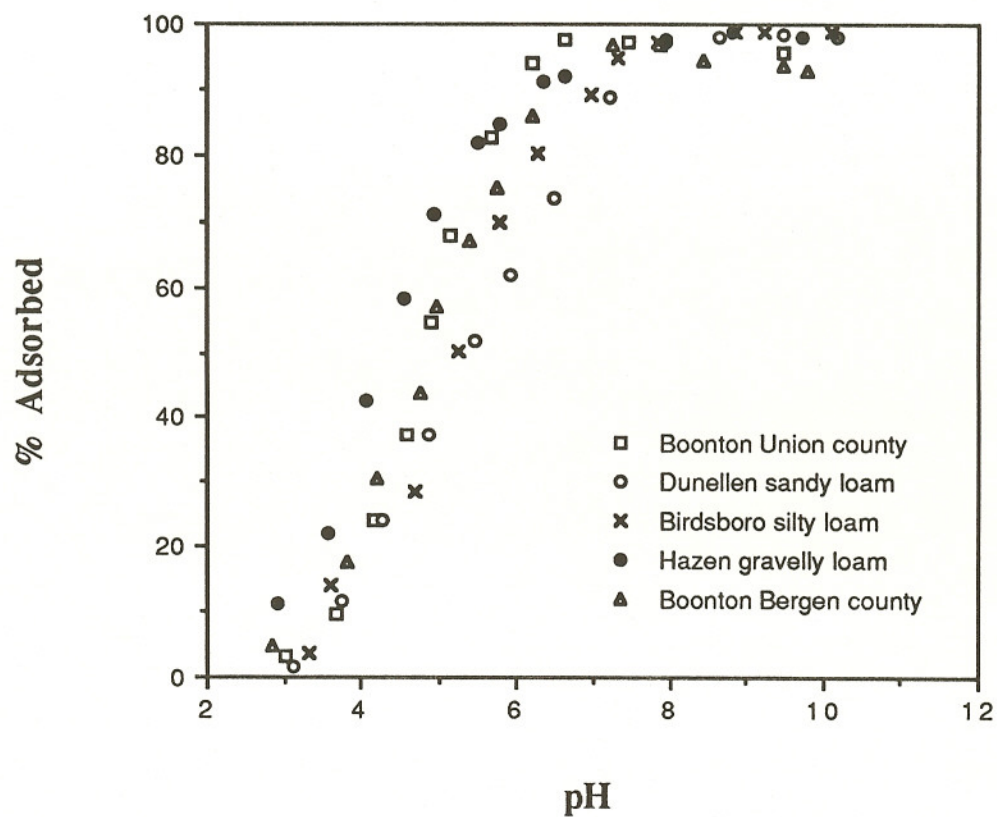
Figure 19. Adsorption of 1×10^{-4} M cadmium onto Boonton Union County soil, Dunellen sandy loam, Birdsboro silt loam, Hazen gravelly loam, and Boonton Bergen County soil. Soil:water = 1g/100mL; I = 0.01 M NaNO$_3$; T = 25°C.
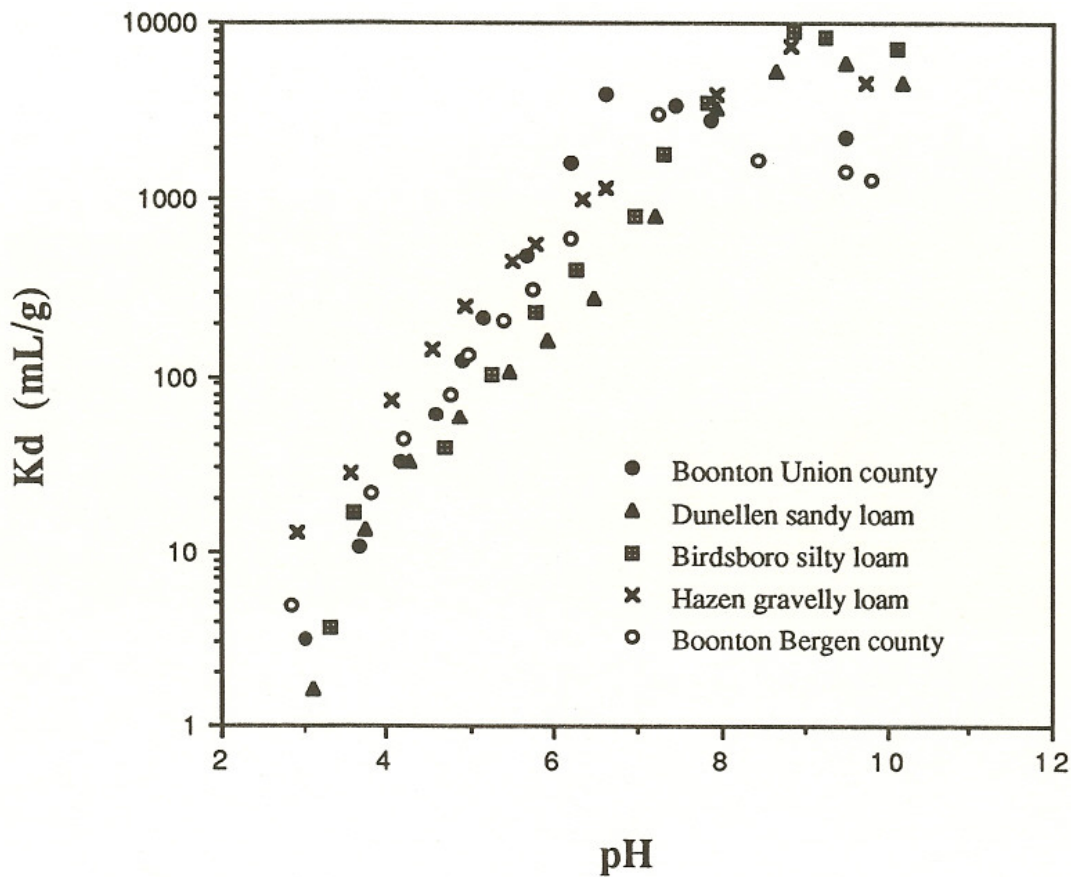
Figure 20. Adsorption coefficient (Kd) for the adsorption of 1 x 10^{-4} M cadmium onto Boonton Union County soil, Dunellen sandy loam, Birdsboro silt loam, Hazen gravelly loam, and Boonton Bergen County soil. Soil:water = 1g/100mL; I = 0.01 M NaNO3; T = 25°C.
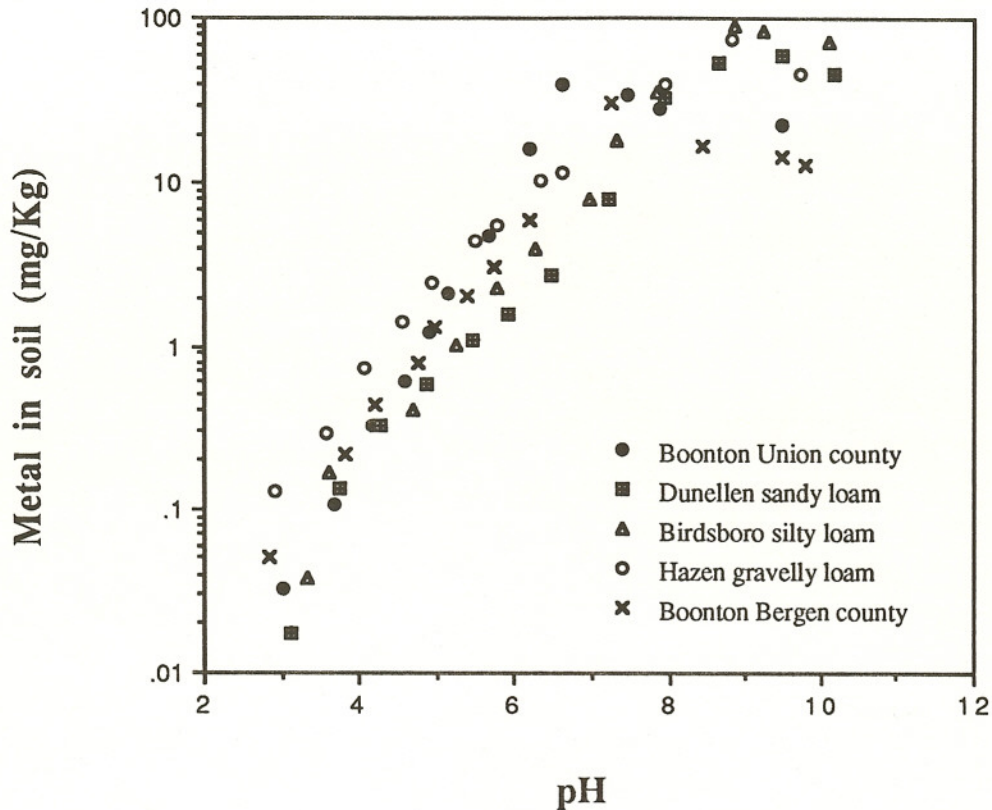
Figure 21. The maximum permissible level of cadmium for   Boonton Union County soil, Dunellen sandy loam,   Birdsboro silt loam, Hazen gravelly loam, and Boonton   Bergen County soil for 1x 10^{-4} M cadmium.
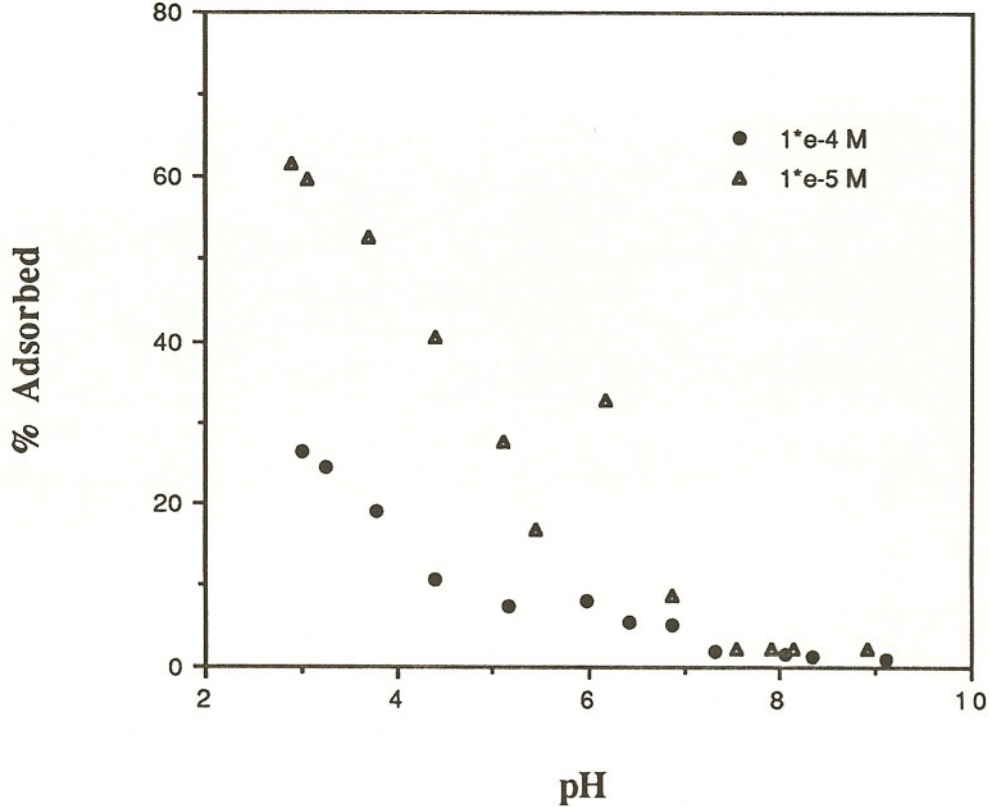
Figure 22. Adsorption of hexavalent chromium onto Birdsboro silt loam Soil:water = 1g/100mL; I = 0.01 M NaNO3; T = 25°C.
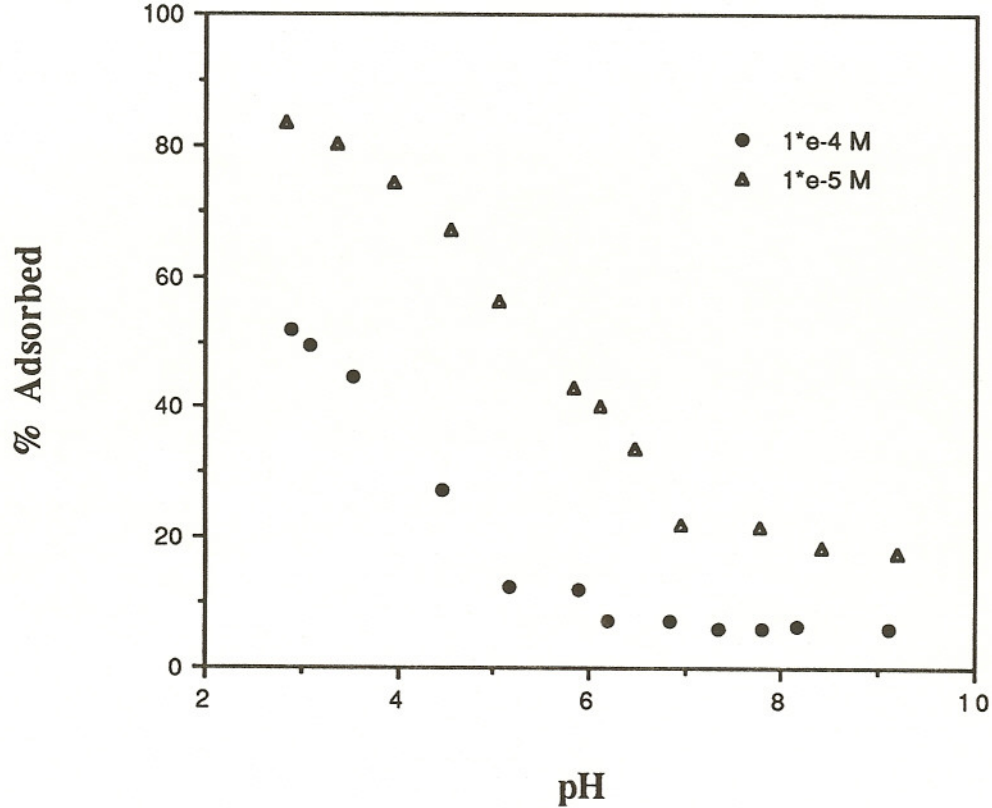
Figure 23. Adsorption of hexavalent chromium onto Boonton Bergen County soil. Soil:water = 1g/100mL; I = 0.01 M NaNO3; T = 25°C.
