ADSORPTION/DESORPTION AND TRANSPORT OF MERCURY AND ARSENIC IN NEW JERSEY SOILS

YEAR 1

Final Report

August 1993 - January 1995

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1. INTRODUCTION

Since the industrial revolution, increases in the use of heavy metals in industries, their disposal at landfill sites, and the application of sewage sludge to land have resulted in a significant rise in environmental pollution. Mercury and arsenic are two of the heavy metals that have caused serious environmental contamination. Heavy metals released to soil have not only resulted in adverse effects on the foodstuff growth, but also are able to leach to groundwater and surface water, posing a serious health threat to both human and aquatic life because of their high toxicity.

A major problem in the remediation of hazardous contaminated sites is the lack of information on the behavior of chemicals in soils. The aqueous concentration of trace inorganic contaminants in soil solution can be characterized using appropriate thermodynamic theory. At high concentrations, these trace contaminants will precipitate (Stumm and Morgan, 1981; 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). However, trace contaminants are typically present at levels below those at which precipitation occurs. Their presence in the solid phase is a result of adsorption to constituents of soils. Therefore, an understanding of the adsorption, desorption, and transport behavior of trace contaminants in soil is vital for soil remediation.

The purpose of this study is to provide quantitative information about the behavior of mercury and arsenic, including Hg(II), As(III) and As(IV), in soils with respect to their adsorption, desorption, kinetics and transport. Mathematical models that are capable of predicting each of the processes will be developed and validated. These models can be used as managerial and regulatory tools by the NJDEPE in the development of management practices to reduce soil and groundwater contamination and environmental cleanup.

2. PROGRESS TO DATE

2.1 Mercury

2.1.1 Development of a Flow Injection Analysis System (FIA) for the Determination of Mercury

2.1.1.1 Introduction

The determination of low concentration of mercury is usually achieved by using the Cold Vapor Atomic Absorption technique (Hatch and Ott, 1968). Mercuric ions are reduced to elemental form by Sn^{+2} or BH_4 (Rooney, 1976). The metallic Hg is then striped by gas to a detection cell where the absorbance of mercury is measured. Various commercially available instruments such as the Coleman Mercury Analyzer system MAS-50A and the MHS-20 from Perkin Elmer Corp., have been developed based on the above principle. However, their operation requires large amounts of sample and is time-consuming as the absorption needs to be determined after reaching the steady state. Furthermore, the manual operations and glassware usage increase the contamination risk. Consequently, a FIA system has been developed and used to measure the mercury. This system has the advantage of a high rate of analysis, good accuracy, and low consumption of sample and reagents (Pasquini et al., 1988).

2.1.1.2 Development of the FIA System

In this study we developed a flow injection analysis system (FIA) combined with an atomic adsorption spectrometer for the determination of mercury. The FIA system is schematically depicted in Fig. 1. The main components are: (1) a Gilson Minipuls peristaltic pump with four channels; (2) a Rheodyne four-way rotary valve with a variable-volume sample loop; (3) a gas-liquid separator of laboratory design and construction; (4) a gas flow meter; (5) a reaction coil of 450 mm x 0.5 mm i.d.; and (6) an open ended quartz T-tube used as the absorption cell, 170 mm long x 14 mm i.d., with a 50 mm long x 2 mm i.d. inlet in the center. All transport tubing is Teflon of 0.5 mm i.d.

2.1.1.3 Optimization of the FIA System

Several factors, including the reagent and sample carrier flow rates, reaction coil length, gas flow rate, the size of gas transport tubing between the separator and adsorption

tube, and the size of sample loop were found to have significant effects on sensitivity. Different sizes of sample loops were tested and the maximum sensitivity was reached for a sample loop of 500 μL. Four different sizes of reaction coil, 250 mm x 0.5 mm i.d., 350 mm x 0.5 mm i.d., 450 mm x 0.5 mm i.d., and 600 mm x 0.5 mm i.d., were tested. The 450 mm x 0.5 mm i.d. coil gave the best results. A short gas transport tube (5 mm) with medium inside diameter (0.9 mm) between the gas-liquid separator and the absorbance cell gave the largest peak.

The flow rates of liquid and gas are closely dependent on each other and have marked effect on the sensitivity. Low gas flow rates cannot maximally strip mercury gas or transport the stripped mercury vapor rapidly into the absorption tube. Therefore, short broad peaks are obtained. High gas flow rates, however, cause excessive dilution of the mercury vapor and reduce the residence time of mercury in the light path. For each combination of sizes of reaction coil, gas transport tubing, and sample loop, we optimized liquid and gas flow rates using the Simplex statistical method (Burton and Nickless, 1987). It was found that for a sample loop of 500 μl, reaction coil of 450 mm x 0.5 mm i.d., gas flow rate of 10 ml/min., acid carrier flow rate of 6 ml/min. and reductant flow rate of 0.6 ml/min., the optimum sensitivity was achieved.

2.1.1.4 Calibration

All reagents were of trace element analytical grade and distilled, deionized water was used throughout. Glassware was cleaned by soaking overnight in 10% v/v nitric acid.

The 1000 ppm mercury stock solution was prepared by dissolving 0.7395 g Hg(II) sulfate in 500 ml of 1 % wt/v nitric acid. From the 1000 ppm stock solution we diluted to 10 ppm by 1 % v/v nitric acid. All standard solutions were prepared daily by diluting 10 ppm stock solution using 1% v/v nitric acid, and stabilized by addition of a few drops of 0.1% sodium dichromate.

After each detection, the FIA system was washed with distilled, deionized water. For each sample, triplicate measurements were made. It is found that the linear range is from 1 μg/L to 30 μg/L with linear regression coefficient R^2=0.9996 (Fig. 2). The detection limit

was calculated to be 0.65 μg/L according to Standard Methods for the Examination of Water and Wastewater (Greenberg et al., 1992).

2.1.1.5 Test of the Effects of Complexation of Hg(II) by Ligands in Soil Solution on the Mercury Measurement by FIA

2.1.1.5.1 Overall Effect of All Ligands

Since Hg(II) can form very strong complexes with ligands existing in soil solution, such as Cl^-, OH^-, and organic matter, it is assumed that the complexation between Hg(II) and these ligands may influence the measurement of mercury by FIA. To test this, nine soil extracts were prepared by shaking 1 g of soil and 100 ml of 0.01 N $NaNO_3$ at different pH values followed by filtering through a 0.45 μm membrane filter. Each soil extract contained the same amounts of chloride and different amounts of dissolved organic matter (Table 1). 20 μg/L of mercury was then spiked to each of the soil extract. After equilibrium, one portion of each solution was analyzed for mercury immediately and another portion analyzed after digestion.

Digestion method:

The methods for solution digestion for metals described in Standard Methods (Greenberg et al., 1992) require evaporating solutions at near boiling temperature after addition of strong acids. These methods may not be suitable for mercury because significant amount of mercury may be lost through volatilization (e.g., Van Delft and Vos, 1988). A preliminary experiment was therefore carried out to ascertain appropriate digestion methods for mercury. The following method was shown to yield the highest recovery.

Procedure:

a. Take a 5 ml aliquot and place into a 10 ml glass test tube;
b. Gently add 0.5 ml of each of concentrated HNO_3, H_2SO_4, and HCl acids;
c. Cap each tube tightly;

d. Place the tubes in a COD Reactor (Model 45600, Hatch Company, Loveland, CO) and maintain the temperature at 90°C for two hours;

e. Analyze after cooling.

The mercury recovery for both digested and non-digested solutions is listed in Table 1. It is evident that some mercury species cannot be reduced by $SnCl_2$ and analyzed by the FIA system. Mercury recovery for non-digested samples ranged from 16.9 to 80.0%, with the lowest recovery occurring at the highest pH (9.70) and dissolved organic carbon (98.84 mg/L). All recoveries were greater than 82% with a average of 92.8% after digestion. To measure the total mercury in soil solution, the digestion of solution is necessary.

2.1.1.5.2 Effect of Individual Ligands

Three types of predominant complexed-mercury species, Hg-OH complexes, Hg-Cl complexes, and Hg-organic matter complexes, may be responsible for the low mercury recovery. Other ligands, such as CN^-, which can form complexes with Hg(II), can be neglected because of their very low concentrations in solutions. The effect of complexation of Hg(II) by each of the three major ligands on mercury determination was further tested.

First we tested the effects of Hg-OH and Hg-Cl complexation on the measurement of Hg(II) by determining the recovery of known additions. The following procedure was used:

a. Take eight 100 ml volumetric flasks and add 100 ml of 1×10^{-5} M Cl^- and 1×10^{-7} M Hg(II) to each flask;

b. Adjust the solution pH from 2 to 11 with 0.1 M NaOH or HNO_3 ;

c. After equilibration, determine Hg(II) concentration and final pH;

Based on chloride concentration and pH for each solution, the fraction of each mercury species was calculated using MINEQL+ program (Schecher, 1991). The results are listed in Table 2. It can be seen that when Hg-Cl complexes, including $HgCl^+$ and $HgCl_2$, are the predominant species (from 99.67 to 99.98%), the Hg(II) recovery ranges from 104 to 102% with a average of 102.8%; when Hg-OH complexes, including $HgOH^+$ and $Hg(OH)_2$, are the predominant species, the Hg(II) recovery ranges from 95 to 97% with an average of

96%. The results indicate that both Hg-Cl and Hg-OH complexes can be reduced by Sn^{2+} and therefore the complexation of Hg(II) by these two ligands has no effect on the measurement of Hg(II). The low recovery of Hg(II) spiked to soil extracts must be caused by the complexation of Hg(II) with dissolved organic matter.

2.1.1.5.3 Results and Conclusions

Based on these results, the mercury other than Hg-dissolved organic matter complexes can be determined without the digestion of solution; with the digestion of the solution, total mercury can be determined. The concentration of organically complexed mercury is the difference between these two values.

2.1.1.6 Selection of Efficient Soil Solution Digestion Method

It was shown in Section 2.1.1.5.1 that in order to measure total mercury in solution, samples must be digested prior to analysis by FIA. Since a large number of samples will be involved in this project, an efficient digestion method is necessary. It was therefore decided to conduct a solution digestion efficiency test using single, two, and three combinations of concentrated HNO_3, H_2SO_4, and HCl.

Treatment:

a. 0.5 ml concentrated HNO_3 ;
b. 0.5 ml concentrated H_2SO_4 ;
c. 0.5 ml concentrated HCl ;
d. 0.5 ml concentrated HNO_3 + 0.5 ml concentrated H_2SO_4 ;
e. 0.5 ml concentrated H_2SO_4 + 0.5 ml concentrated HCl ;
f. 0.5 ml concentrated HNO_3 + 0.5 ml concentrated HCl ; or
g. 0.5 ml concentrated HNO_3 + 0.5 ml concentrated H_2SO_4 + 0.5 ml concentrated HCl.

The procedure was the same as that described in Section 2.1.1.5.1.

The results are listed in Table 3. The combinations of nitric acid and hydrochloric acid yielded recoveries over 92% for all three soils. Single acids were not sufficient to release all mercury complexed with DOM.

2.1.2 Mass Balance Study for Adsorption Experiment

2.1.2.1 Introduction

It is speculated that during the adsorption experiment, the added mercury (II) may be reduced to elementary mercury by reducing agents such as soil organic material. As a result, mercury may be lost through volatilization during the reduction. We therefore decided to digest both soil and solution after 24 hours of adsorption equilibration to see the mass recovery. Two soils of low and high organic matter content were used for this study. The procedure described in Fig. 3 was followed.

2.1.2.2 Methods

The digestion of the solution was carried out followed the method described previously. The method described in Methods of Soil Analysis (Page, 1982) was followed for the digestion of soils. The procedure is as following:

a. Weigh 1 g of air-dried soil and put into a 125 ml Erlenmeyer flask;
b. Moisten the soil with a few drops of deionized water;
c. Add 15 ml of 2:1 concentrated H_2SO_4:HNO_3 to each of the flasks, gently shake the mixture, cover each flask with a rubber stopper, and cool the mixture by placing the flasks in a cold water bath;
d. Add 2 ml concentrated HCl to each of the flasks;
e. Place the flasks in a water bath at 55 ^{o}C and shake for 3 hours at 50 strokes per minute;
f. Remove the flasks from the bath and let them cool to room temperature;
g. Carefully add 6% (w/v) $KMnO_4$ solution to each flask with gentle stirring until purple color of permanganate ions persists for at least 15 min.;

h. Leave the mixture overnight, and then dilute to 100 ml; and

j. Filter the suspension and determine mercury concentration by FIA.

2.1.2.3 Results and Conclusions

The results are listed in Table 4. The recoveries for both soils at a variety of pHs are greater than 80%. However, there is still about 15-20% of the mass unaccounted for, which may be due to volatilization during shaking, and/or irreversible adsorption.

2.1.3 Adsorption of Hg(II) on Fifteen New Jersey Soils: Effects of pH, Chloride and Organic Matter

2.1.3.1 Introduction

Adsorption of solutes on soil solid surface can be by weak physical, Van der Waals forces (e.g., partitioning) and electrostatic forces (e.g., ion exchange) as well as chemical interactions that include ligand exchange, covalent bonding, hydrophobic bonding, hydrogen bonding, hydrogen bridges, and steric or orientation effects (Stumm and Morgan, 1981).

Adsorption of metals on soil solid surface greatly depends on solid surface charge characteristics and metal speciation in solution.

2.1.3.1.1 Soil Solid Surface Charge

Soil solid surface charge consists of permanent charge and variable charge. The permanent charge results from structural isomorphous substitution in 2:1 soil clay minerals. High permanent surface charge in soil could result in high adsorption of metals through ion exchange. The variable charge results from the protonation and deprotonation of surface functional groups and is pH dependent.

Upon hydration, a protonation-deprotonation equilibrium exists on the solid surface

$$\equiv S-OH_2^+ \leftrightarrow \equiv S-OH + H_s^+ \qquad (1)$$

$$\equiv S-OH \leftrightarrow \equiv S-O^- + H_s^+ \tag{2}$$

Surface acidity, i.e. the total number of the surface ionizable groups can be expressed

$$N_t = [\equiv S-OH_2^+] + [\equiv S-OH] + [\equiv S-O^-] \tag{3}$$

Assuming that the concentration of protons near the solid surface in the electrical double layer is related to the bulk concentration by the Boltzmann distribution involving only electrostatic work, then

$$[H_s^+] = [H^+]\exp(-\frac{e\varphi_0}{kT}) \tag{4}$$

The corresponding intrinsic constants are

$$K_{a1}^{int} = \frac{[\equiv S-OH][H^+]}{[\equiv S-OH_2^+]}\exp(-\frac{e\varphi_0}{kT}) \tag{5}$$

$$K_{a2}^{int} = \frac{[\equiv S-O^-][H^+]}{[\equiv S-OH]}\exp(-\frac{e\varphi_0}{kT}) \tag{6}$$

where [ ] designates the concentration in moles/L, φ_0 is the surface potential, k is the Boltzmann's constant, e is electron charge, and T is the absolute temperature.

From the intrinsic constants, the fraction of positive, neutral and negative surface groups, α_+, α_0, α_- , can be calculated for any given pH value.

$$\alpha_+ = \frac{[H_s^+]^2}{[H_s^+]^2 + K_{a1}^{int}[H_s^+] + K_{a1}^{int}K_{a2}^{int}} \tag{7}$$

$$\alpha_0 = \frac{K_{a1}^{int}[H_s^+]}{[H_s^+]^2 + K_{a1}^{int}[H_s^+] + K_{a1}^{int}K_{a2}^{int}} \tag{8}$$

$$\alpha_{-} = \frac{K_{a1}^{int} K_{a2}^{int}}{[H_s^+]^2 + K_{a1}^{int}[H_s^+] + K_{a1}^{int} K_{a2}^{int}} \tag{9}$$

The values of K_{a1}^{int}, K_{a2}^{int}, and φ_0 can be obtained by titrametric, electrophoretic, or other methods. Therefore, the densities of different surface groups can be easily calculated for any given pH value. At pH < pH_{ZPC}, the main surface groups are $[\equiv S-OH_2^+]$ and $[\equiv S-OH]$ and therefore the surface bear positive charge. At pH > pH_{ZPC}, the main surface groups are $[\equiv S-O^-]$ and $[\equiv S-OH]$, the surface is negatively charged. Increase in pH results in the increase of negatively charged surface sites and consequently increases the adsorption of positively charged metals by solids.

The pH dependence of adsorption of metals and anions onto soils has been extensively documented (Christensen, 1989; Zachara et al., 1989; Goldberg and Glaubig, 1987). The data from our laboratory have shown that the adsorption of cadmium, lead and both trivalent and hexavalent chromium to fifteen New Jersey soils are all highly pH dependent (Allen et al., 1994). For cadmium, chromium (III) and lead, the adsorption increases with increasing solution pH. For Cr(VI), however, the adsorption decreased with increasing solution pH. The solution pH controls the adsorption of solute by controlling the relative fraction of differently charged surface groups of soil solids and the speciation of solute in solution.

2.1.3.1.2 Metal Speciation in Solution

Much research has been conducted on the effect of complex formation on the adsorption of metal ions. Comprehensive reviews given by Elliott and Huang (1979) and Bourg (1988) indicated that difficulties still remain in generalizing about the influence of ligands on metal adsorption. There are three possible outcomes, i.e. enhancement, inhibition or no effect. However, which one is predominant depends on the ligand/metal ratio, adsorbability of the free ligand, and pertinent solution chemistry which acts collectively or independently on the extent of adsorption of metals (Huang and Lin, 1981; Davis, 1984). Vuceta (1976) suggested that the addition of ligand may generally result in (i) an inhibition of metal adsorption because of a strong complex formation with the metal ion or by competing with the surface for available adsorption sites; (ii) no perceptible change in the extent of

adsorption if the ligand has weak complex forming ability and exhibits a lack of affinity for the solid surface: or (iii) an enhanced adsorption of the ligand if the ligand is capable of strong complex formation and also possesses a substantial affinity for the solid surface. Benjamin (1979) also suggested that there are at least three possible ways by which the metal-ligand complex may interact with the surface: (i) adsorption of complexed metal ions depends upon the adsorbability of uncomplexed metal (metal-like adsorption); (ii) adsorption of the complexed metal ions is related to the adsorption characteristics of the free ligand (ligand-type adsorption); and (iii) the complexed metal ions may not be adsorbed at all. Based on the study of the adsorption characteristics of Cu(II) and Co(III) in the presence of chelating agents, Elliott and Huang (1979, 1980) and Huang and Lin (1981) asserted that the effect of complex formation on metal adsorption must be assessed by the adsorbability of the complexed metal ions.

Mercury differs from other heavy metals in that it is a strong Lewis acid. The hydrolysis constants are 3.49 for pK_1 and 2.77 for pK_2 at an ionic strength of 0.01 N (Baes and Mesmer, 1976). Mercury rarely exists predominantly as a free ion in natural systems.

Mercury also differs form most of the other metals in that it is more prone to form complexes with chloride. Hg-Cl complexes begin to form at Cl^- concentration above 10^{-9} M. Hg-Cl complexes are expected in soil solution where high concentrations of Cl^- usually occur.

$$Hg^{2+} + H_2O \Leftrightarrow HgOH^+ + H^+ \qquad pK_{OH,1} = 3.49 \qquad (10)$$

$$HgOH^+ + H_2O \Leftrightarrow Hg(OH)_2 + H^+ \qquad pK_{OH,2} = 2.77 \qquad (11)$$

$$Hg^{2+} + Cl^- \Leftrightarrow HgCl^+ \qquad pK_{Cl,1} = -7.02 \qquad (12)$$

$$Hg^{2+} + 2Cl^- \Leftrightarrow HgCl_2 \qquad pK_{Cl,2} = -13.70 \qquad (13)$$

$$Hg^{2+} + 3Cl^- \Leftrightarrow HgCl_3^- \qquad pK_{Cl,3} = -14.78 \qquad (14)$$

$$Hg^{2+} + 4Cl^- \Leftrightarrow HgCl_4^{2-} \qquad pK_{Cl,4} = -15.23 \qquad (15)$$

$$Hg^{2+} + H_2O + Cl^- \Leftrightarrow Hg(OH)Cl + H^+ \qquad pK_{OH,Cl} = -3.87 \qquad (16)$$

A fraction of each species in the solution is given by the ratio of the concentration of the species to the sum of the concentration of all the species. This may be calculated using the reaction constants corrected for an ion strength of 0.01 N from Baes and Mesmer (1976). For instance, the fraction of Hg^{2+} is:

$$\alpha_{Hg^{2+}} = \frac{1}{1 + K_{OH,1}/[H^+] + K_{OH,1}K_{OH,2}/[H^+]^2 + \sum_{i=1}^{4} K_{Cl,i}[Cl^-]^i + K_{OH,Cl}[Cl^-]/[H^+]} \qquad (17)$$

Given total concentrations of chloride and mercury in solution, the fraction of each of the mercury species in solution can be calculated as a function of pH. For instance, given the Cl^- concentration to be 10^{-6} and mercury concentration to be 10^{-7} M, at low pH the predominant species of mercury are $HgCl_2$, $HgCl^+$, and small amount of Hg^{2+}. As pH increases, the proportion of $Hg(OH)_2$ increases, and when pH is greater than 5.5 almost all mercury exists as $Hg(OH)_2$ (Fig. 4).

In the presence of dissolved organic matter in solution, mercury tends to form very stable complexes with the dissolved organic matter. For example, Peng and Wang (1982) showed that most of the mercury in river water may be present as organic complexes.

Assuming 1:1 stoichiometry for mercury-organic ligand complex, the complexation reaction between Hg^{2+} and a ligand (L) can be written as

$$Hg^{2+} + L \Leftrightarrow HgL; \qquad K = \frac{[HgL]}{[L][Hg^{2+}]} \qquad (18)$$

where K= conditional stability constant and the charge on the ligand and complex are not considered.

The fraction of Hg^{2+} in solution containing the Hg-organic matter complex becomes:

$$\alpha_{Hg^{2+}} = \frac{1}{1 + K_{OH,1}/[H^+] + K_{OH,1}K_{OH,2}/[H^+]^2 + \sum_{i=1}^{4} K_{Cl,i}[Cl^-]^i + K_{OH,Cl}[Cl^-]/[H^+] + K[L]} \quad (19)$$

2.1.3.1.4 Previous Studies

The complexation of Hg(II) by ligands, such as OH^-, Cl^-, and organic matter, has been found to significantly affect the adsorption of Hg(II) by soil colloids and soils. MacNaughton and James (1974) found that without the presence of chloride in solution, the adsorption of Hg(II) by silica increases abruptly in the pH range of 2 to 3. Newton et al. (1976) reported that the maximum adsorption of Hg(II) by bentonite clay occurred in the pH range of 4.5 and 5.5 regardless of initial mercury concentration or the concentration of electrolyte $Ca(NO_3)_2$. Kinniburgh and Jackson (1978) examined the Hg(II) adsorption by freshly prepared iron hydrous oxide gel and found that at pH 5 to 8.6 more than 90% of the Hg(II) was adsorbed. The adsorption of Hg(II) by goethite was investigated by several researchers. In a recent study, Barrow and Cox (1992a) reported that in the absence of chloride, the adsorption maximum was just below pH 4. In all these studies with pure minerals as adsorbents, the addition of chloride to colloid suspensions has been found to significantly reduce Hg(II) adsorption at low pH and caused the pH at which the adsorption maximum occurred to increase.

Some attempts have been made to study the adsorption of Hg(II) by soils. Semu et al. (1987) studied the effect of pH on the Hg(II) adsorption by tropical soils within a pH range of 5 to 8 and observed that the adsorption increased with increasing pH. Barrow and Cox (1992b), however, reported that in the absence of added chloride, there was little effect of pH on mercury adsorption between pH 4 and 6. Further increase of pH resulted in a decrease in the adsorption. They also reported that the addition of chloride decreased the Hg(II) adsorption by soil at low pH but had little effect at high pH.

Trost and Bisque (1970) examined the adsorption capacity of various clay minerals and organic substances and found that humus rich materials had a far higher adsorption capacity than pure clays. Fang (1978) and Landa (1978) also reported the same results. By comparing Hg-adsorption by soils of identical mineralogy and humus content but varying vegetation cover, Semu et al. (1987) further suggested that not only the amount but also the

quality of organic matter decided the adsorption capacity of Hg. Ramamoorthy and Rust (1976) examined the correlation between the adsorption maximum and binding strength of Hg(II) and soil properties and suggested that the adsorption maximum was related to soil properties in the order of surface area > organic content > cation exchange capacity (CEC) > grain size, whereas the bonding constant was correlated in the order organic matter > grain size > CEC > surface area.