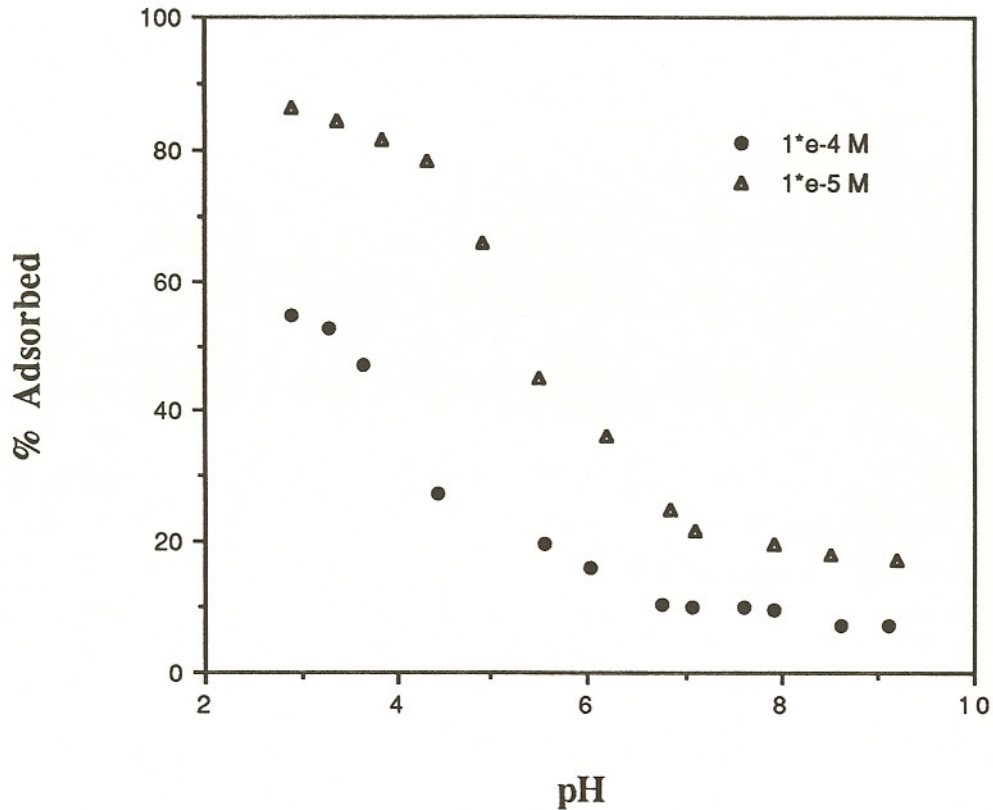
Figure 24. Adsorption of hexavalent chromium onto Boonton Union County soil.
Soil:water = 1g/100mL; I = 0.01 M NaNO3; T = 25°C.
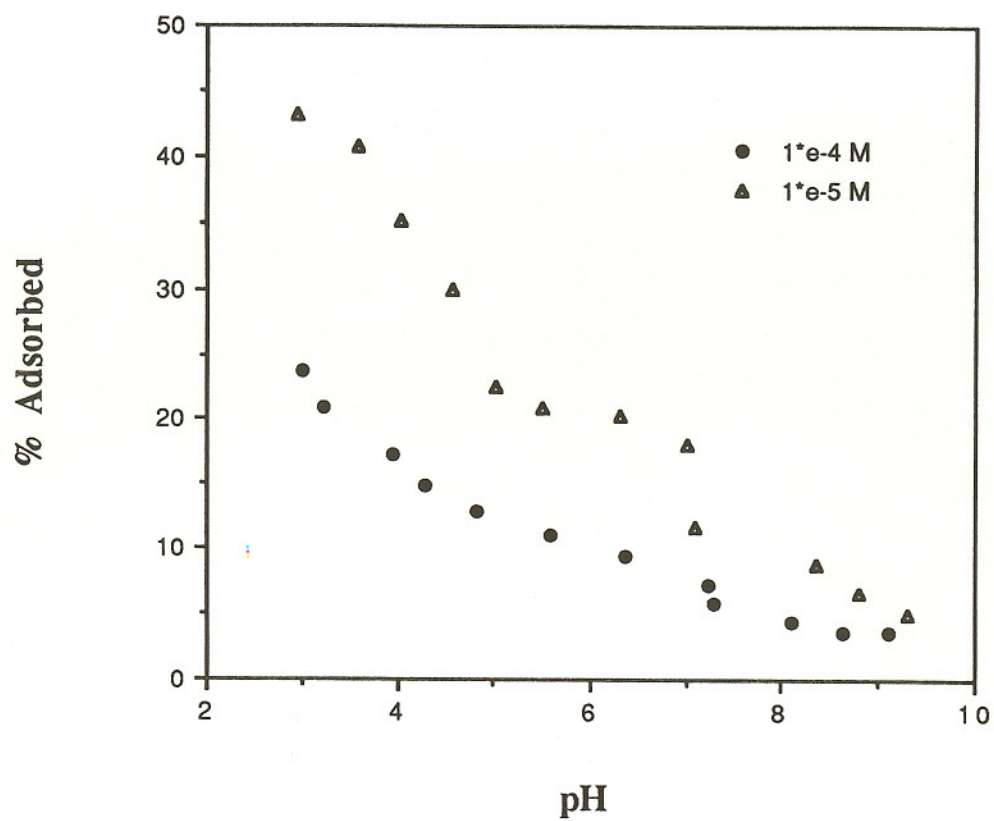
Figure 25. Adsorption of hexavalent chromium onto Downer loamy sand. Soil:water = 1g/100mL; I = 0.01 M NaNO3; T = 25°C.
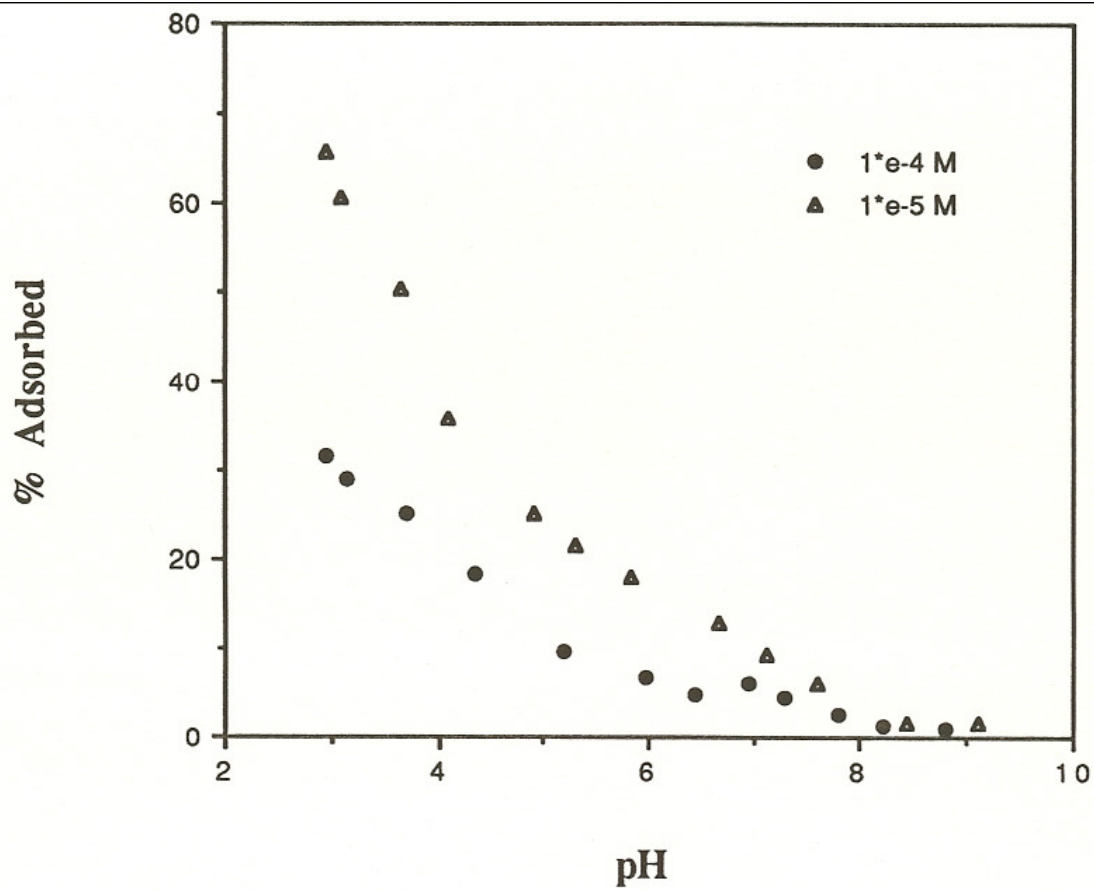
Figure 26. Adsorption of hexavalent chromium onto Dunellen sandy loam. Soil:water = 1g/100mL; I = 0.01 M NaNO3; T = 25°C.
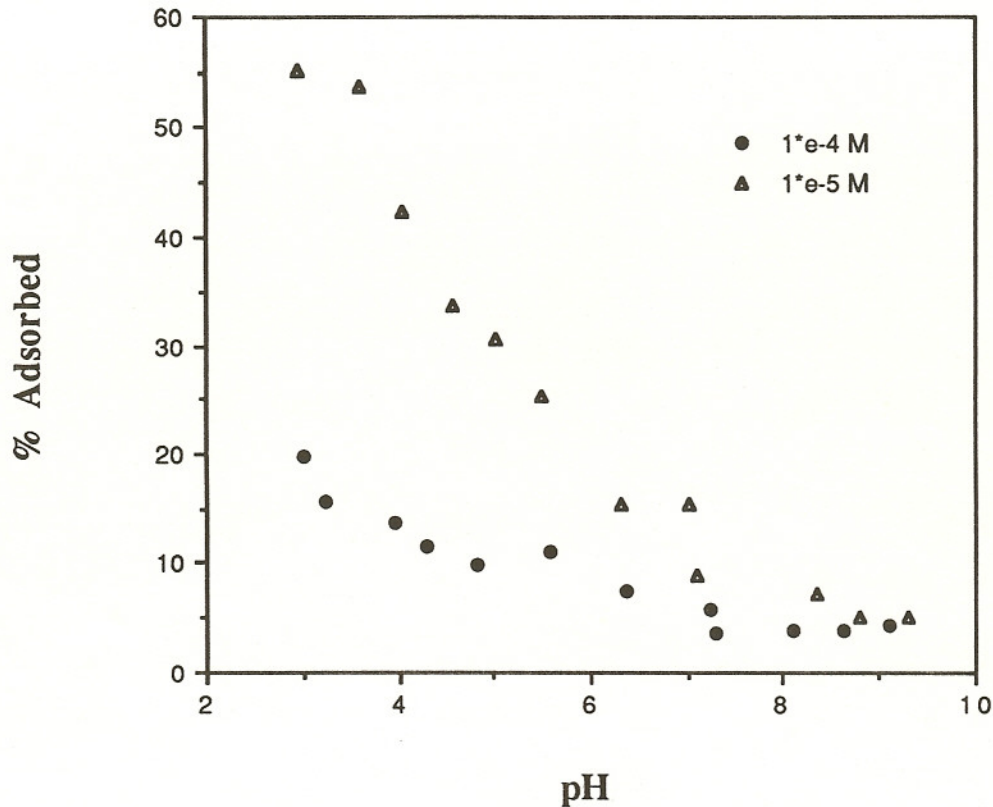
Figure 27. Adsorption of hexavalent chromium onto fill material dredged from the Delaware River. Soil:water = 1g/100mL; I = 0.01 M NaNO$_3$; T = 25°C.

79
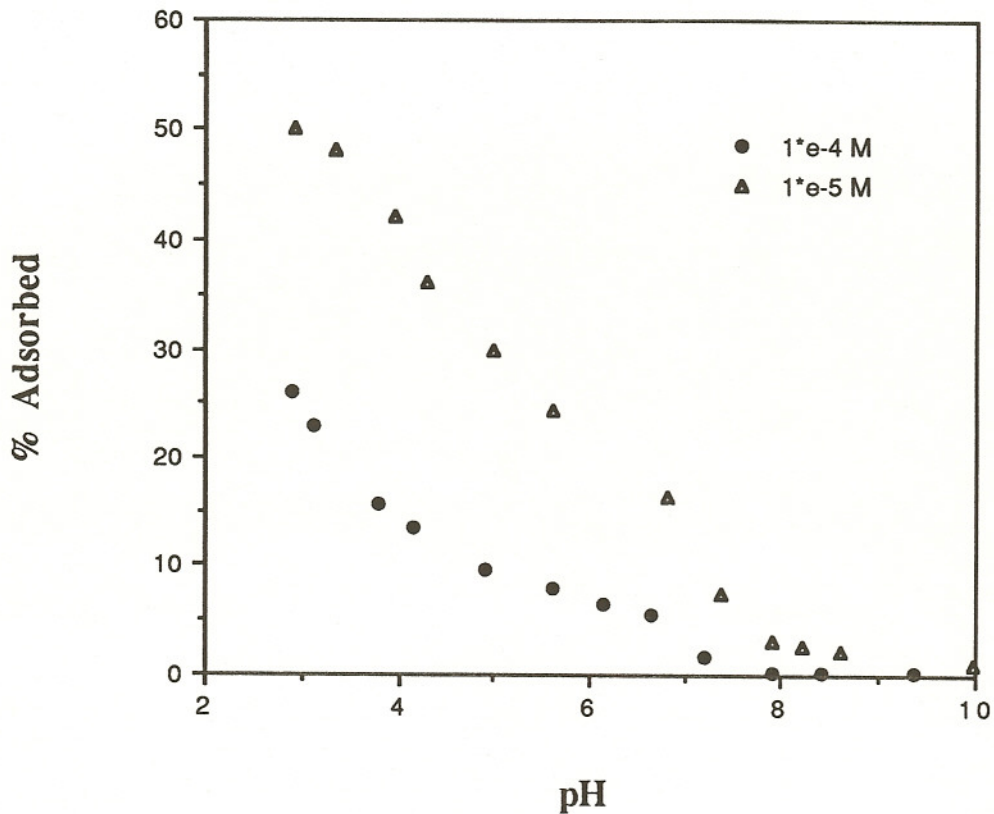
Figure 28. Adsorption of hexavalent chromium onto Freehold sandy loam (surface). Soil:water = 1g/100mL; I = 0.01 M NaNO$_3$; T = 25°C.