Lindberg et al. (1979) reported that the organic associated fraction (extracted with $NaHCO_3$) of mercury adsorbed by a soil near the Almadén mercury mine accounted for nearly 200 times more than the cation exchangeable fraction. Lindberg et al. (1975) also reported that soil fulvic acid exerted a stronger affinity for Hg than a strong cation-exchange resin. This explains the observation that podzolic soils may contain maximum Hg-concentrations in the horizons of humus accumulation (McKeague and Kloosterman, 1974). Kerndorff and Schnitzer (1980) further examined the retention of mercury and other 10 metal ions by humic acid at different pH. They reported that the order of adsorption of these metals by humic acid is:

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

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

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

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

It can be seen that mercury and iron are always adsorbed most readily by humic acid. The effect of dissolved organic matter on the adsorption of mercury was also studied by some researchers. Peng and Wang (1982) reported that the dissolved organic matter tended to form very stable complexes with Hg(II). The Hg-organic matter complexes may account for 90% of the total mercury existing in river water. Laboratory experiments showed that the presence of dissolved organic matter, such as humic acids, glycine, leucine, acetate, cyanide or NTA, generally reduced the adsorption of Hg(II) on mineral surfaces (Trost and Bisque, 1970;

MacNaughton and James, 1974; Farrah and Pickering, 1978). However, the dependency of this effect on environmental conditions is not fully understood.

2.1.3.2 Methods and Materials

A batch equilibration technique described in Figure 5 was followed in all studies. An initial mercury (prepared form $Hg(NO_3)_2$) concentration of 10^{-7} M, a soil/solution ratio of 1 g/100 ml and an ionic strength of 0.01 M were employed. Fifteen New Jersey soils used in this study were well characterized in terms of particle size distribution, MnO_2, Fe_2O_3, Al_2O_3, total organic carbon, cation and anion exchange capacity, and BET surface area (Tables 5-10).

A preliminary kinetics study was first conducted to establish equilibration time. It was found that the equilibrium was reached after 24 hours of shaking on a reciprocating shaker (Orbit, No. 3590, Lab-line Instruments, Inc., Melrose Park, IL) at a rate of 100 strokes. Therefore, this setup was used throughout the entire study. After equilibration, the suspensions were filtered through 0.45 μm Nuclepore membrane filters. An aliquot of each supernatant was then digested and analyzed for Hg(II). The difference between initial mercury concentration and the mercury remaining in solution at equilibrium is calculated as that adsorbed by soil.

For the study of the adsorption of Hg(II) as a function of pH, ten pH values ranging from 3 to 10 were used and the ionic strength was kept at 0.01 M $NaNO_3$.

For the study of effect of chloride concentration on the Hg(II) adsorption, three soils of low, medium and high organic matter content were used for this study. The chloride concentrations were adjusted to range from the background concentration to 1 x 10^{-2} M by adding NaCl. The concentration of $NaNO_3$ was adjusted correspondingly to maintain a constant ionic strength of 0.01 M. The experiments were carried out at constant low, medium, and high pH.

For the effect of organic matter on the Hg(II) adsorption, two kinds of studies were conducted. The first one includes adding different amount of organic matter (3 mg/L to 130 mg/L) to soil suspensions at constant pH and adding same amount of organic matter (95

mg/L) to soil suspensions at different pH (3 to 10). The organic matter was extracted from Boonton Union loam with dilute NaOH solution. The second one includes removing organic matter from soils and then studying the adsorption as a function of pH (3 to 10). The organic matter was removed by treatment with 30% H_2O_2 following the method of Jackson (1962). The soils were then washed by shaking in distilled deionized water followed by centrifuge for 30 min. at 3000 rpm until no H_2O_2 in supernatants was detected using Quantofix Peroxide test paper. The samples were air-dried prior to weighing for use. In both studies, the ionic strength was kept at 0.01 M $NaNO_3$.

2.1.3.3 Results and Discussion

Effect of pH. Fig. 6-20 show the adsorption behavior of Hg(II) as a function of pH. It can be seen that like other heavy metals, mercury adsorption on soils is also highly pH dependent. At low pH, Hg(II) is strongly adsorbed by all soils. The maximum adsorption occurred in the pH range from 3 to 5 for all soils and ranged from 98% to 86% depending on soil properties.

It was noticed that Hg(II) behaves differently from other heavy metals for which the maximum adsorption on soils usually occurs at a higher pH range (Allen et al., 1994). This was also observed in studying the adsorption of Hg(II) on pure minerals such as silica, hydrous manganese oxides, hydrous iron oxide, bentonite and goethite (Lockwood and Chen, 1973; MacNaughton and James, 1974; Newton et al., 1976; Kinniburgh and Jackson, 1978; Barrow and Cox, 1992). The principal reason for this difference is the strong Lewis acid character of mercury. The hydrolysis constants are 3.87 for $pK_{OH,1}$ and 2.77 for $pK_{OH,2}$ corrected for an ionic strength of 0.01 M from Baes and Mesmer (1976). In the soil solutions of our study which had a typical chloride concentration of approximately 1×10^{-6} M, the hydroxo mercury species $Hg(OH)_2$ was calculated to significantly increase in the pH range from 3 to 5 (Fig. 1). The hydroxo metal species have been found to be more readily adsorbed by soil colloids and soil (MacNaughton and James, 1974; James and Healy, 1972; Elliott et al., 1986). This results in the maximum adsorption of Hg(II) by soil occurring at a low pH range from 3 to 5, while the adsorption of other metals in this pH range is very small because the major species of these metals are free metal ions in this pH range.

At higher pH, the Hg(II) adsorption decreases. Two factors suggested by MacNaughton and James (1974), including the decrease of the maximum adsorption sites with increasing pH and the decrease of the chemical adsorption free energy $\Delta G_{chem,\ hydroxo\ species}$ which contains terms that decrease in magnitude with pH, could contribute to the decrease in Hg(II) adsorption. However, a more important factor is the complexation of Hg(II) by the desorbed soil organic matter. This will be discussed latter.

Effect of Organic Matter. The adsorption/desorption of soil organic matter is pH dependent. At low pH, almost all soil organic matter exists in particulate phase (Fig. 21). The percent adsorption of Hg(II) at this pH range is positively correlated with soil organic matter content (Fig. 22). As pH was raised, the amount of desorbed soil organic matter increased significantly. One effect of the increase in desorbed organic matter is a corresponding decrease in surface adsorption sites which may be responsible for the decrease in the Hg(II) adsorption.

Because desorbed organic matter tends to form very stable complexes with Hg(II), this may also reduce the adsorption. This effect was studied by adding organic matter to soil suspensions at both constant pH and variable pH. It was found that the Hg(II) adsorption at pH 6.5 decreased from approximately 60% to 28% when the added dissolved organic matter increased from 3 to 130 mg/L (Fig. 23). When 93 mg/L organic matter was added to soil suspensions at pH range 2.5 to 10, the Hg(II) adsorption generally decreased over most of the pH range for all soils except at very low pH (Fig. 24-26). For Rockaway sandy loam, at pH less than 4, more than 50% of the added organic matter was adsorbed by soil particles (Fig. 27) and the addition of organic matter had no effect or slightly increased the Hg(II) adsorption. At pH greater than 4, more than 50% of the added organic matter remained in solution phase at equilibrium, which caused the Hg(II) adsorption to decrease. For Freehold surface sandy loam and Dunellen sandy loam, only at pH near 3, was more than 50% of the added organic matter adsorbed by soil particles. At this pH range the addition of organic matter had no effect on the Hg(II) adsorption. At higher pH, more than 50% of the added organic matter remained in solution phase at equilibrium and caused the Hg(II) adsorption to decrease.

When soil organic matter was removed, the adsorption of Hg(II) was significantly reduced at low pH. Two hypotheses seem reasonable. First, when soil organic matter was removed, some inorganic surface areas were exposed. Compared with organic matter, soil inorganic components usually have smaller surface areas. Therefore the total soil surface area decreased. This may contribute to the decrease of the Hg(II) adsorption. Second, organic matter generally has stronger adsorbability for Hg(II) than does soil inorganic components. This may also contribute to the decrease of the Hg(II) adsorption. As pH increased, for Dunellen sandy loam, the adsorption increased and reached maximum at pH 7 to 8. For Freehold surface sandy loam and Rockaway sandy loam, the adsorption increased and reached maximum at pH near 4. Further increases in pH resulted in a decrease of the adsorption. However, the extent of the decrease is much smaller than that for the adsorption of Hg(II) by soils without organic matter changes. The results further verified that the complexation of Hg(II) by desorbed organic matter is the major factor that caused the Hg(II) adsorption by original soils to significantly decrease at higher pH.

Effect of Chloride. From Fig. 28-30, It can be seen that at higher pH, chloride has little effect on the adsorption of Hg(II) by any of the soils. In this pH range, only small amount of Hg-Cl complexes is formed. At low pH, chloride may affect the adsorption. However, the extent of this affect depends on soil organic matter content. For the soil of low organic matter content (0.2%), the addition of chloride significantly reduced the adsorption (Fig. 28). The predominant adsorption sites in this soil are inorganic. Due to coordination selectivity, Hg^{2+} prefers Cl^- as an electron donor to O^{2-} as a donor (negative surface group). As a result, most of the Hg(II) forms $HgCl_2$ complex which has been found to be poorly adsorbed by inorganic surfaces (Lockwood and Chen, 1973; MacNaughton and James, 1974; Newton et al., 1976; Kinniburgh and Jackson, 1978; Barrow and Cox, 1992). Therefore, as the concentration of chloride was increased, $HgCl_2$ become more and more predominant which resulted in the decrease of Hg(II) adsorption (Fig. 31). For the soil of medium organic matter content (1.9%), the addition of chloride slightly reduced the adsorption (Fig. 29). For the soil with very high organic matter content (8.6%), the addition of chloride had almost no effect on the adsorption of Hg(II) (Fig. 30). This suggests that $HgCl_2$ is predominantly adsorbed by organic matter.

2.1.3.4 Conclusions

This study has demonstrated that the adsorption of Hg(II) on soils is highly pH dependent. At low pH, Hg(II) can be strongly adsorbed by all soils. At higher pH, the Hg(II) adsorption decreased. The complexation of Hg(II) by desorbed soil organic matter at higher pH is the most important factor contributing to the decrease of the adsorption. The presence of chloride in soil solution has no effect on the adsorption of Hg(II) at high pH, but can significantly reduce the adsorption of Hg(II) at low pH. However, Cl^- has little effect on the adsorption of Hg(II) on soils of high organic matter content regardless of pH.

2.1.4 Column Leaching Study

2.1.4.1 Introduction

In order to understand the bonding strength of Hg(II) on soil particles, the column leaching study was conducted. The effects on both flux and soil types on the leachability of Hg(II) was investigated.

2.1.4.2 Methods and Materials

Three soils of different physical and chemical properties, Downer loamy sand, Sassafras sandy loam, and Birdsboro silt loam, were used for this study. The following procedure was used to conduct the experiments:

a. Conducted batch adsorption experiment using initial mercury concentration of 20 μg/L at soil pH;
b. After equilibration, the suspension was transferred to a column with a 0.45 μm Nuclepore filter membrane at the bottom of the column;
c. Once the dripping stopped, the soil was leached with 0.01 M $NaNO_3$ solution at flow rates of 1.0, 5.0, and 10.0 ml/min. The effluent was collected in 10 ml fractions;
d. The samples were analyzed using FIA.

2.1.4.3 Results and Discussion

The results are shown in Fig. 32-34. The adsorbed mercury in all soils was desorbed through leaching. This suggests that freshly adsorbed mercury is not tightly bonded on soil particles.

With respect to the affect of flux on mercury desorption, the general trend is that the greater the flux is, the smaller the solution concentration results. This is true for all three soils, although the degree to which the concentration changes are different. This is because at higher fluxes, the leaching solution has insufficient contact time with the soil for the solution phase concentration of mercury to reach its maximum value.

The desorption curves at three flow rates on Downer loamy sand almost coincided each other. This is due to the fact that less mercury was adsorbed by sand comparing to loam soil and the adsorption by sand was weaker.

2.2 Arsenic

2.2.1 Establishment of the Experimental Protocol for the Determination of Arsenic

A colorimetric method modified from the work of Johnson (1971) and Johnson and Pilson (1972) was used for determination of arsenic. A mixed reagent containing ammonium molybdate, sulfuric acid, ascorbic acid, and potassium antimonyl-tartrate is used to develop color by complexation of As(V) to form molybdenum blue complex. The samples were then determined using a HACH DR/2000 spectrophotometer at a wavelength of 865 nm.

2.2.1.1 Calibration

All solutions were prepared using distilled deionized water and analytical-grade reagents. Standard solutions for calibration were prepared fresh by diluting from 1000 ppm As(III) standard solution (Fisher, Atomic Absorption Standard). The mixed reagent was freshly prepared by mixing 0.024 M ammonium molybdate, 3.5 N sulfuric acid, ascorbic acid, and potassium antimonyl-tartrate solutions with a ratio of 2:5:2:1.

8 ml of each standard solution was taken and put into 10 ml test vials. 0.2 ml of 3.5 N HCl and 0.2 ml of 0.04 M potassium iodate were subsequently added to each vial to oxidize As(III) to As(V). The mixtures were allowed to equilibrate for 30 minutes. 1 ml of mixed reagent was then added to each vial and were allowed 4 hours to develop color. The absorbance of each standard was determined by a HACH DR/2000 spectrophotometer at 865 nm.

The calibration curve was shown in Fig. 35. The linear range is about 40 μg/L to 5 mg/L with regression coefficient of 0.9998.

In the presence of phosphate in solution, the reaction of phosphate with mixed reagent can also form a molybdenum blue complex. Since the reaction between As(III) and mixed reagent does not develop color, both As(III) and As(V) and phosphate can be determined by treating samples in different ways, i.e., oxidation, reduction, and non-treatment. The difference between the concentrations of untreated and reduced samples is the concentration of As(V). The difference between the concentrations of the oxidized and reduced samples represents the total arsenic concentration. The concentration of As(III) is calculated as the difference between the concentrations of total arsenic and As(V).

The reducing reagent was prepared fresh by mixing 0.74 M sodium metabisulfide, 0.056 M sodium thiosulfate, and 3.5 N sulfuric acid solutions with a ratio of 2:2:1.

2.2.1.2 Accuracy Test

A standard addition method was used to test the accuracy of the colorimetric method with soil extracts as matrixes. The recoveries of added arsenic at low and high levels are more than 90% for both soil extracts which contained high and low organic matter contents (Table 11).

2.2.2 Preliminary Results on Arsenic Adsorption onto Soil

2.2.2.1 Materials and Methods

As(III) adsorption on Downer loamy sand was measured as a function of pH. A soil/solution ratio of 0.3 g/30 ml, an initial As(III) concentration of 5 mg/L, and an ionic strength of 0.01 M $NaNO_3$ were employed. 0.1 M HNO_3 and 0.1 M NaOH was used to adjust pH from 3 to 10. The suspensions were shaken on a reciprocating shaker for 24 hours at a rate of 50 strokes. After equilibration, the suspensions were filtered through 0.45 μm membrane filters. 8 ml of each filtrate was placed in a 10 ml test vial and 0.2 ml 3.5 N HCl and 0.2 ml 0.04 M potassium iodate were added to each vial to oxidize all forms of arsenic to As(V). 0.4 ml of reducing reagent was added to another 8 ml of each samples to reduce all forms of arsenic to As(III). 30 minutes was allowed for the oxidation and reduction reactions. 1 ml of mixed reagent was then added to all samples and 4 hours were allowed for color to develop. The concentration of arsenic was determined at last.

2.2.2.2 Results and Discussion

The results are shown in Fig. 36. Less than 10% of added arsenic was adsorbed by soil and the maximum adsorption occurred at pH near 9. Similar results were observed by Gupta and Chen (1978). The adsorption behavior of As(III) is closely correlated with its speciation chemistry. At pH less than 9, the predominant As(III) species in solution is H_3AsO_3. The species can be adsorbed by negatively charge surface group of solids through hydrogen bonding. Therefore, the adsorption increased with increase of negatively charged surface group as pH increased. At pH greater than 9, almost all soil particles bear negative charges, and the predominant As(III) species in solution are negatively charge species, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-}. As a result of the repulsion reaction between the charges of As(III) species and particles, the adsorption decreased.

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APPENDIX A (Tables

Table 5 The fraction of material larger than 2 mm.

Soil Name	< 2 mm	> 2 mm	> 2 mm
	(g)	(g)	(%)
Birdsboro silt loam	20203.0	10555.5	34.32
Boonton 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 materials 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	0.70
Penn silt loam	21666.5	3372.2	15.60
Rockaway stony loam	15188.5	5902.0	27.98
Sassafras sandy loam	25501.7	761.2	3.00
Washington loam	14807.9	4379.4	29.60
Whippany silty clay loam	18370.8	3946.3	21.50

Table 6 Analysis of particle size distribution, and soil pH

Soil	Particle Size Distribution			pH*	
Name	Sand %	Silt %	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 materials 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	37	6.17	5.72

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

Table 7 Analysis of soil cation exchange capacity, and soil organic matter.

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

Table 8 Total Fe, Al, and Mn oxides extracted by perchloric - nitric acids.

Soil Name	Fe_2O_3	Al_2O_3	MnO_2
		(%)	
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 materials 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
Hazen gravelly loam	4.307	4.372	0.116
Lakewood sand	0.657	0.321	0.008
Penn silt loam	4.851	6.397	0.077
Rockaway stony loam	3.538	5.047	0.096
Sassafras sandy loam	2.674	3.191	0.018
Washington loam	5.556	7.072	0.136
Whippany silty clay loam	3.282	5.047	0.023

Table 9 Amorphous and crystalline Fe, Al, and Mn oxides extracted by sodium dithionite - citrate - bicarbonate.

Soil Name	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 materials 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
Hazen gravelly loam	1.493	0.958	0.189
Lakewood sand	1.600	0.201	0.016
Penn silt loam	1.654	0.546	0.142
Rockaway stony loam	3.839	1.731	0.179
Sassafras sandy loam	1.973	0.365	0.032
Washington loam	1.813	0.415	0.236
Whippany silty clay loam	1.494	0.184	0.025

Table 10 Amorphous Fe, Al, and Mn oxides extracted by ammonium oxalate.

Soil	Fe_2O_3	Al_2O_3	MnO_2
Type		(%)	
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 material 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
Hazen gravelly loam	1.117	0.574	0.034
Lakewood sand	0.344	0.096	0.0002
Penn silt loam	0.743	0.593	0.022
Rockaway stony loam	0.832	1.181	0.028
Sassafras sandy loam	0.699	0.461	0.005
Washington loam	0.900	0.684	0.038
Whippany silty clay loam	0.736	0.388	0.004

Table 1 Study of the influence of matrix on the mercury determination

Solution pH	Total Dissolved Organic C (mg/L)	Hg(II) Addition (μg/L)	Recovery (%) Non-digested	Digested
3.27	16.54	20	80.00	82.98
3.40	15.90	20	76.25	96.56
3.69	14.81	20	80.00	93.25
4.05	14.12	20	80.00	100.32
5.24	17.02	20	74.38	96.35
6.05	23.56	20	55.63	82.27
6.56	29.57	20	40.00	95.43
8.93	75.92	20	35.63	83.53
9.70	98.84	20	16.88	94.47
Average				91.68

Table 2 Test of the effects of Hg-Cl and Hg-OH complexation on the Hg(II) measurement by FIA

Hg Standard Addition (µg/L)	Hg-Cl Complexes of Total (%)	Hg-OH Complexes of Total (%)	Recovery (%)
20	99.97		102.90
20	99.96		102.90
20	99.96		102.90
20	99.96		100.70
20	99.96		105.20
20	99.95		105.20
20		100	95.10
20		100	97.90

Table 3 Efficiencies of seven solution digestion methods

Soil Name	Solution pH	Digestion Method	Recovery (%)
Freehold sandy loam (A)	10.16	a	67.5
		b	81.1
		c	86.1
		d	90.5
		e	114.5
		f	101.5
		g	100.0
Rockaway sandy loam	9.74	a	51.1
		b	70.1
		c	66.8
		d	57.7
		e	79.4
		f	116.0
		g	82.2
Matapeake silt loam	10.09	a	38.7
		b	63.2
		c	56.9
		d	46.9
		e	71.9
		f	91.6
		g	101.0

Table 4 Mass balance for mercury recovery from soil and soil solution

Hg(II) Addition (mg/L)	pH	Total Mass Recovery (µg/L)	Recovery (%)
	Soil with low organic matter content (0.6%)		
0		0.25	
10	3	8.773	85.23
10	6.58	8.497	82.48
10	10.83	8.337	80.87
5	11.15	4.267	80.18
	Soil of high organic matter content (5.4%)		
0		0.286	
10	3.18	8.705	84.19
10	6.25	8.324	80.38
10	8.84	8.419	81.33
5	9.16	4.24	79.55

Table 11 Accuracy test for analysis of arsenic in soil extracts

Soil Extract	As(III) Addition (mg/L)	Total Organic Carbon (mg/L)	Recovery (%)
1	0.6	47	94.69
1	2.0	47	93.39
1	0.0	47	
2	0.6	2	95.69
2	2.0	2	95.19
2	0.0	2	

APPENDIX B (Figures

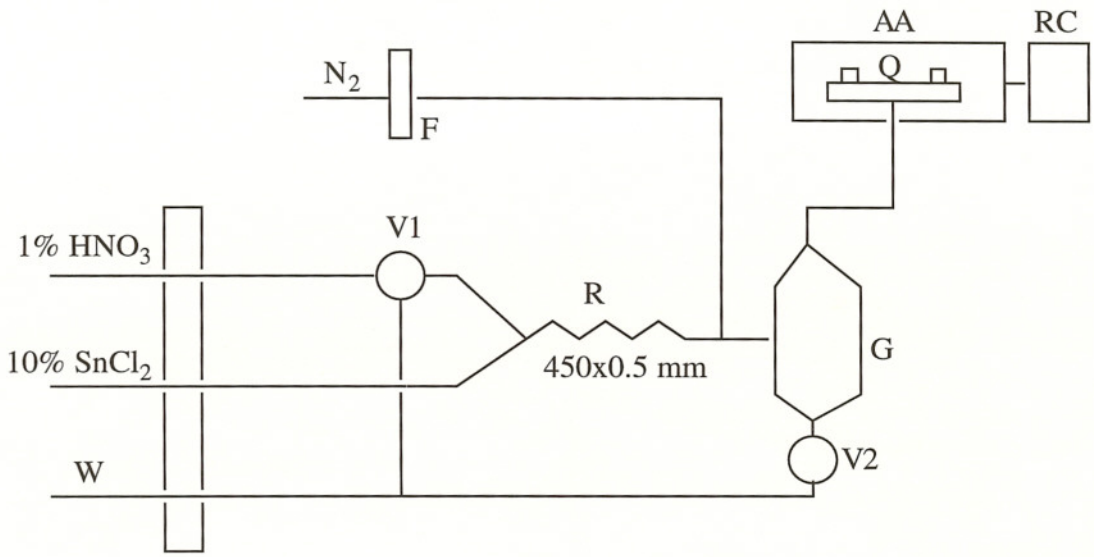

Fig. 1 Schematic of flow injection system. P: Pump; V1: Six-way valve; V2: Two-way valve; R: Reaction coil; Q: Quartz tube; F: Flow meter; RC: Recorder; W: Waste; AA: Atomic absorption spectrophotometry; G: Gas-liquid separator.

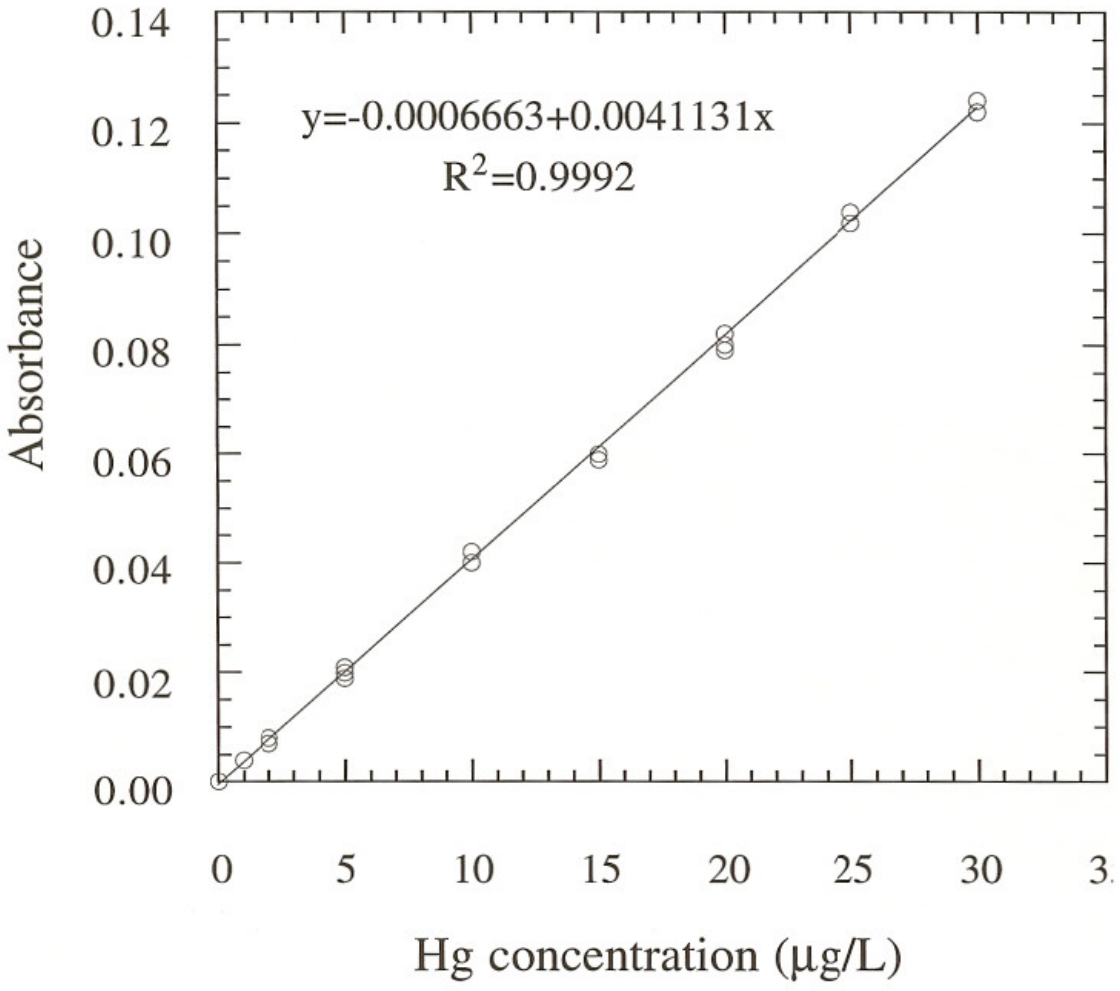

Fig. 2 Mercury calibration curve.