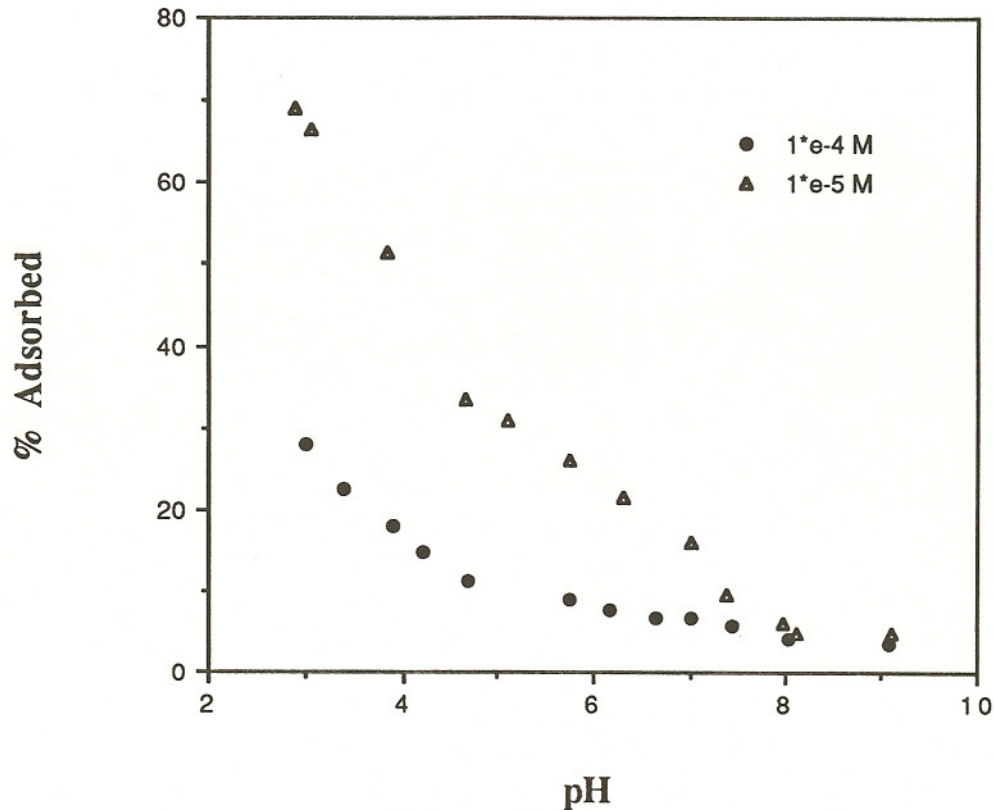
Figure 29. Adsorption of hexavalent chromium onto Freehold sandy loam (subsurface). Soil:water = 1g/100mL; I = 0.01 M NaNO$_3$; T = 25°C.
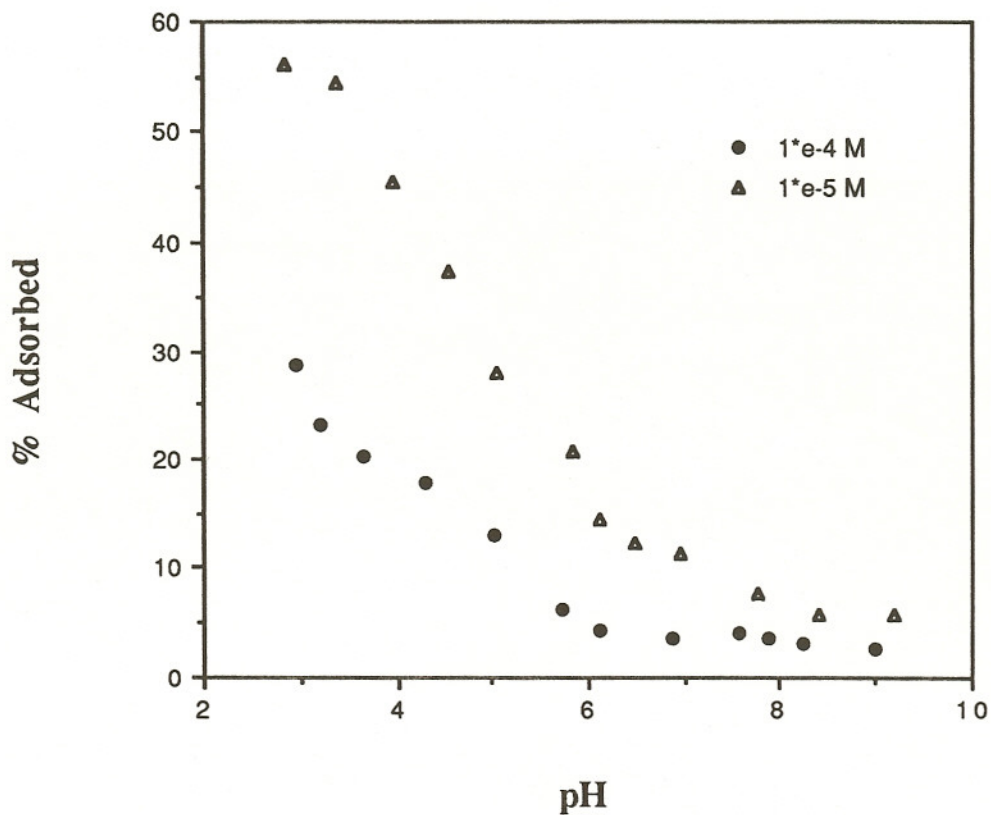
Figure 30. Adsorption of hexavalent chromium onto Hazen gravelly loam Soil:water = 1g/100mL; I = 0.01 M NaNO$_3$; T = 25°C.
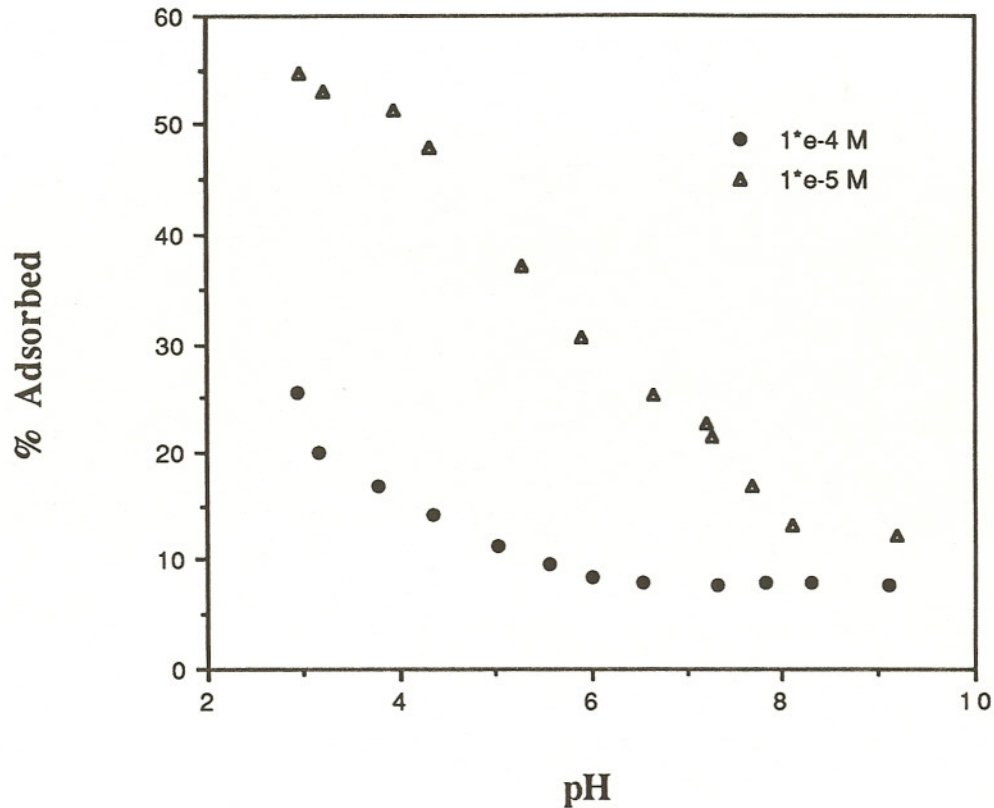
Figure 31. Adsorption of hexavalent chromium onto Lakewood sand. Soil:water = 1g/100mL; I = 0.01 M NaNO₃; T = 25°C.
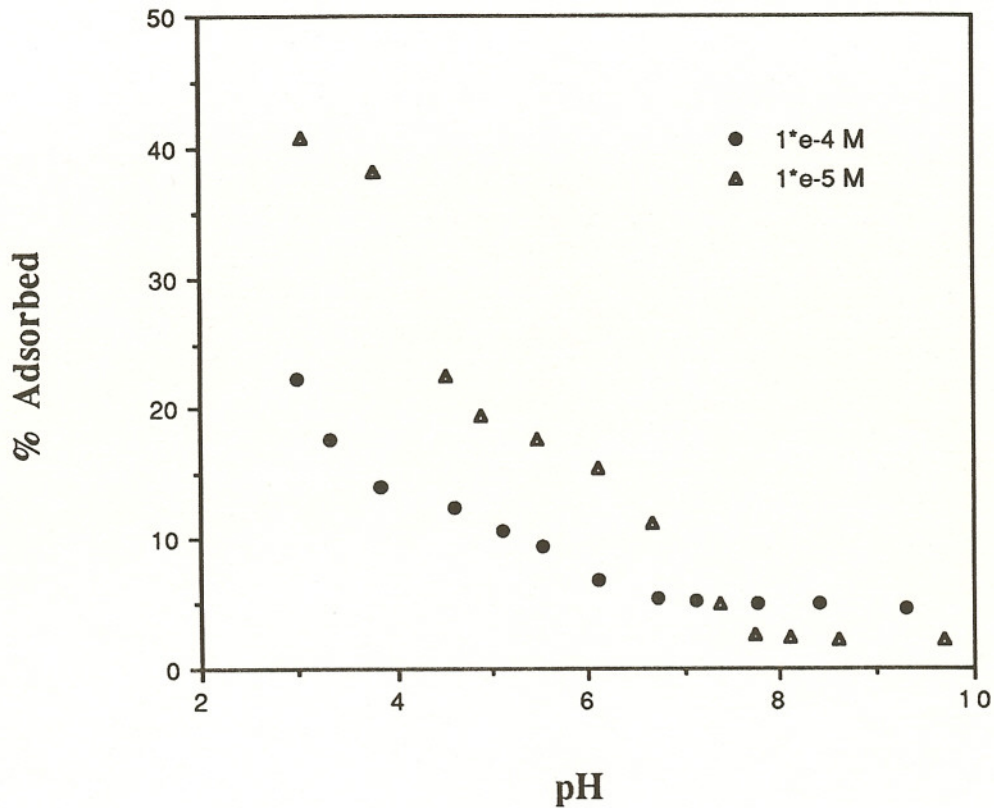
Figure 32. Adsorption of hexavalent chromium onto Penn silt loam. Soil:water 1g/100mL; I = 0.01 M NaNO₃; T = 25°C.
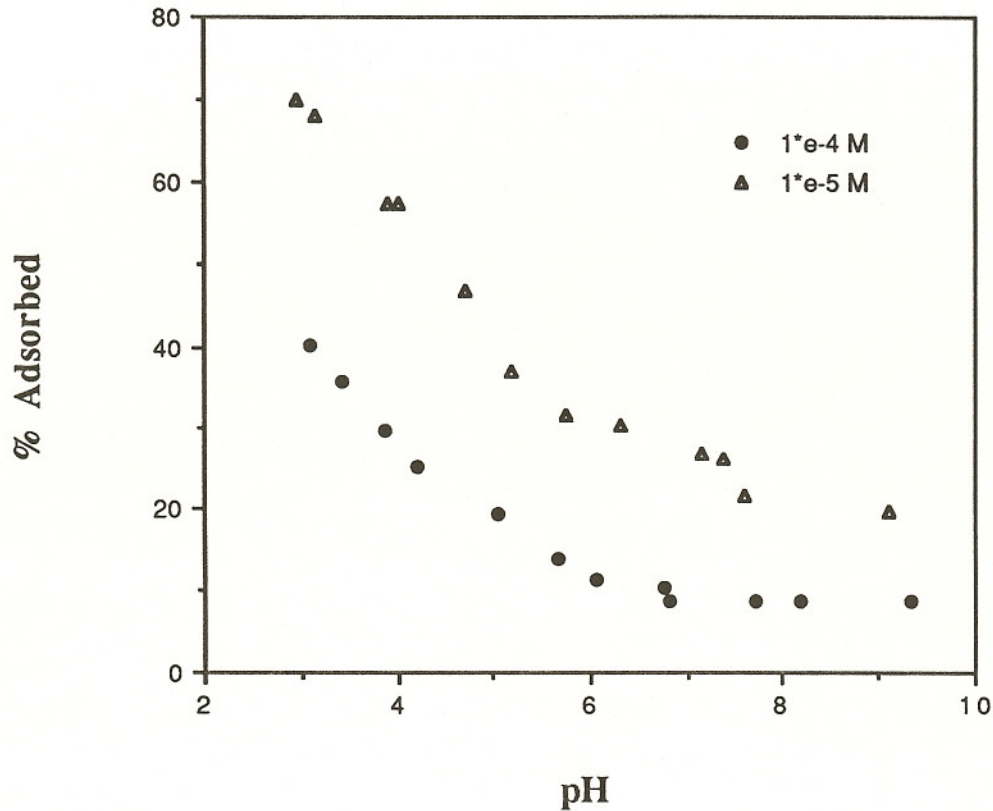
Figure 33. Adsorption of hexavalent chromium onto Rockaway stony loam. Soil:water = 1g/100mL; I = 0.01 M NaNO3; T = 25°C.
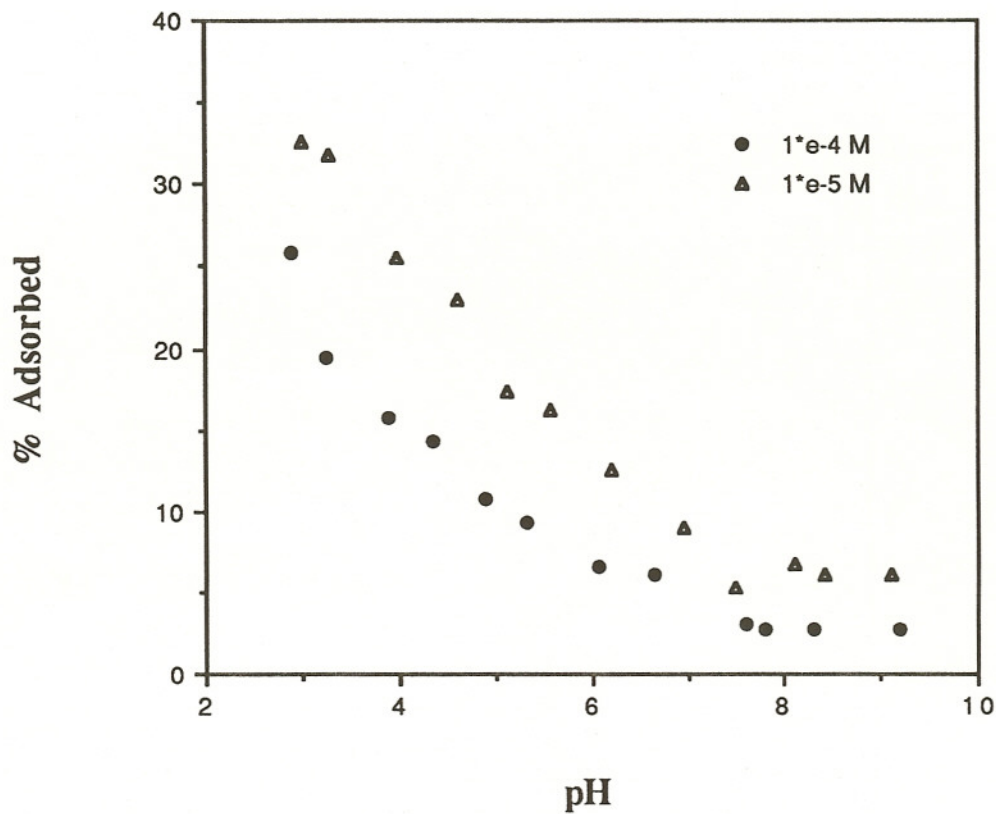
Figure 34. Adsorption of hexavalent chromium onto Sassafras sandy loam. Soil:water = 1g/100mL; I = 0.01 M NaNO$_3$; T = 25°C.
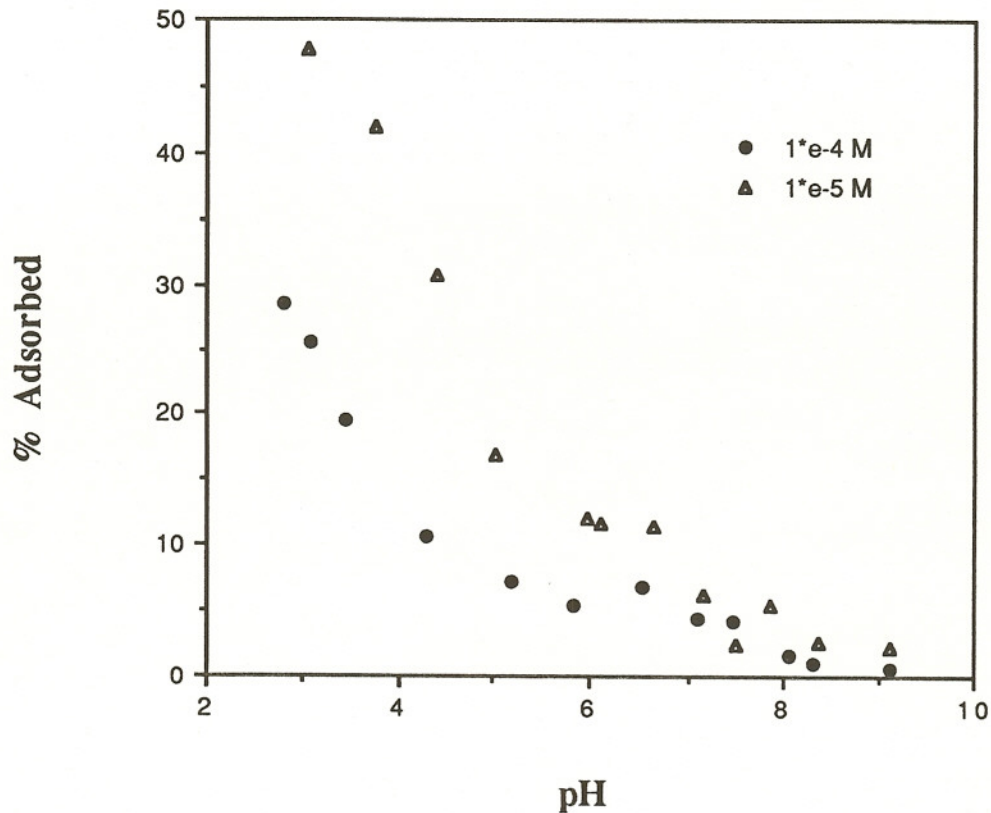
Figure 35. Adsorption of hexavalent chromium onto Washington loam. Soil:water = 1g/100mL; I = 0.01 M NaNO$_3$; T = 25°C.
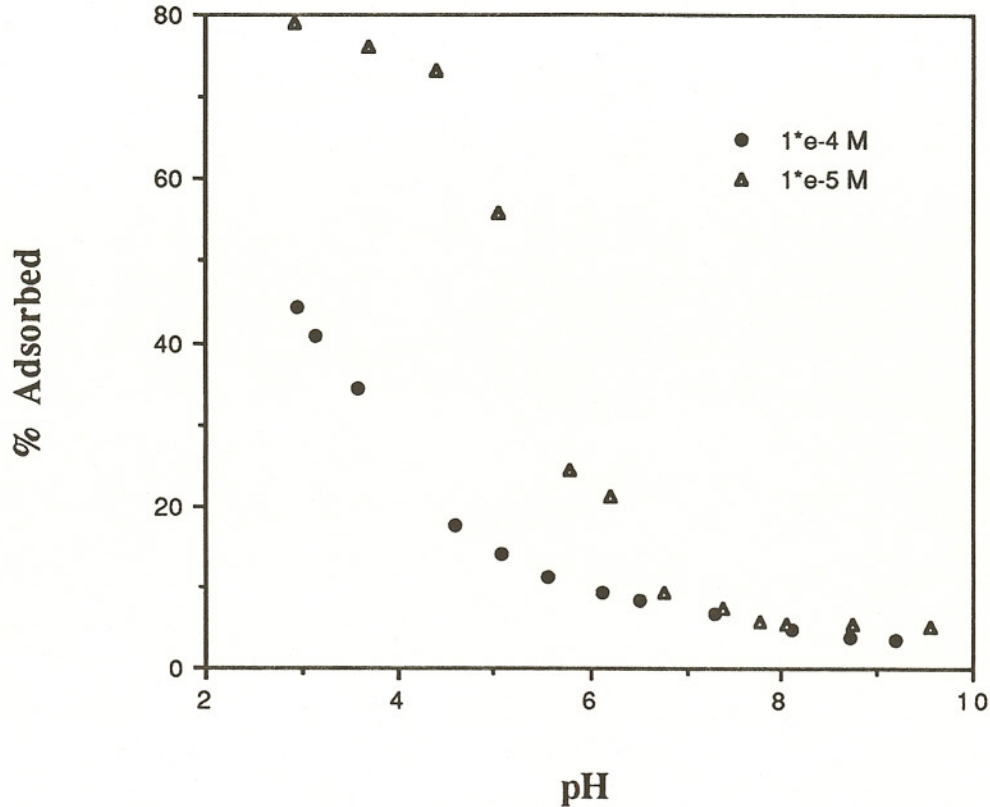
Figure 36. Adsorption of hexavalent chromium onto Whippany silty clay loam. Soil:water = 1g/100mL; I = 0.01 M NaNO₃; T = 25°C.
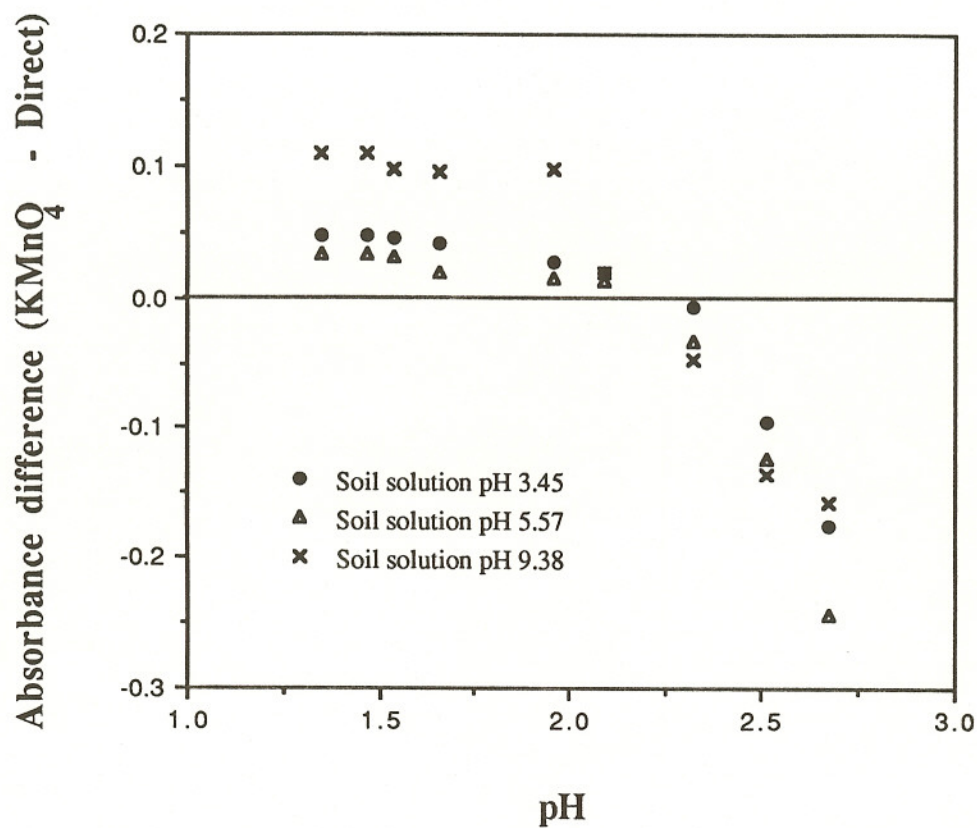
Figure 37. Absorbance difference of hexavalent chromium as a function of analysis pH for KMnO₄ procedure minus directly determined procedure for Freehold sandy loam (subsurface), at three different soil solution pH values.
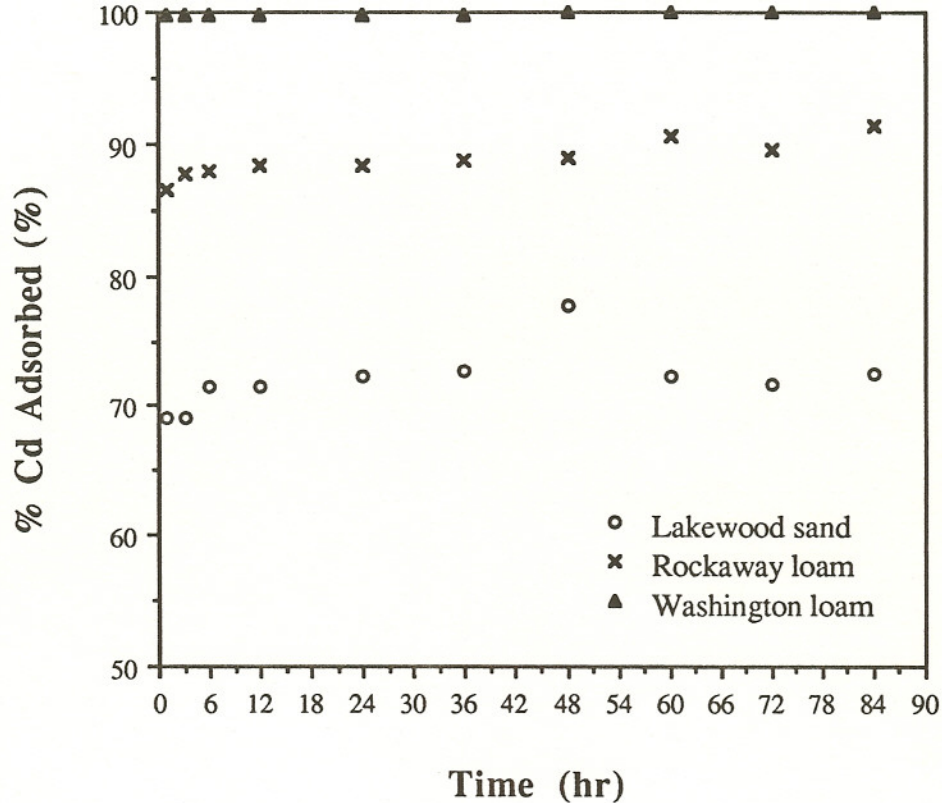
Figure 38 Cadmium adsorption on three different soils at pH 5±0.05. Soil:water = 15g/15mL; I = 0.1 M NaNO$_3$; T = 25^{0}C; C$_0$ = 8×10^{-5} M Cd solution.