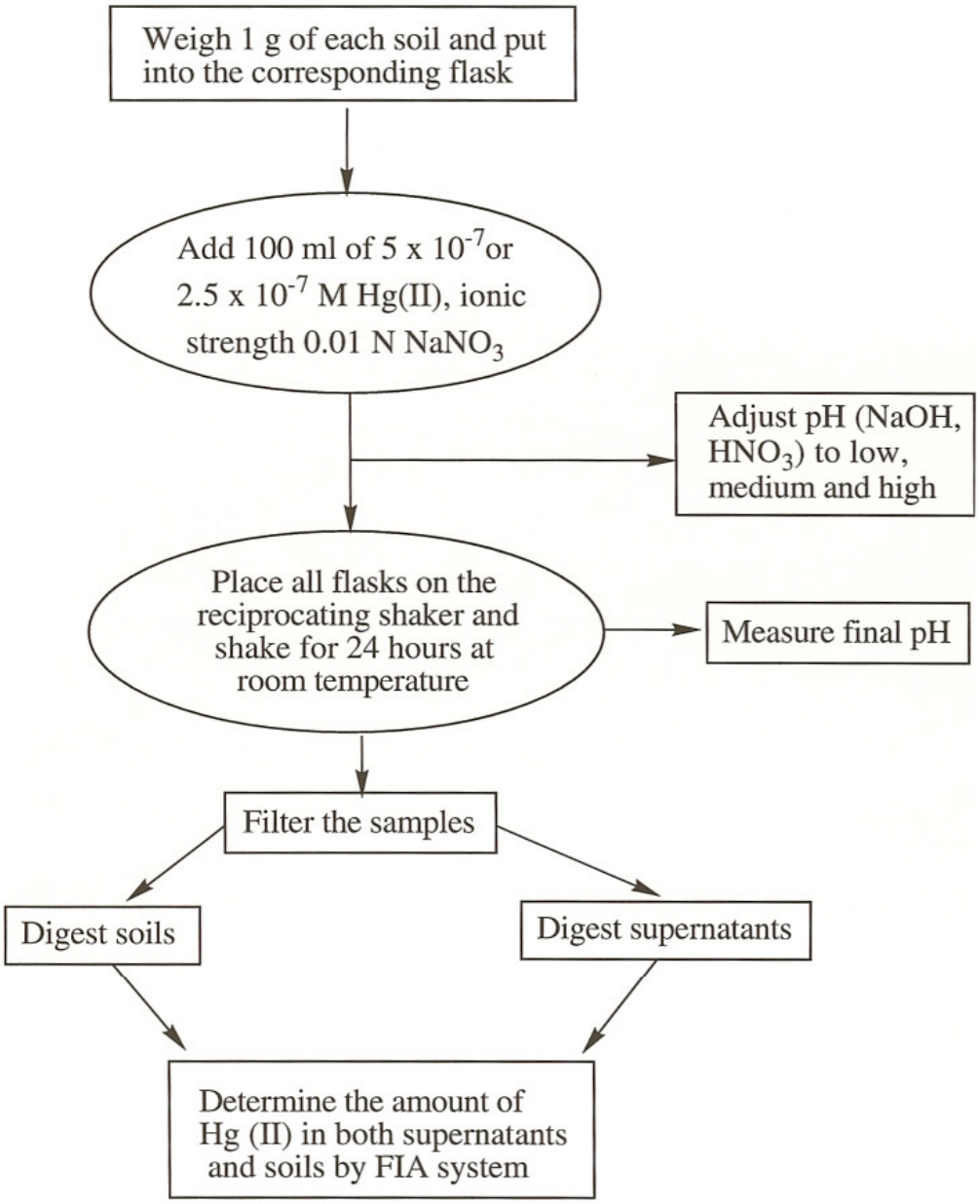

Fig. 3 Experimental protocol for mass balance study.

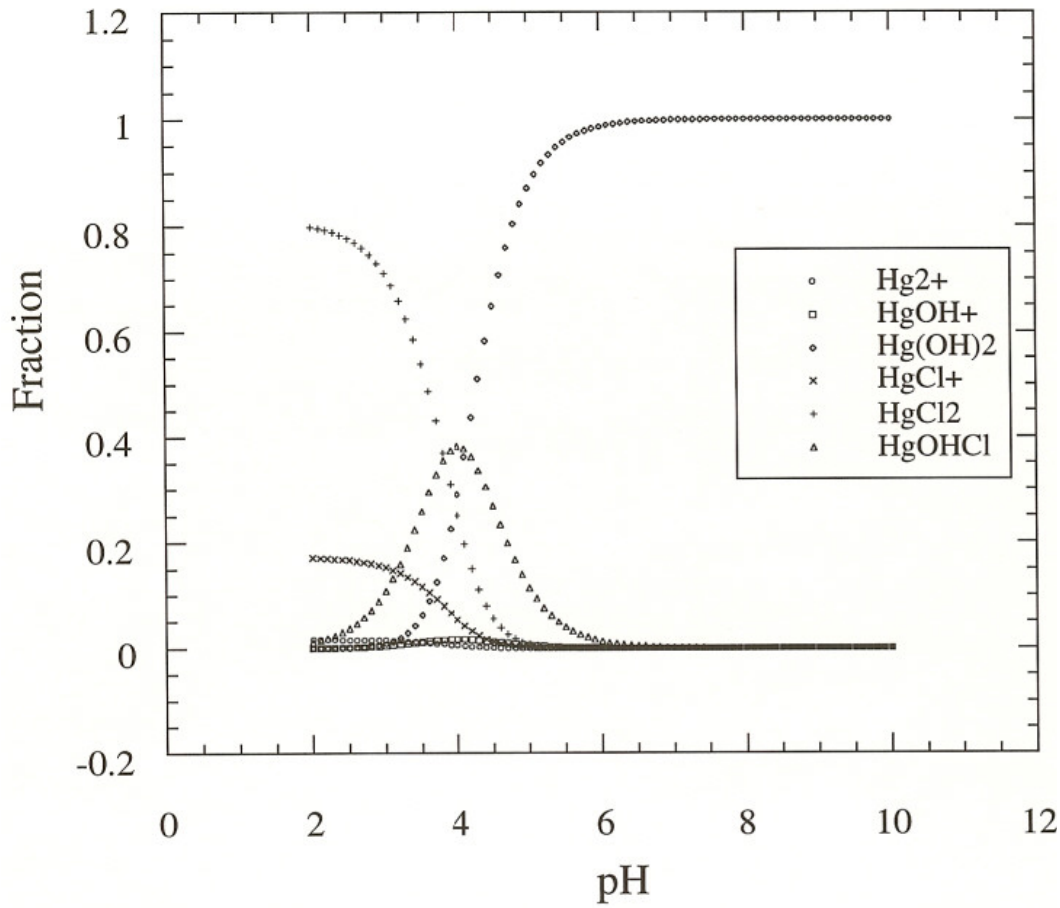

Fig. 4 Hg speciation diagram ($[C^-] = 10^{-6}$ M)

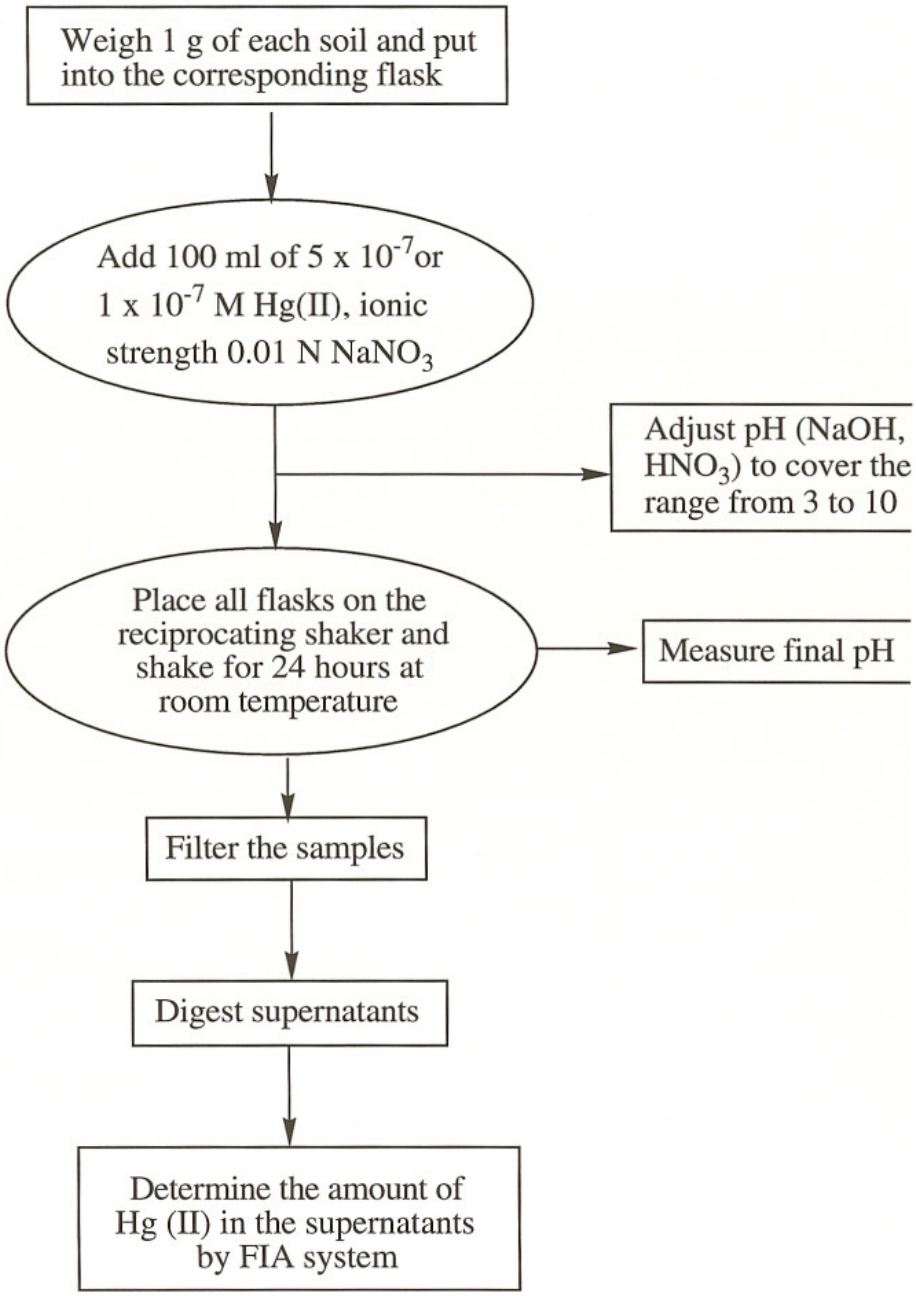

Fig. 5 Flow chart for the batch experimental protocol.