90
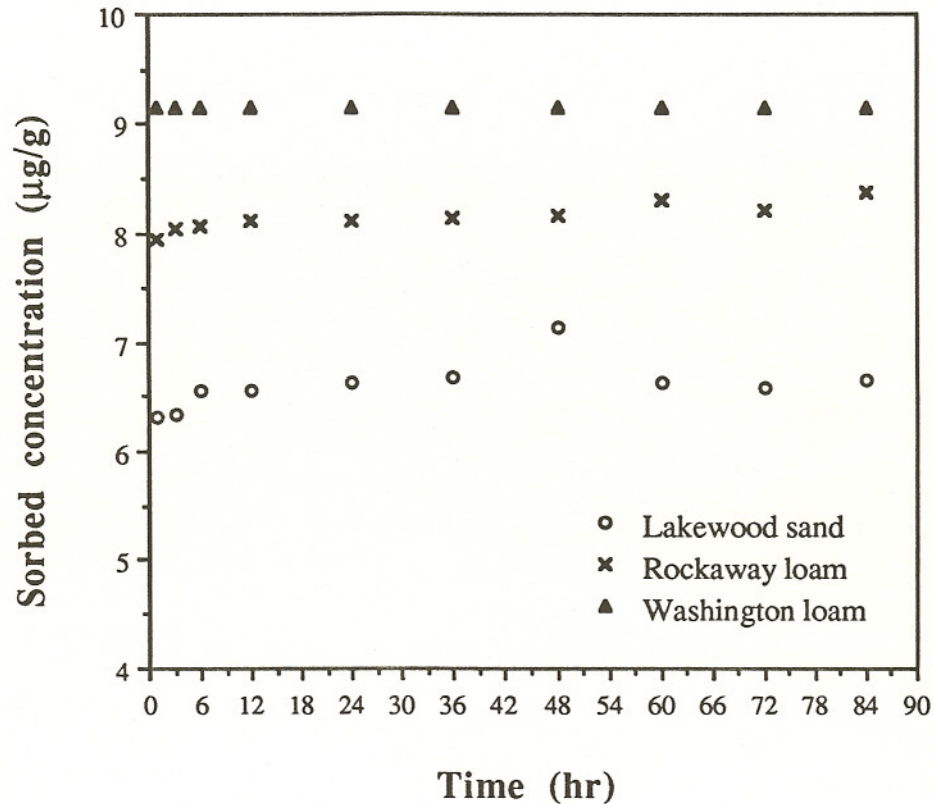
Figure 39 Cadmium adsorption on three different soils at pH 5±0.05 Soil:water = 15g/15mL; I = 0.1 M NaNO$_3$; T = 25^{0}C; C$_0$ = 8×10^{-5} M Cd solution.
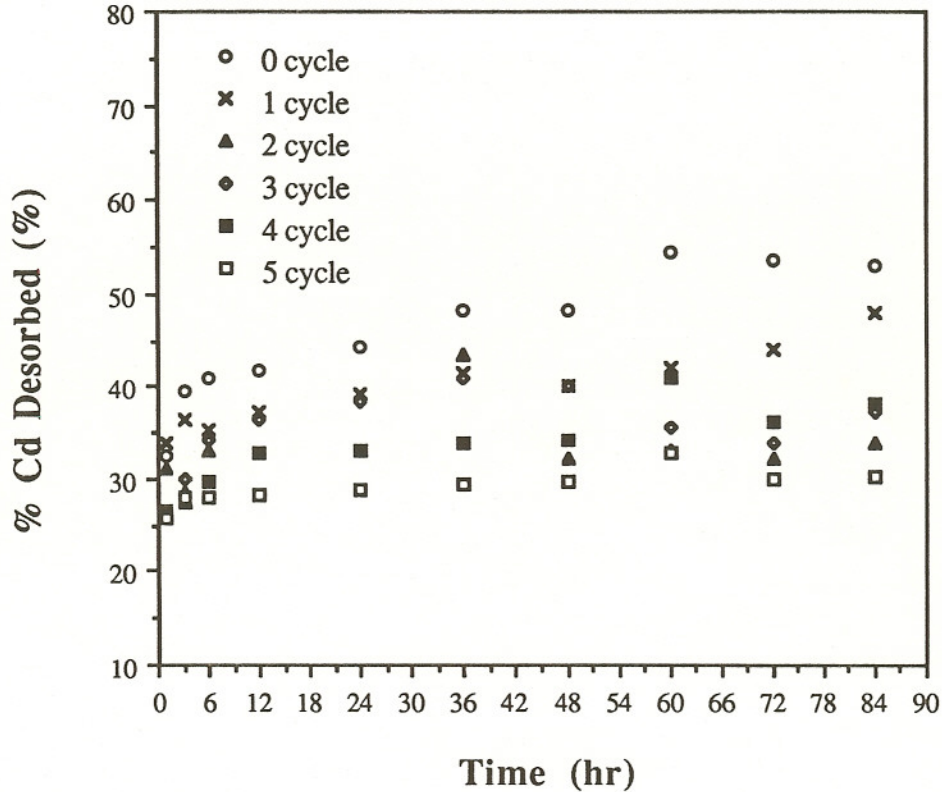
Figure 40 Cadmium desorption from the Lakewood sand after treatment by wet-dry cycles at pH 5.00±0.05. Soil:water = 15g/15mL; I = 0.1 M NaNO3; T = 25⁰C.
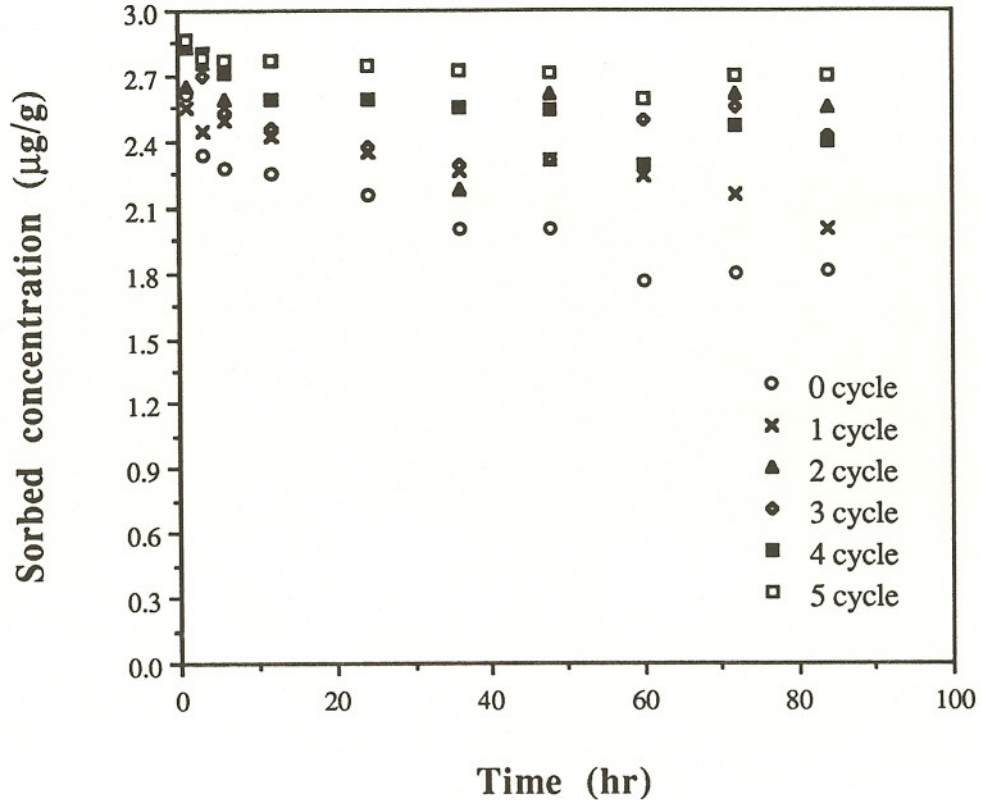
Figure 41 Cadmium desorption from the Lakewood sand after treatment by wet dry cycles at pH 5±0.05. Soil:water = 15g/15mL; I = 0.1 M NaNO3 T = 25⁰C.
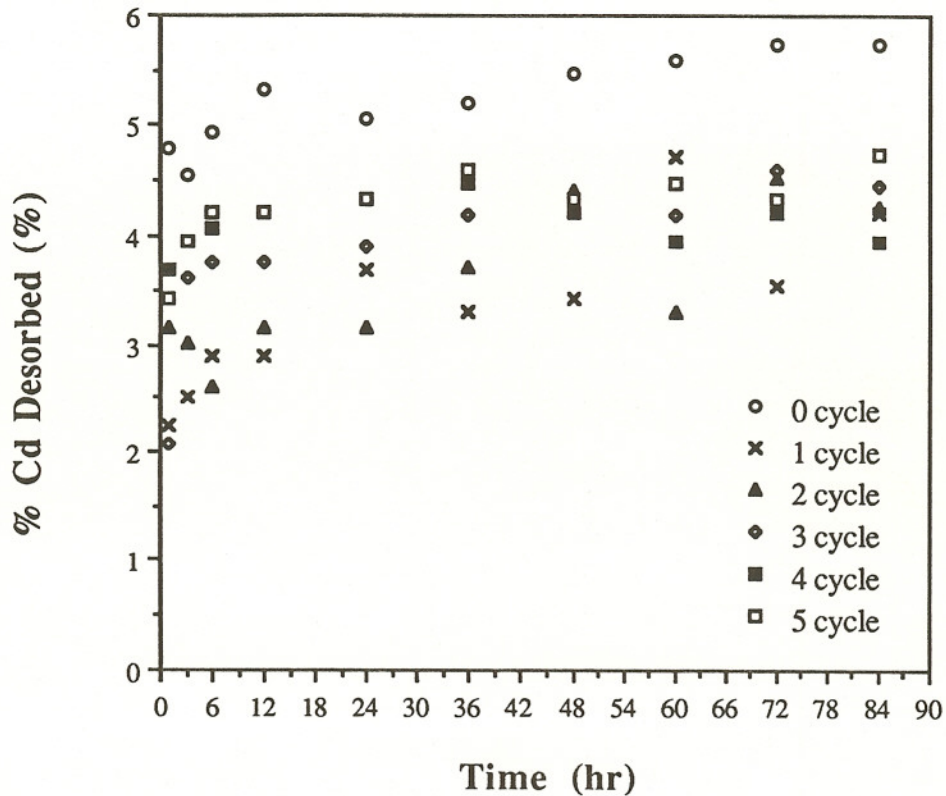
Figure 42 Cadmium desorption from the Rockaway Stony sand loam after treatment by wet-dry cycles at pH 5±0.05. Soil:water = 15g/15mL; I = 0.1 M NaNO₃; T = 25⁰C.
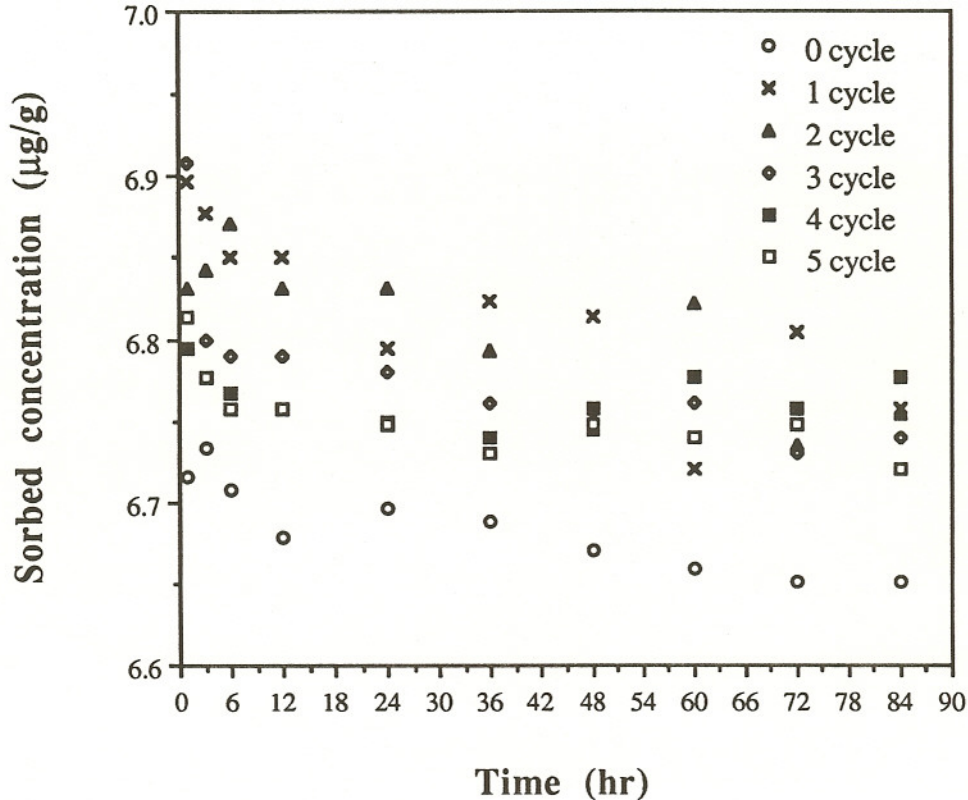
Figure 43 Cadmium desorption from the Rockaway Stony sand loam afte
treatment by wet-dry cycles at pH 5±0.05. Soil:water = 15g/15mL;
= 0.1 M NaNO$_3$; T = 25^{0}C.
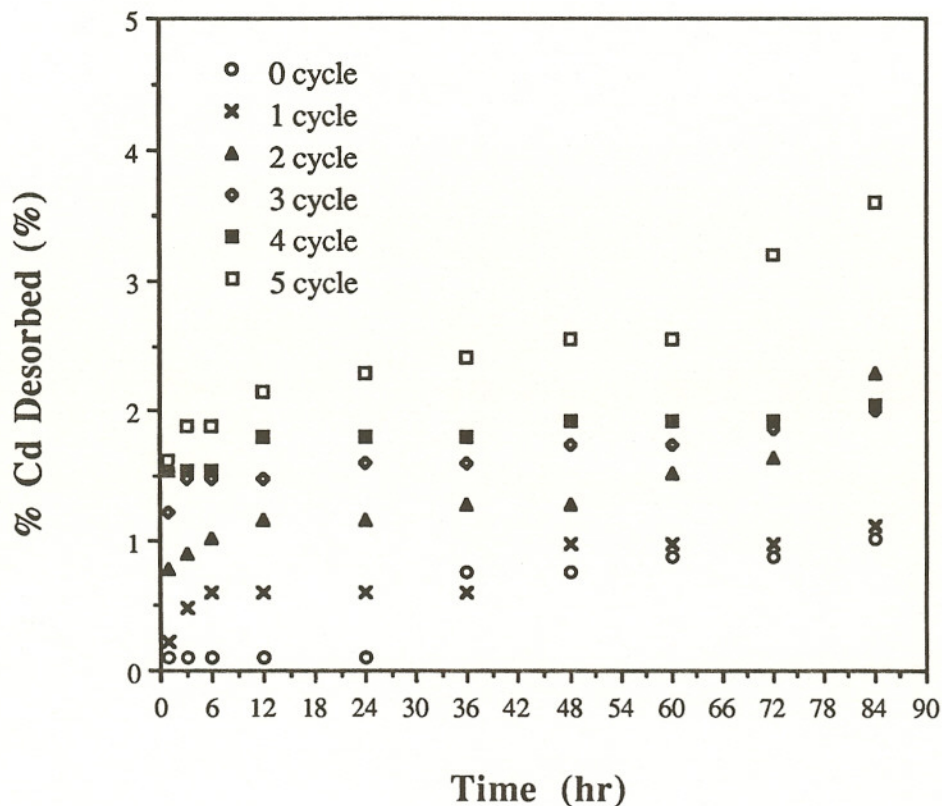
Figure 44 Cadmium desorption from the Washington loam after treatment by wet dry cycles at pH 5±0.05. Soil:water = 15g/15mL; I = 0.1 M NaNO$_3$; T = 25^{0}C.
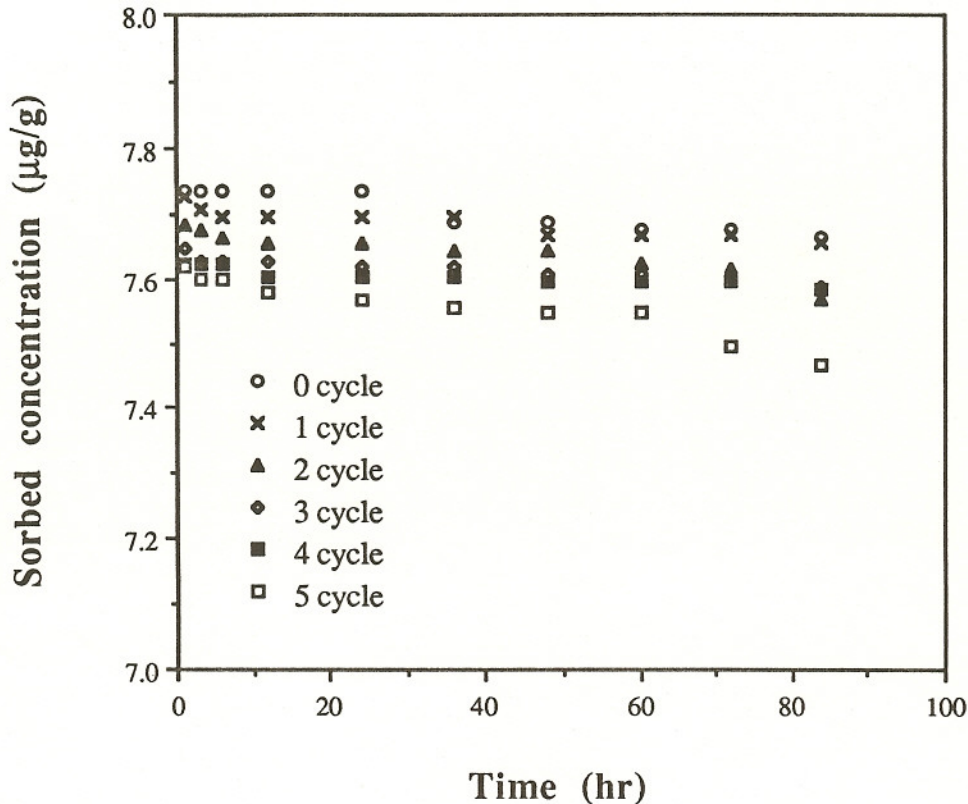
Figure 45 Cadmium desorption from the Washington loam after treatment by wet
dry cycles at pH 5.00±0.05. Soil:water = 15g/15mL; I = 0.1 M
NaNO$_3$; T = 25^{0}C.
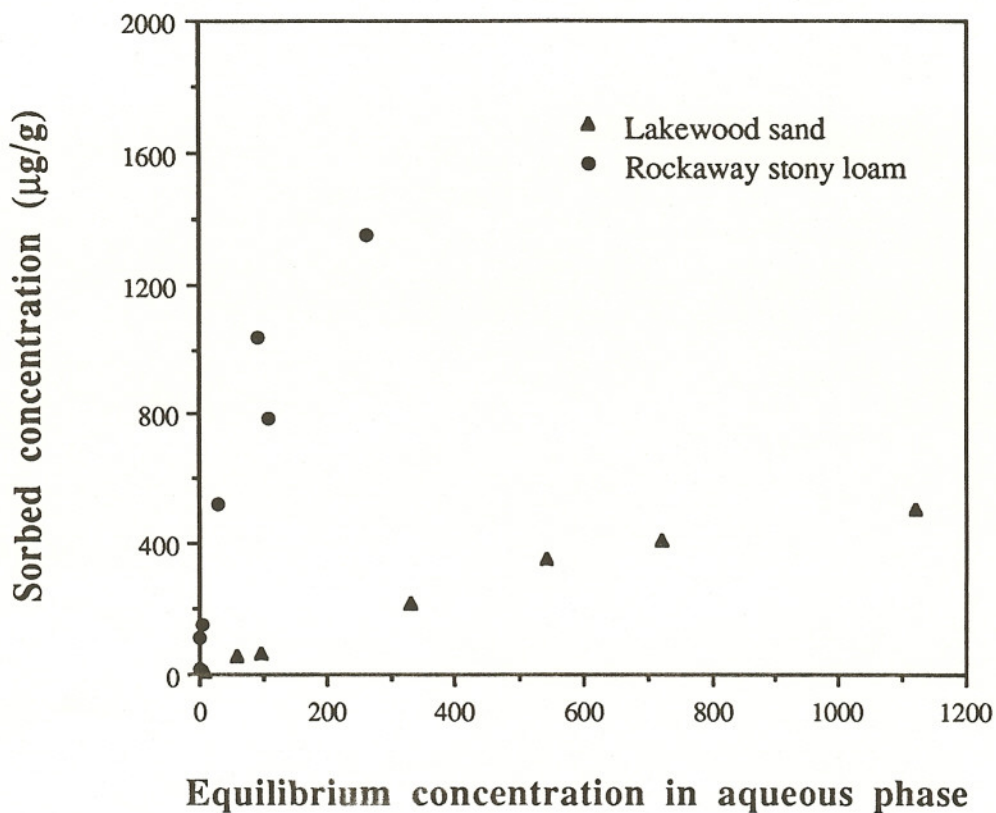
Figure 46 Cadmium adsorption isotherm for two soils. Soil:water =15g/15mL; I
= 0.1 M NaNO3; T = 25⁰C.
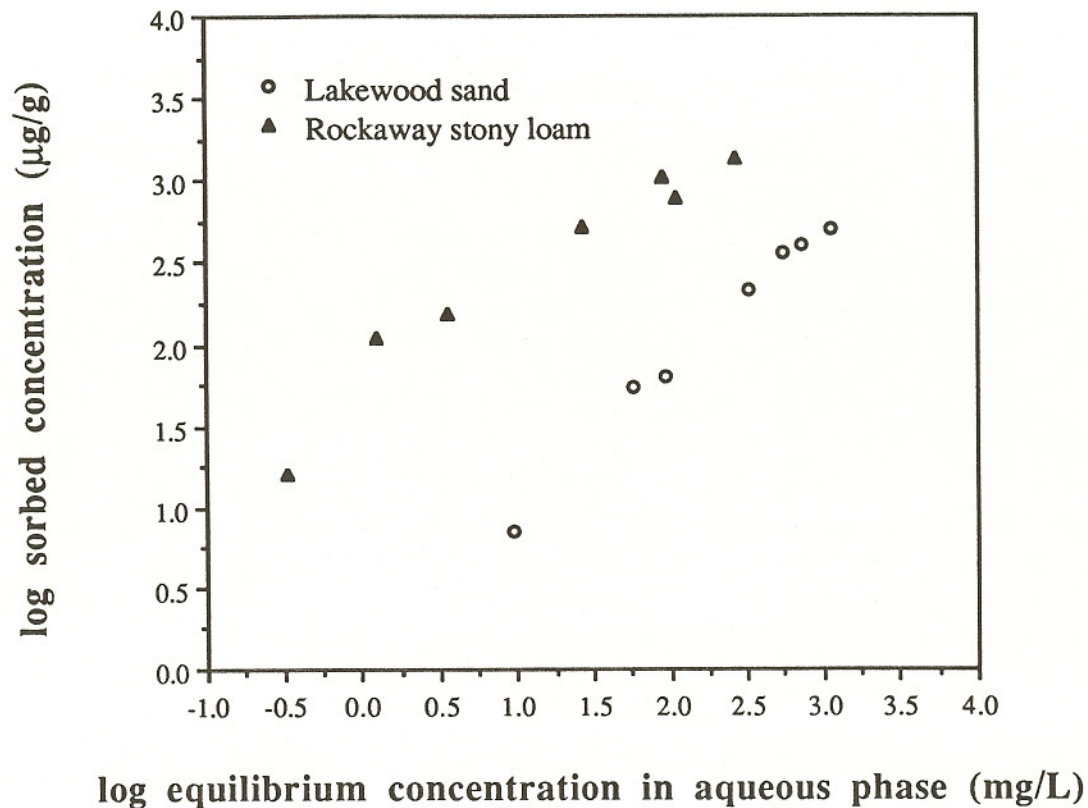
Figure 47 log-log cadmium adsorption isotherm for two soils. Soil:water =
15g/15mL; I = 0.1 M NaNO$_3$; T = 25 ^{0}C.
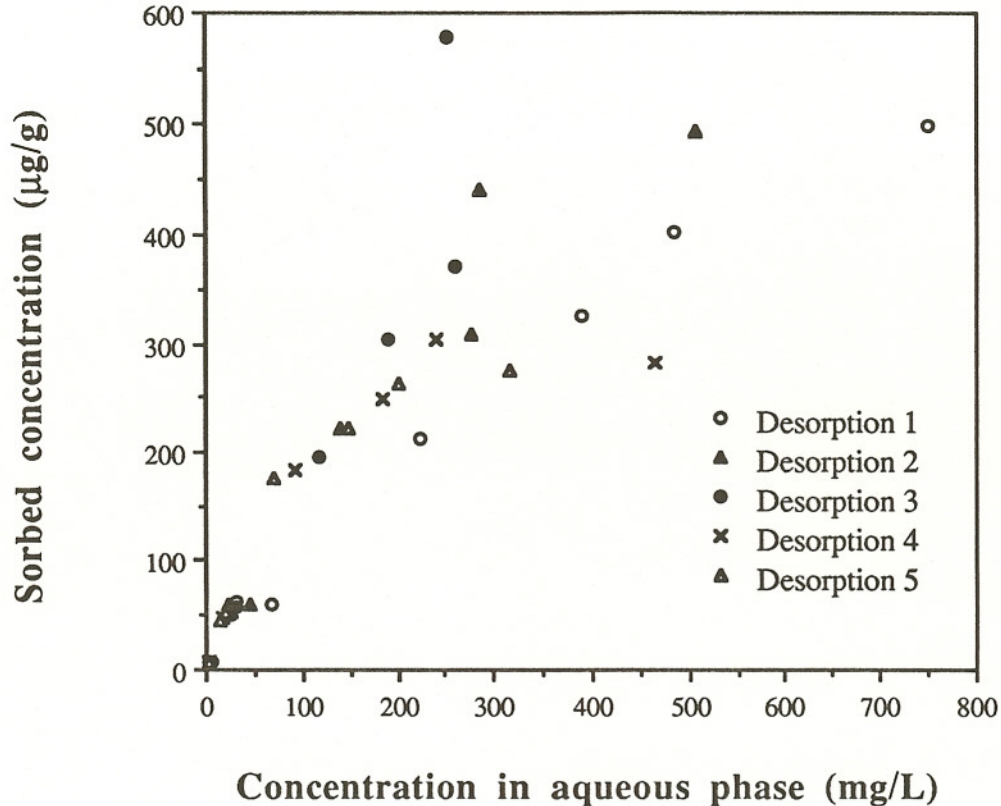
Figure 48 Cadmium desorption isotherm on the Lakewood sand for 5 sequential desorption experiments. Soil:water = 15g/15mL; I = 0.1 M NaNO$_3$; T = 25 ^{0}C.