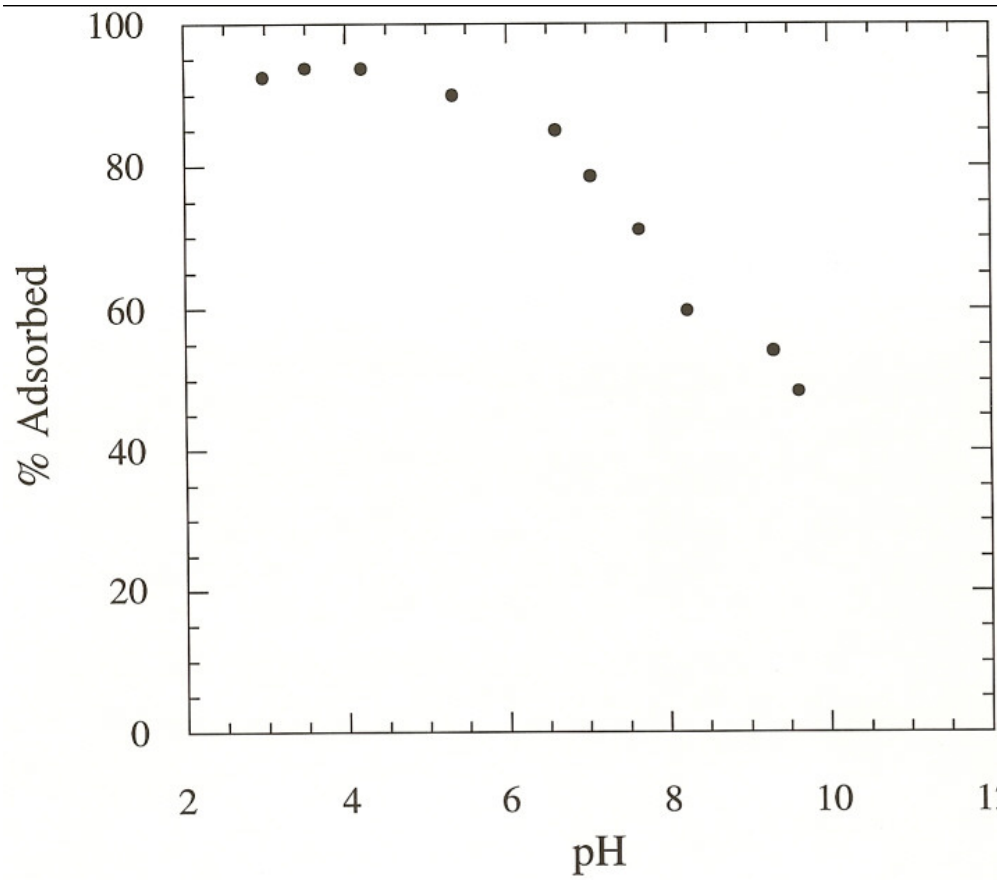

Fig. 6 Adsorption of 1 x 10^{-7} M Hg(II) onto Sassafras sandy loam
Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

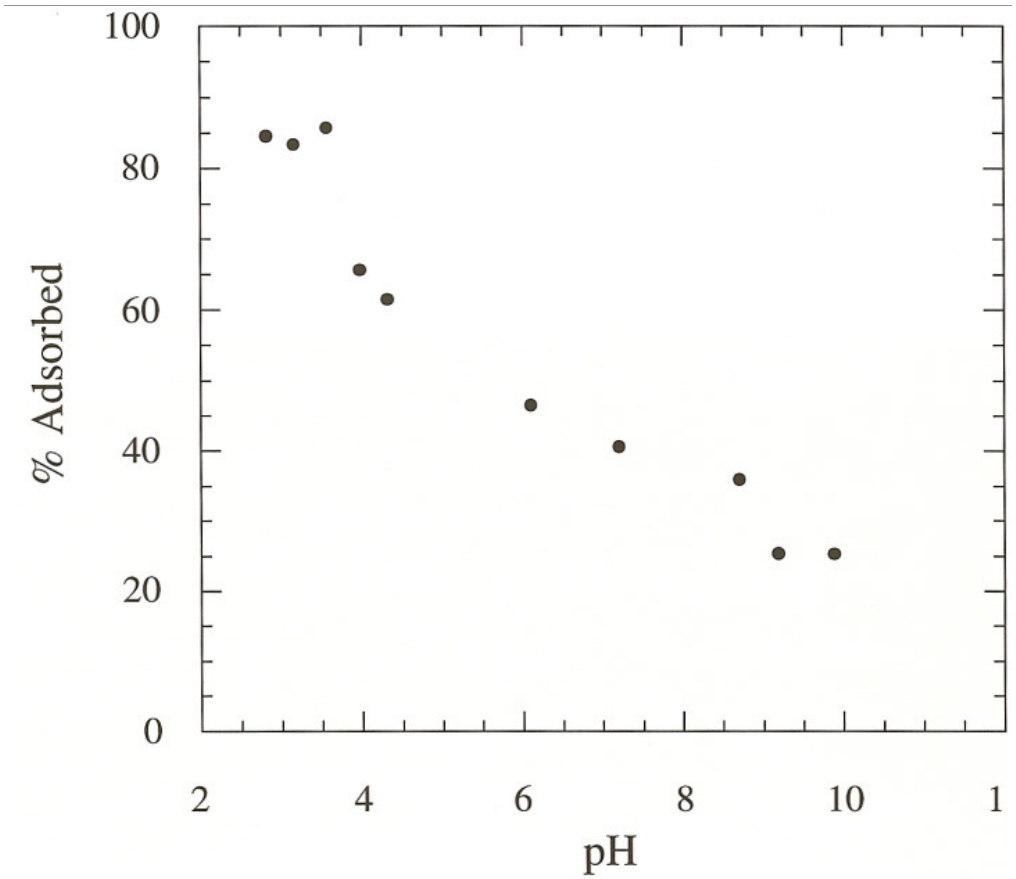

Fig. 7 Adsorption of 1 x 10^{-7} M Hg(II) onto Lakewood sand. Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

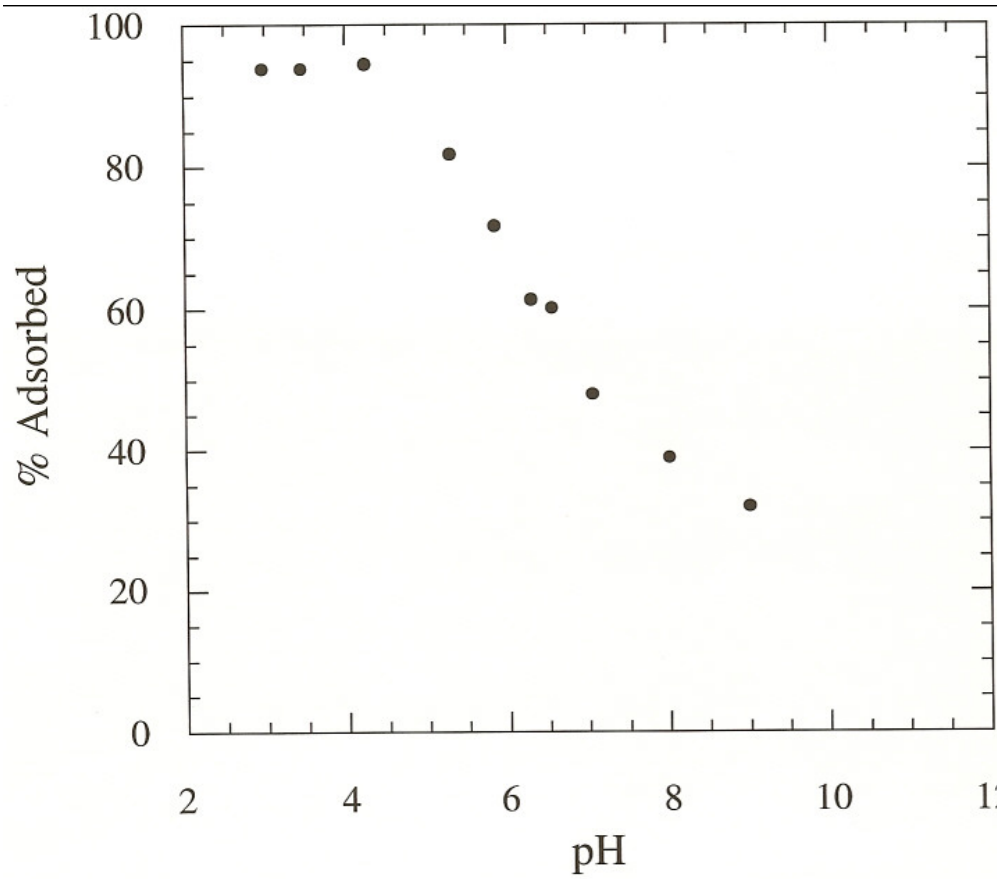

Fig. 8 Adsorption of 1 x 10^{-7} M Hg(II) onto Penn silt loam. Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

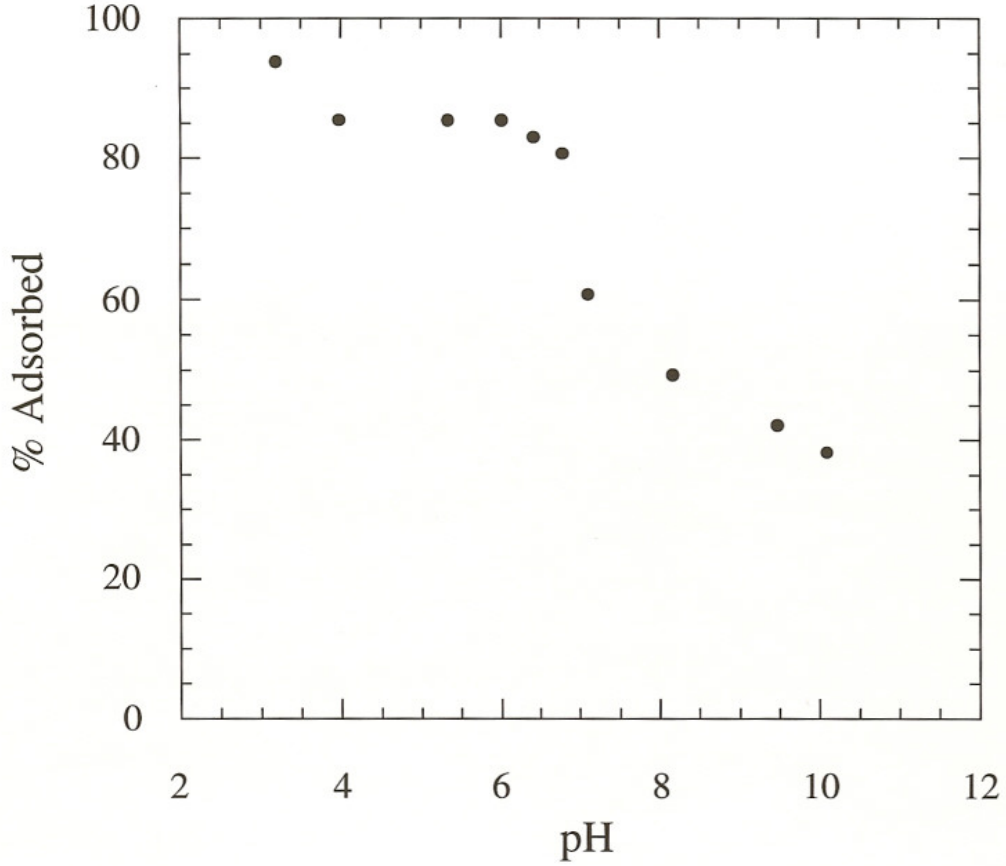

Fig. 9 Adsorption of 1 x 10^{-7} M Hg(II) onto Whippany silty clay loan
Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

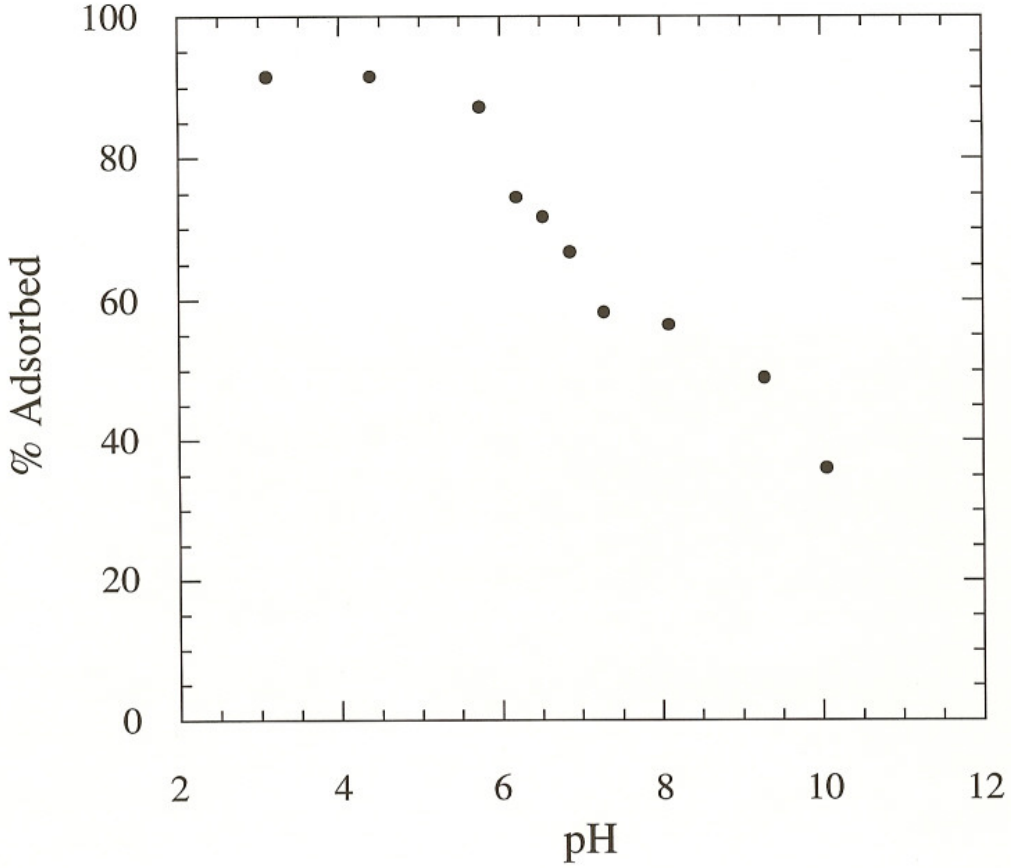

Fig. 10 Adsorption of 1 x 10^{-7} M Hg(II) Washington loam. Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C