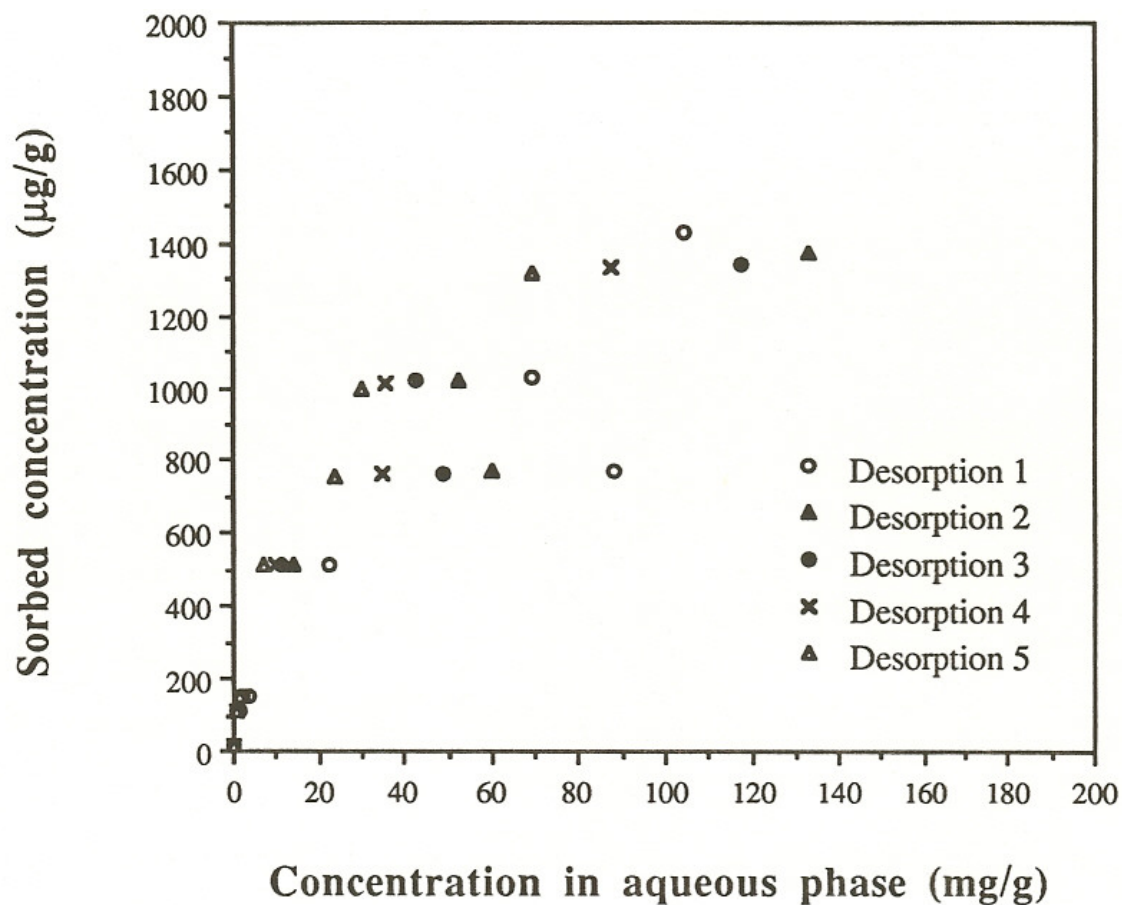
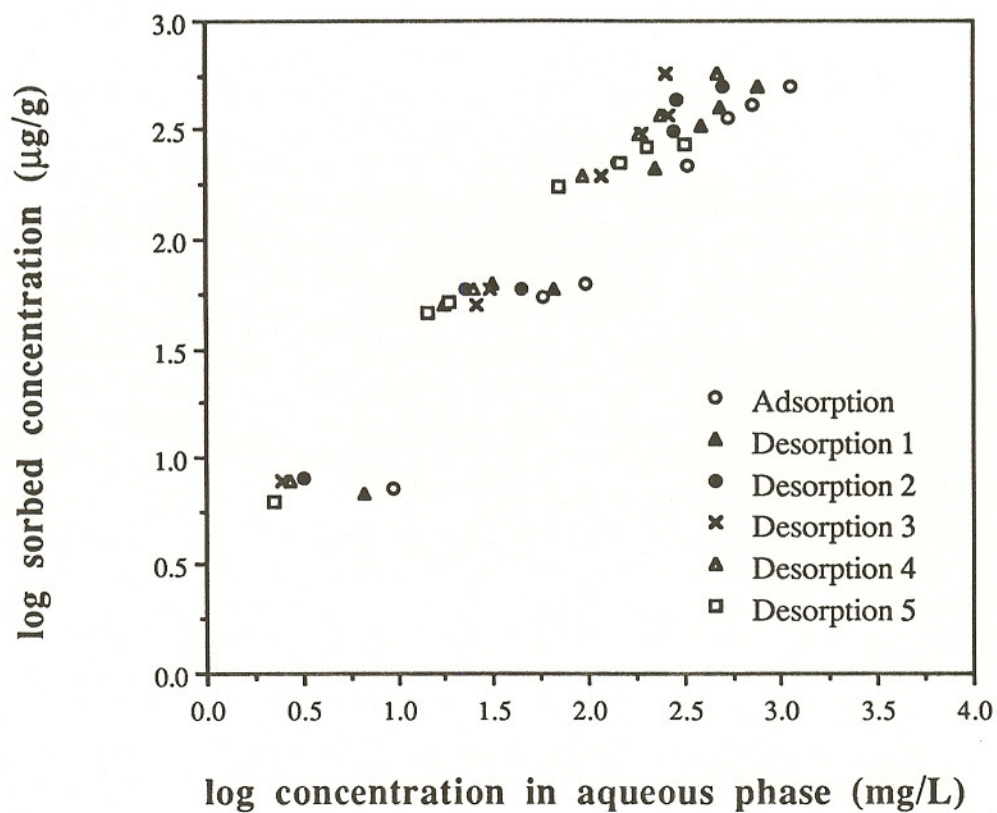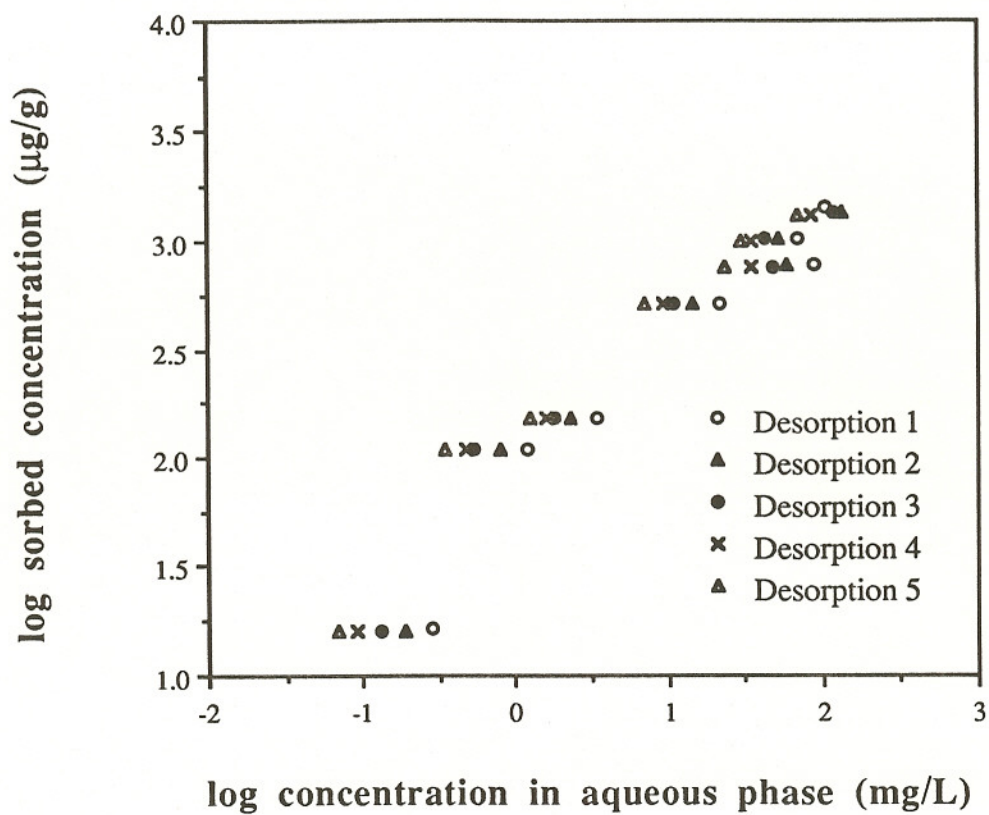**Figure 49** Cadmium desorption isotherm on the Rockaway Stony sand loam for 5 sequential desorption experiments. Soil:water = 15g/15mL; I = 0.1 M NaNO$_3$; T = 25 ^{0}C.
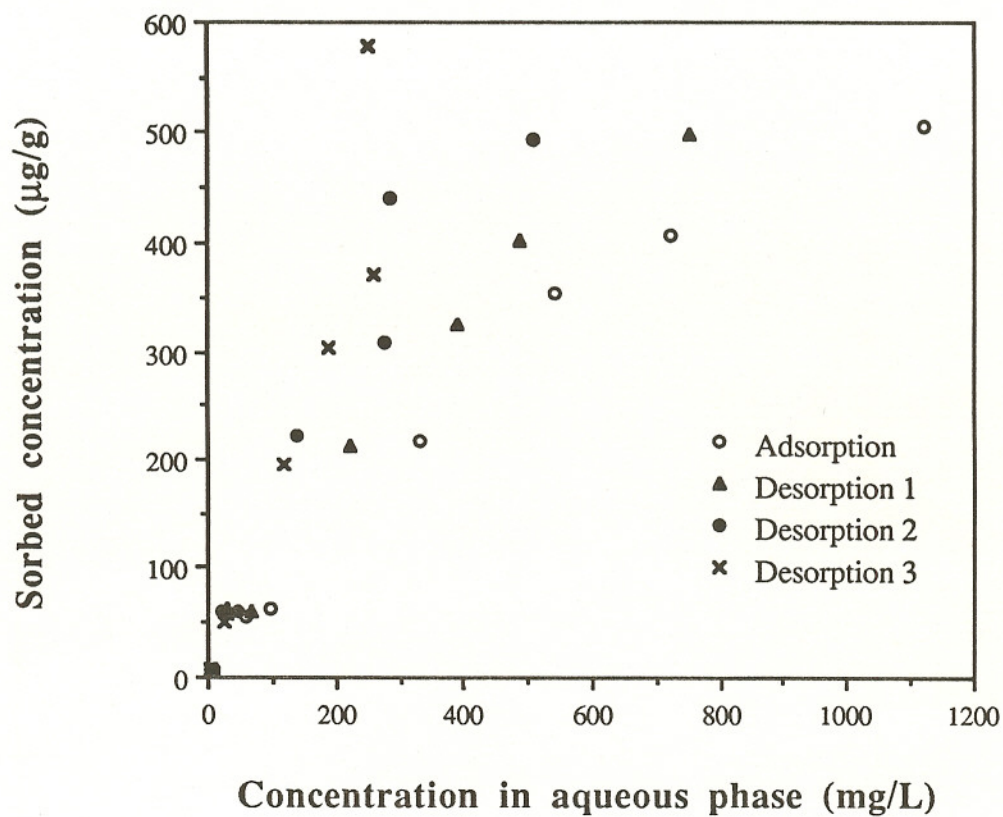
Figure 50 Cadmium adsorption-desorption isotherm on the Lakewood sand for an adsorption and three sequential desorption experiments.Soil:water = 15g/15mL; I = 0.1 M $NaNO_3$; T = 25 ^{0}C.
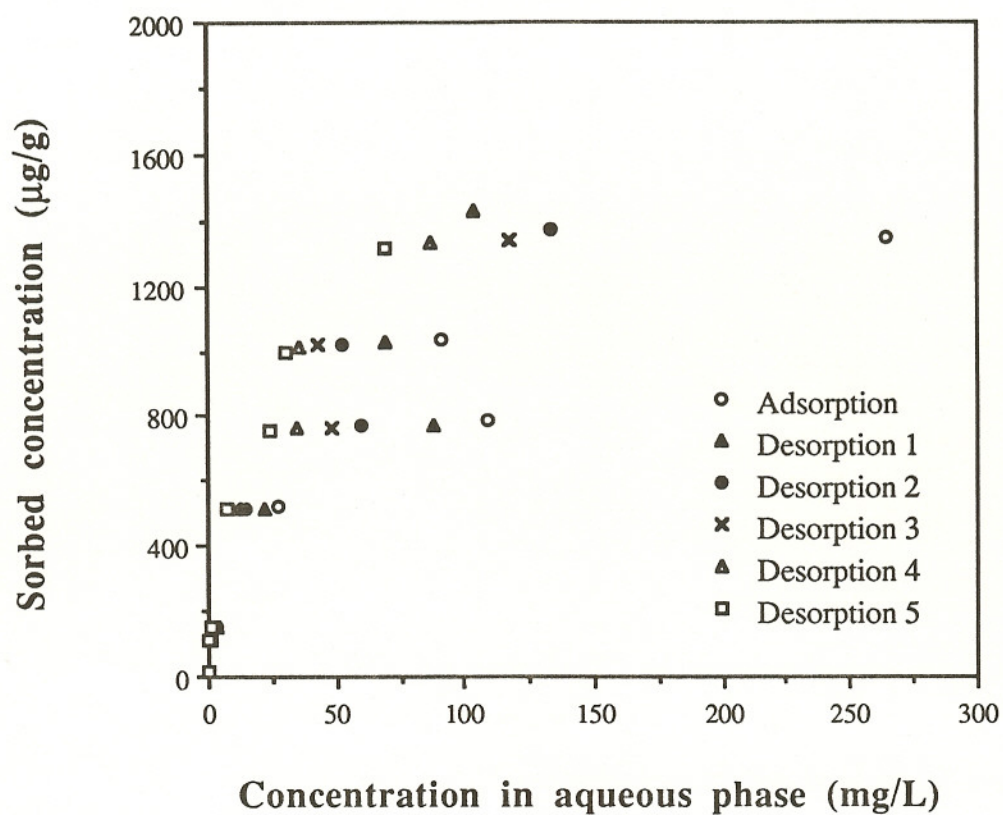
Figure 51 Cadmium adsorption-desorption isotherm on the Rockaway Stony sand loam for an adsorption and 5 sequential desorption experiments. Soil:water = 15g/15mL; I = 0.1 M NaNO3; T = 25 ^{0}C.