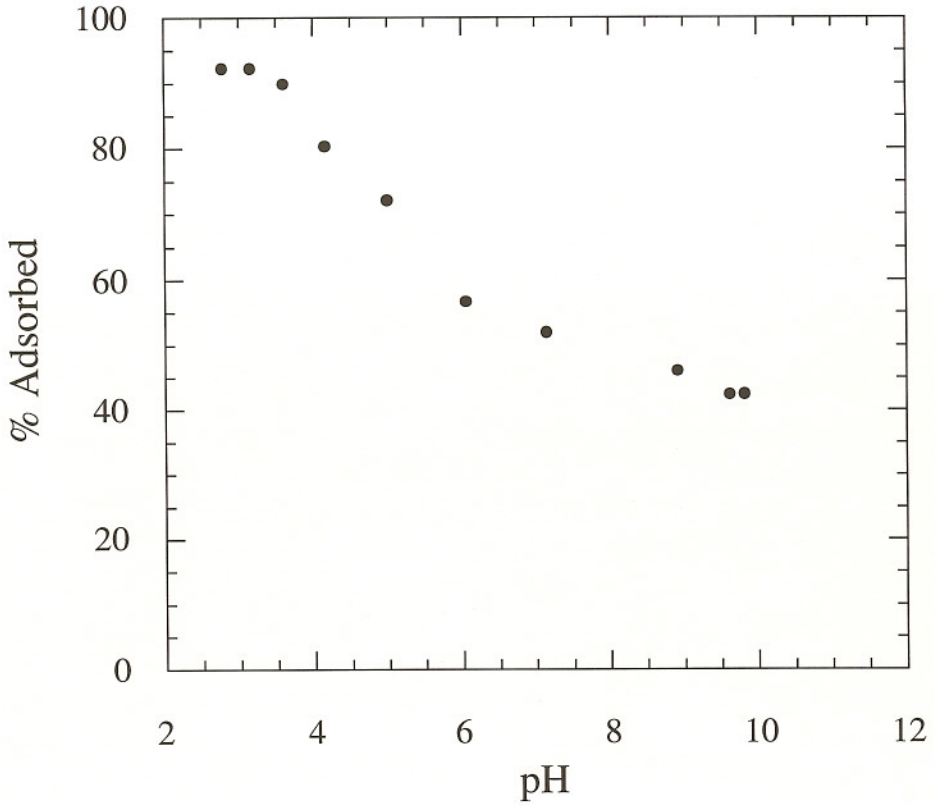

Fig. 11 Adsorption of 1 x 10^{-7} M Hg(II) onto Freehold sandy loam (A horizon). Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

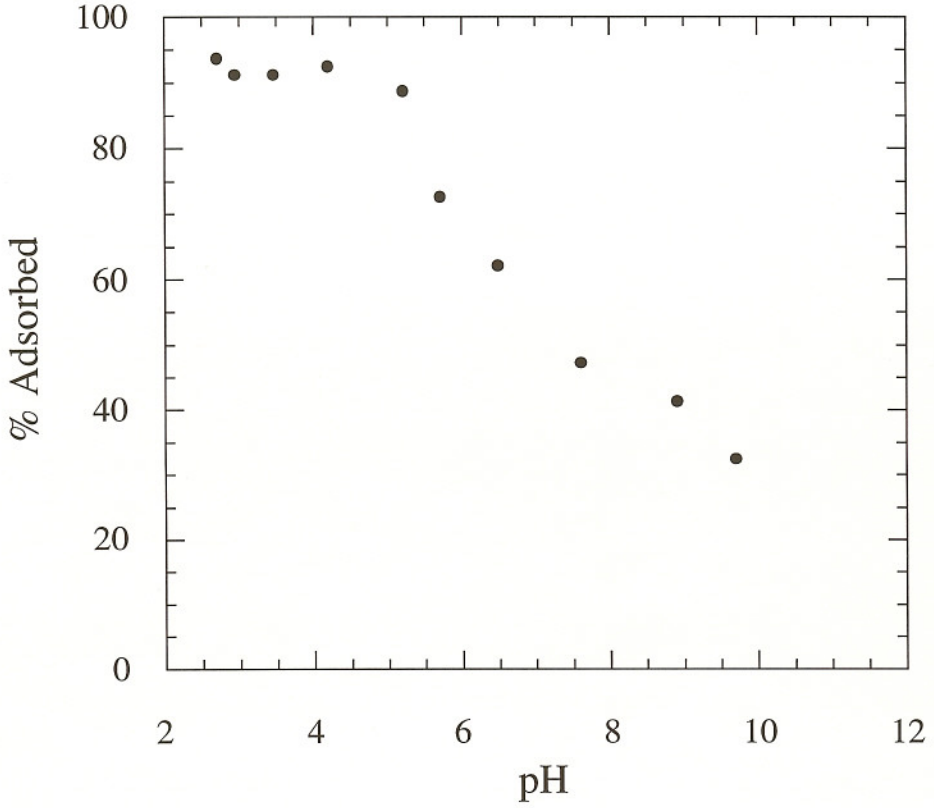

Fig. 12 Adsorption of 1 x 10^{-7} M Hg(II) onto Freehold sandy loam (B horizon). Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

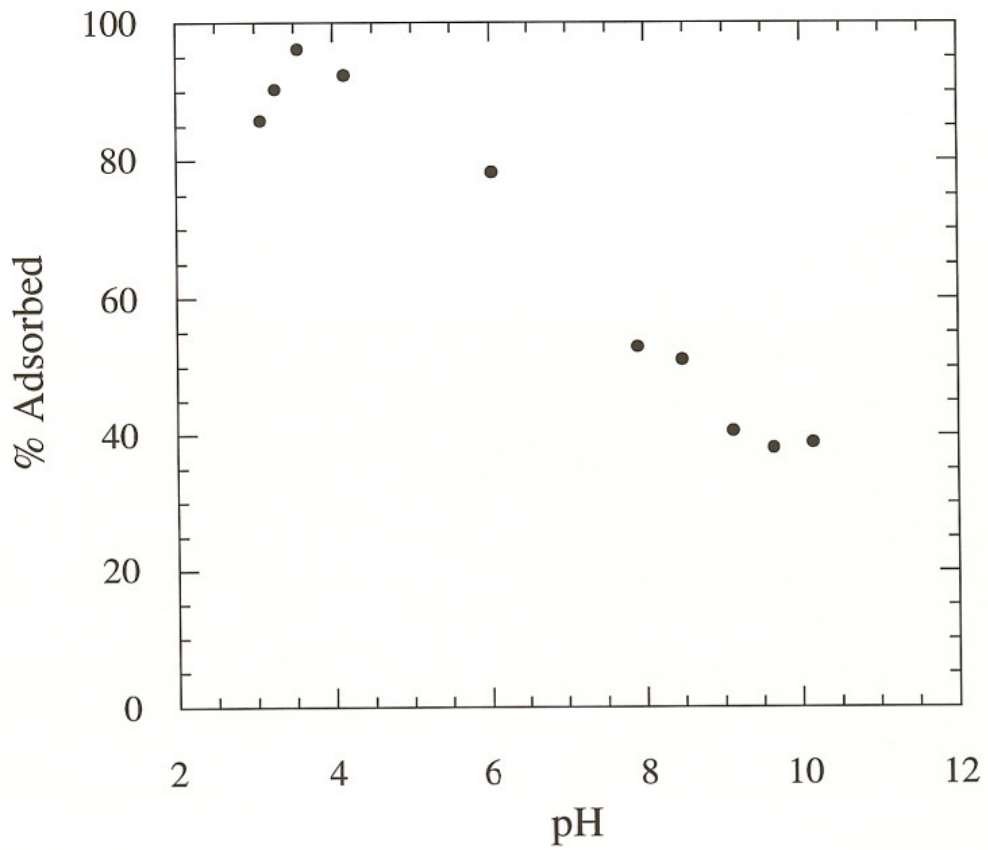

Fig. 13 Adsorption of 1 x 10^{-7} M Hg(II) onto Rockaway stony loam
Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

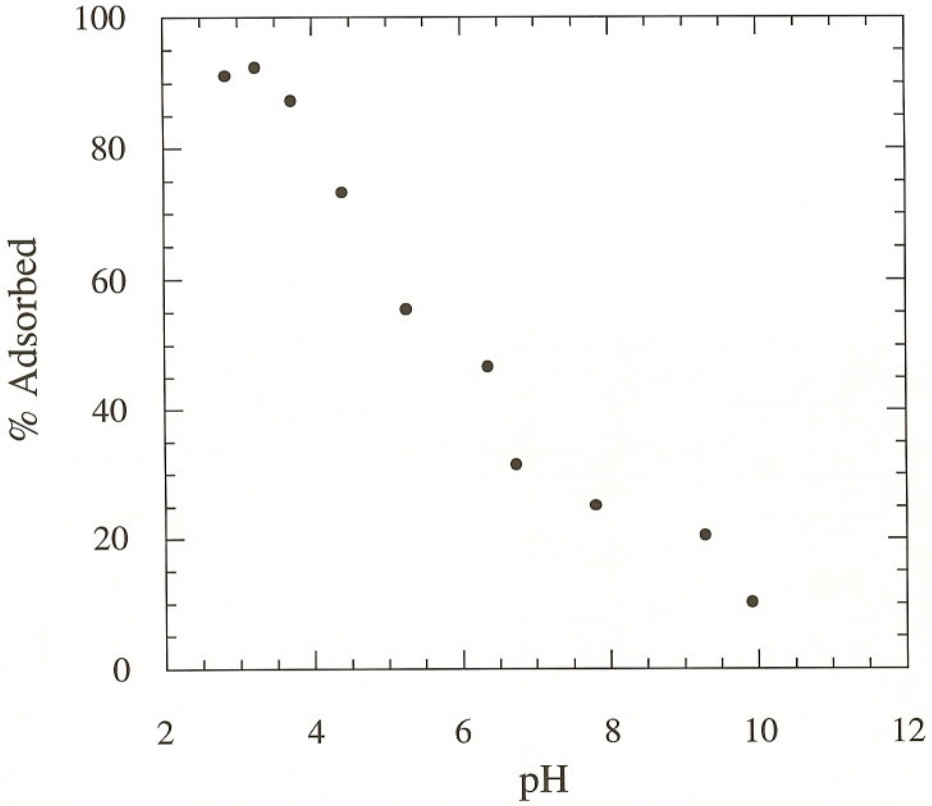

Fig. 14 Adsorption of 1 x 10^{-7} M Hg(II) onto Fill materials from Del. River. Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