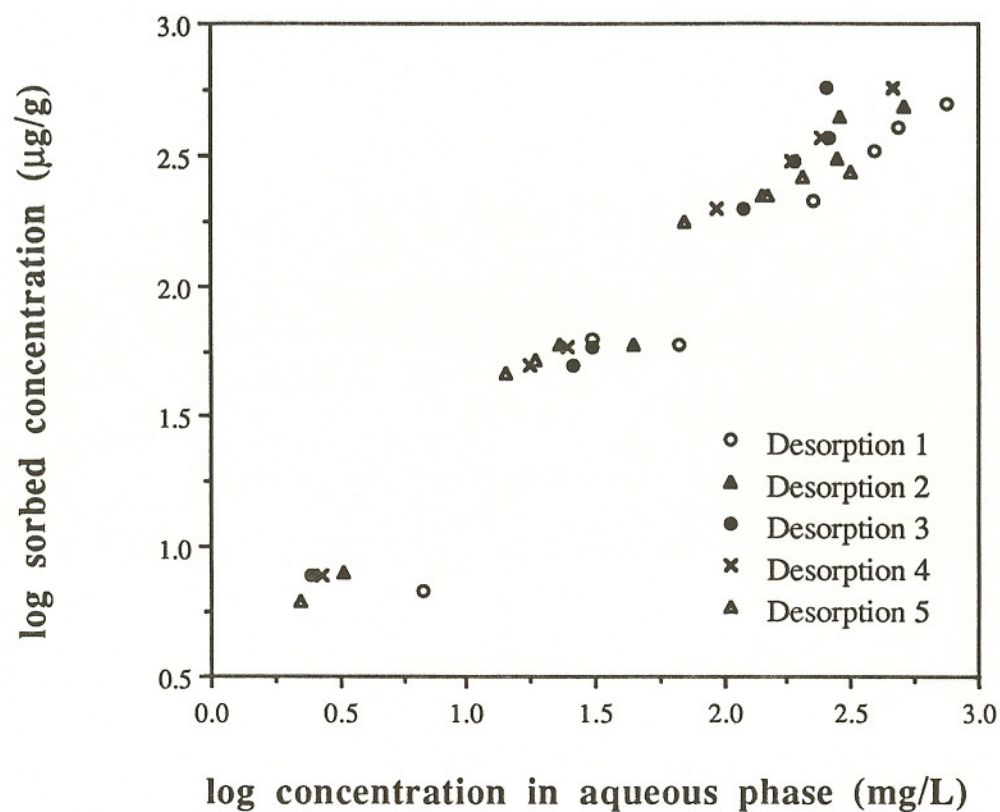
Figure 52 Freundlich isotherm of cadmium desorption on the Lakewood sand for 5 sequential desorption experiments. Soil:water = 15g/15mL; I = 0.1 M NaNO$_3$; T = 25 ^{0}C.
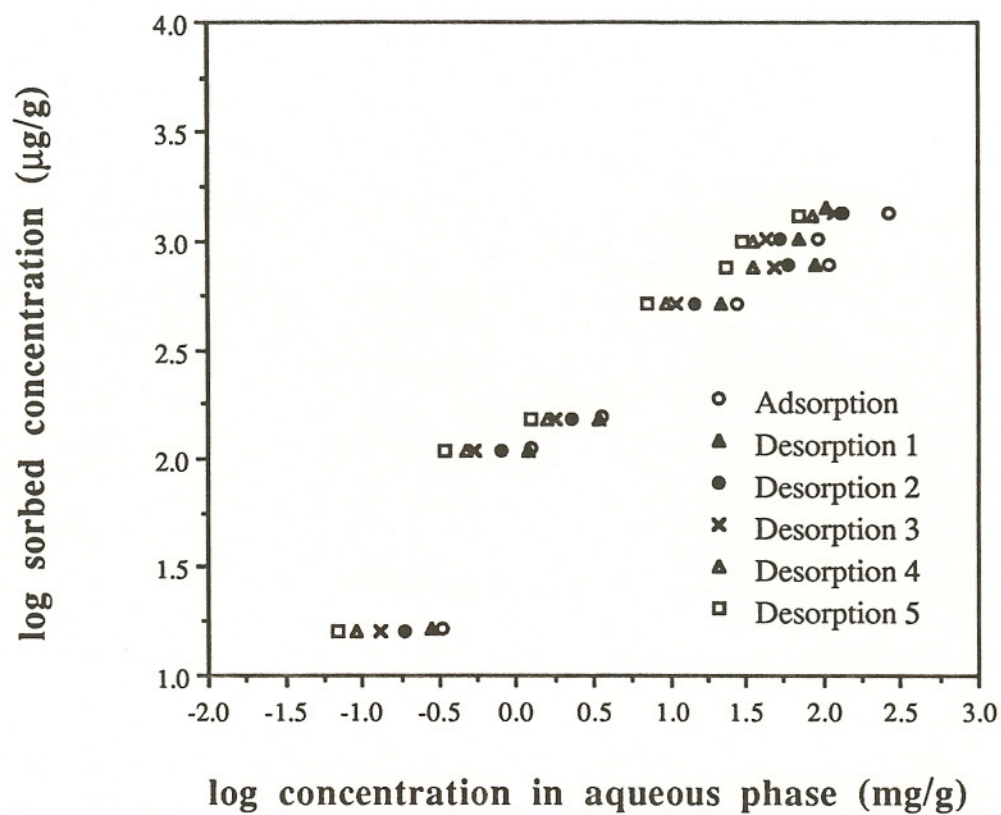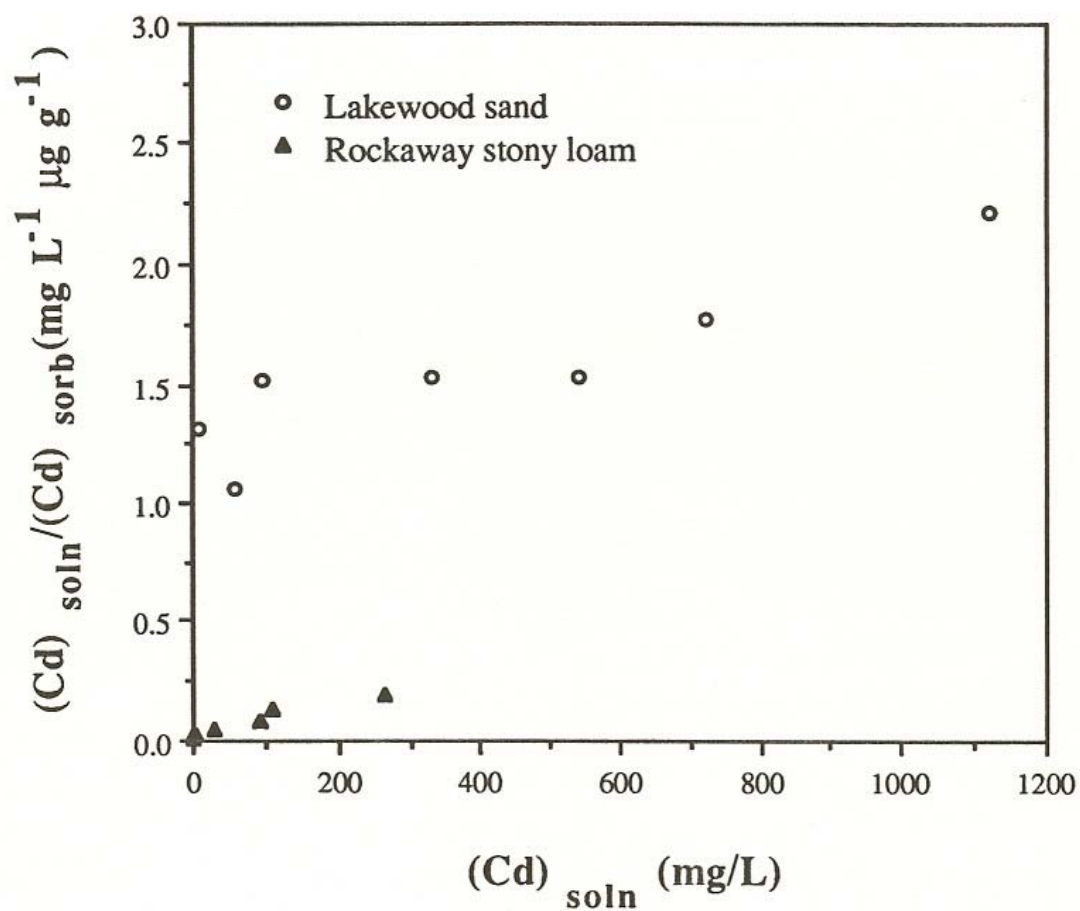
Figure 53 Freundlich isotherm of cadmium adsorption-desorption on the Lakewood sand. Soil:water = 15g/15mL; I = 0.1 M NaNO3; T = 25 0C.

Figure 54 Freundlich isotherm of cadmium desorption on the Rockaway Stony sand loam for 5 sequential desorption experiments. Soil:water = 15g/15mL; I = 0.1 M NaNO$_3$; T = 25 ^{0}C.

Data from "Untitled Data #2"

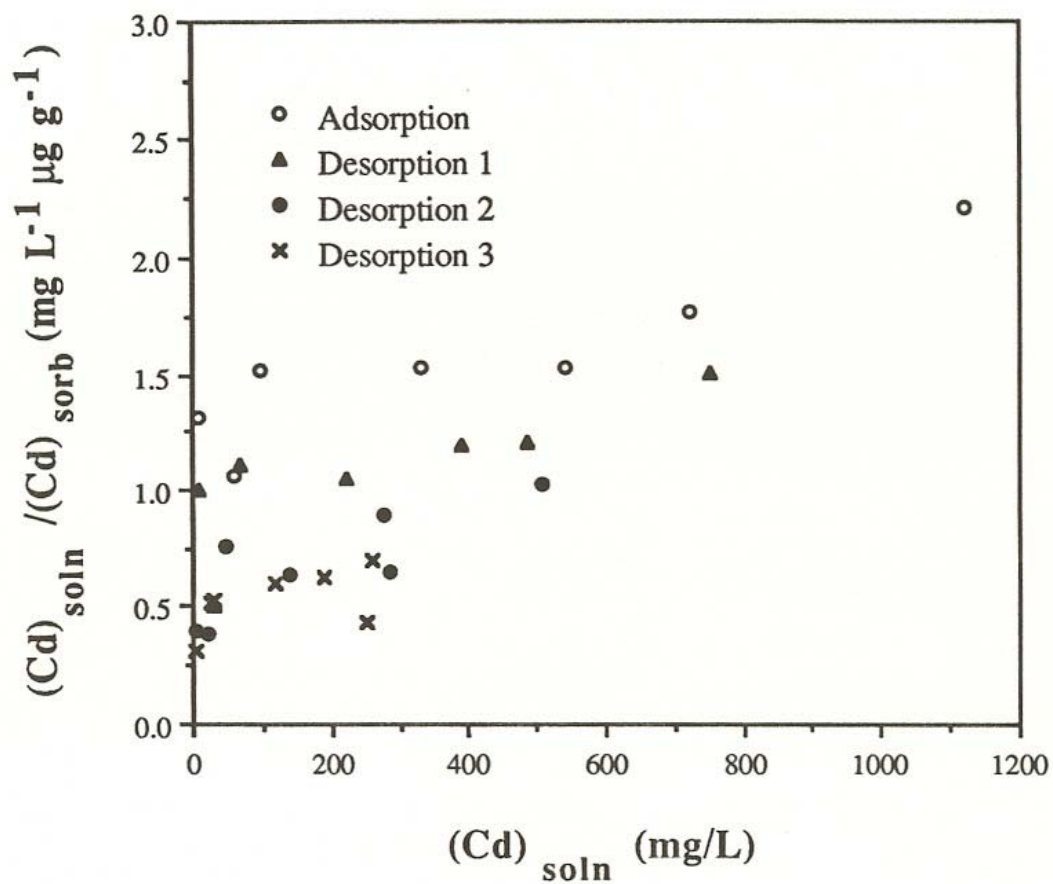Figure 55 Freundlich isotherm of cadmium adsorption-desorption on the Rockaway Stony sand loam. Soil:water = 15g/15mL; I = 0.1 M NaNO$_3$; T = 25 ^{0}C.

Figure 56 Langmuir isotherm of cadmium adsorption for two soils. soil:water = Soil:water = 15g/15mL; I = 0.1 M NaNO3; T = 25 ^{0}C.

Figure 57 Langmuir isotherm of cadmium adsorption-desorption on the Lakewood sand. Soil:water = 15g/15mL; I = 0.1 M $NaNO_3$; T = 25 ^{0}C.
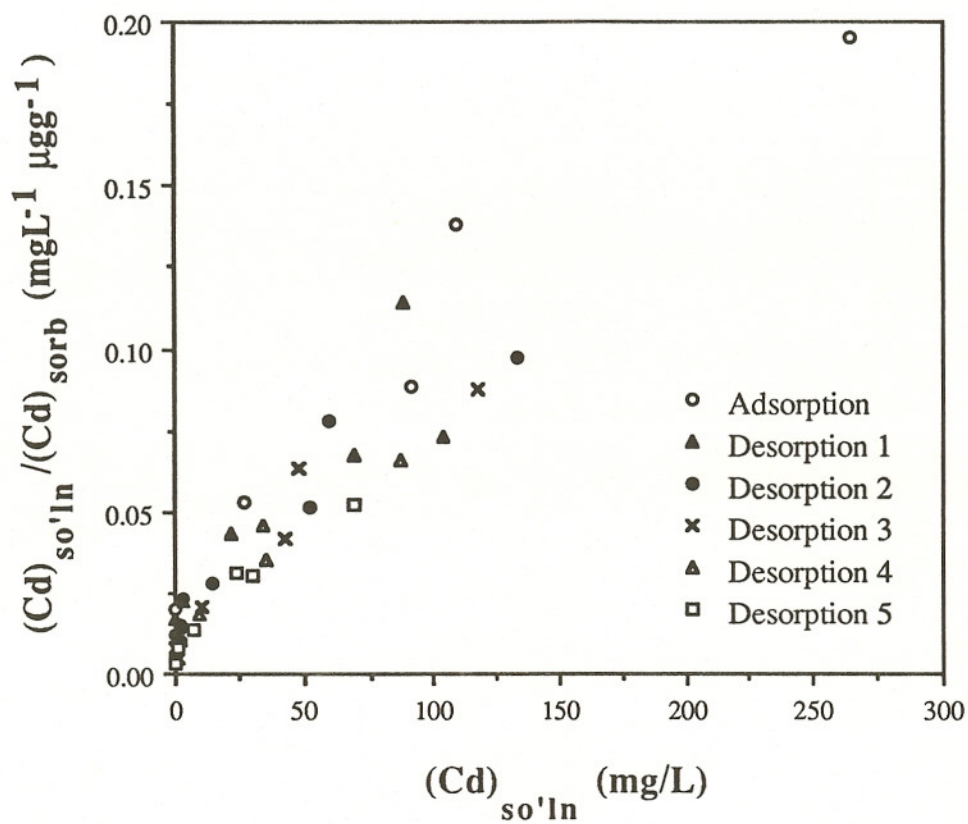
Figure 58 Langmuir isotherm of cadmium adsorption-desorption on the Rockaway Stony sand loam. Soil:water = 15g/15mL; I = 0.1 M NaNO3; T = 25 ^{0}C.