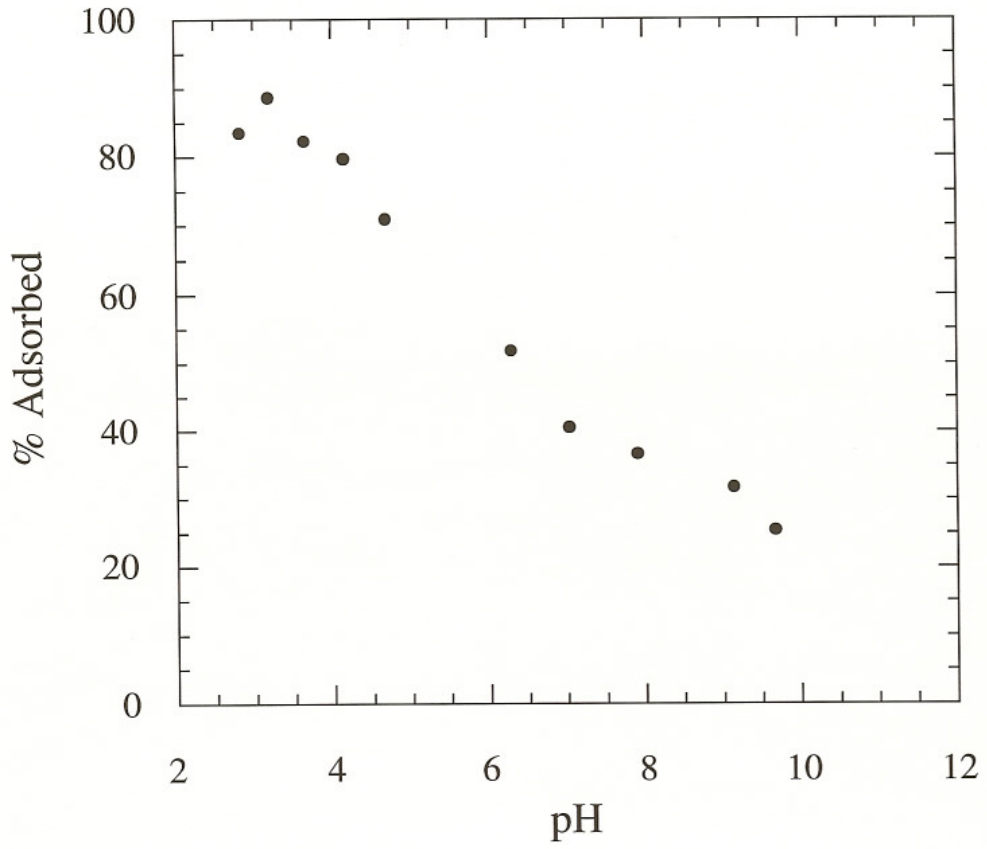

Fig. 15 Adsorption of 1 x 10^{-7} M Hg(II) onto Dowmer loamy sanc
Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

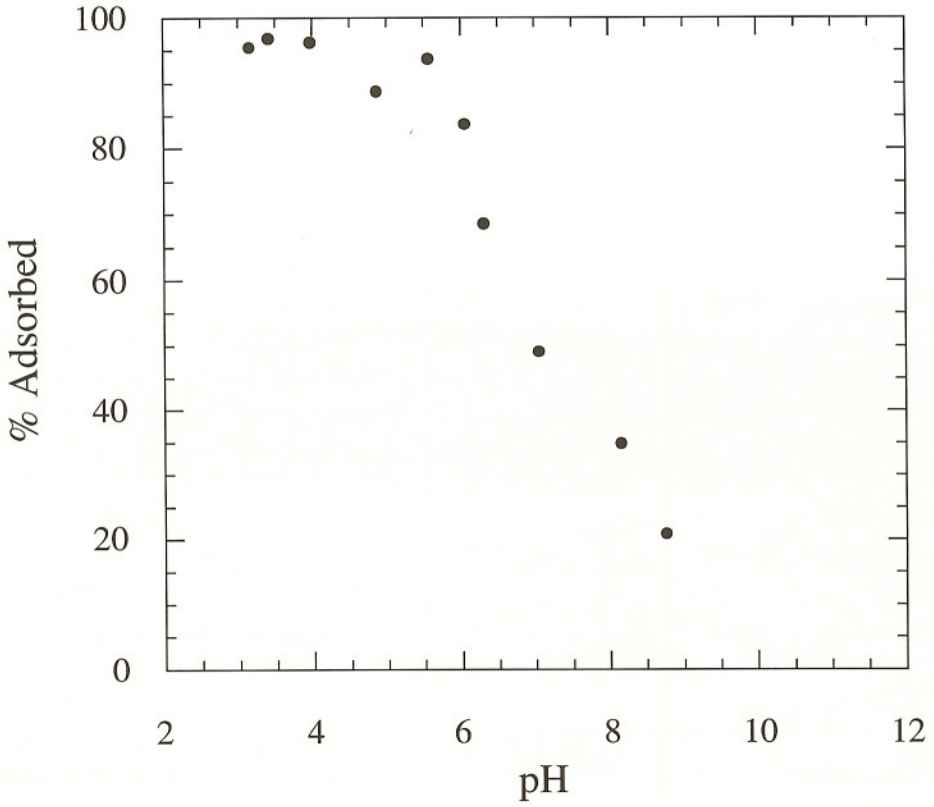

Fig. 16 Adsorption of 1 x 10^{-7} M Hg(II) onto Boonton loam (Union County). Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

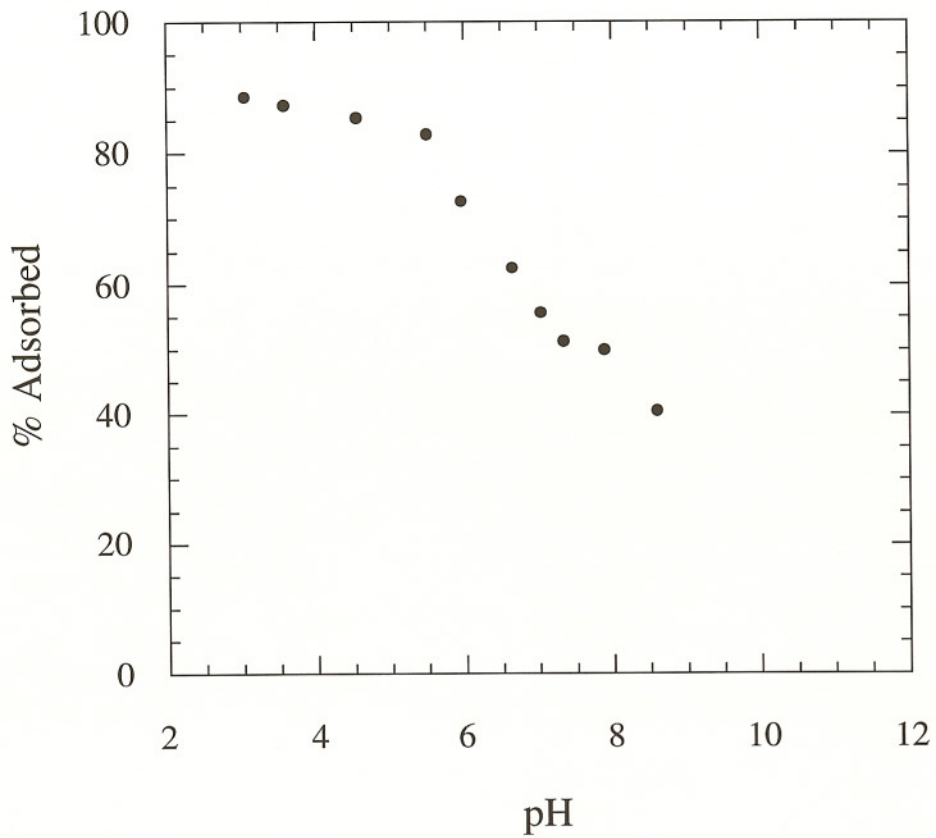

Fig. 17 Adsorption of 1 x 10^{-7} M Hg(II) onto Dunellen sandy loam
Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

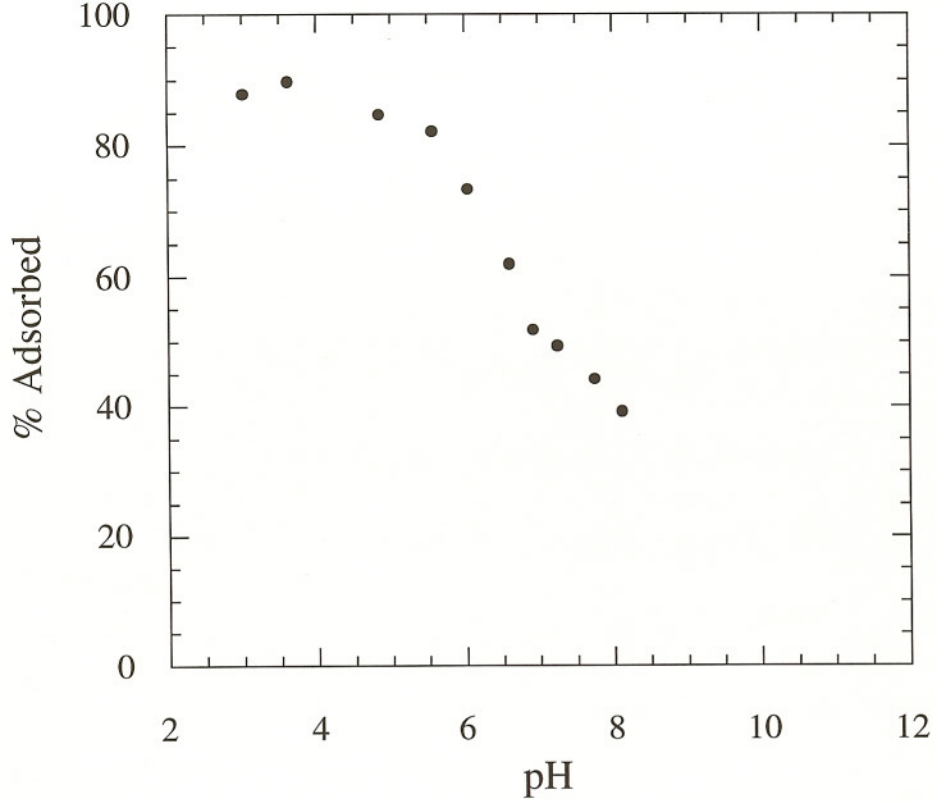

Fig. 18 Adsorption of 1 x 10^{-7} M Hg(II) onto Birdsboro silt loam
Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

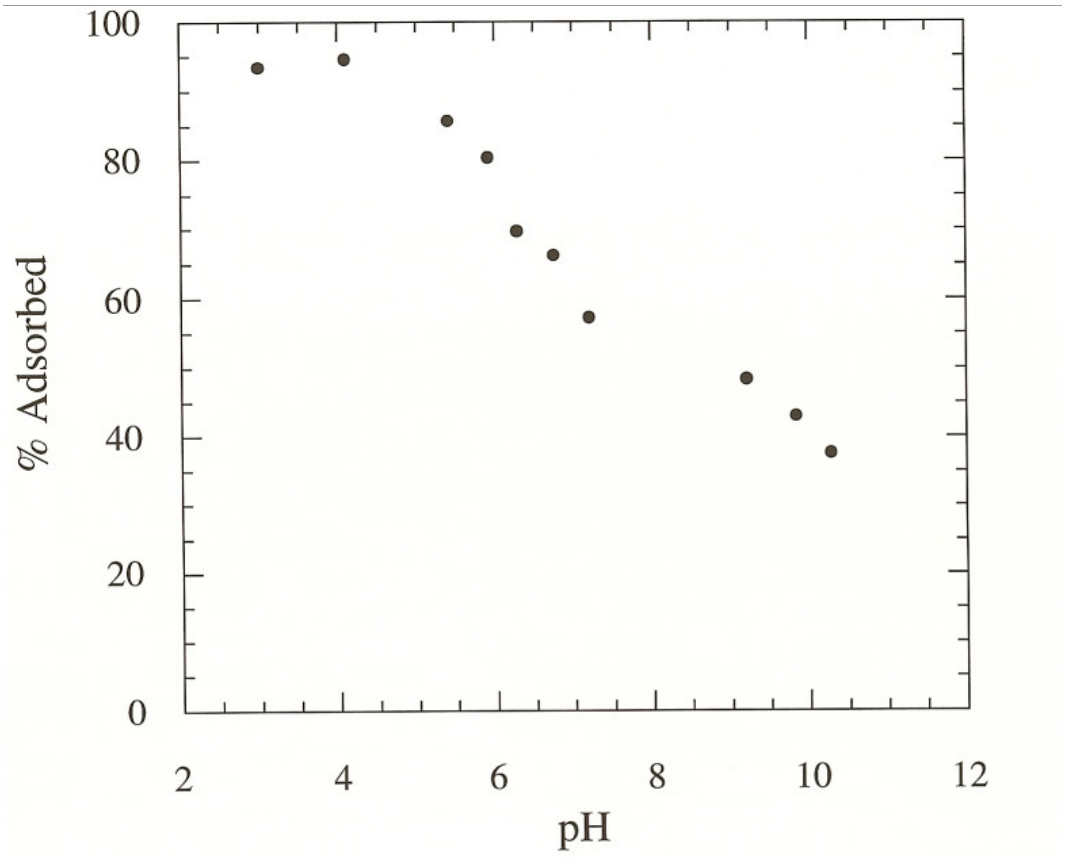

Fig. 19 Adsorption of 1 x 10^{-7} M Hg(II) onto Hazen gravelly loan
Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

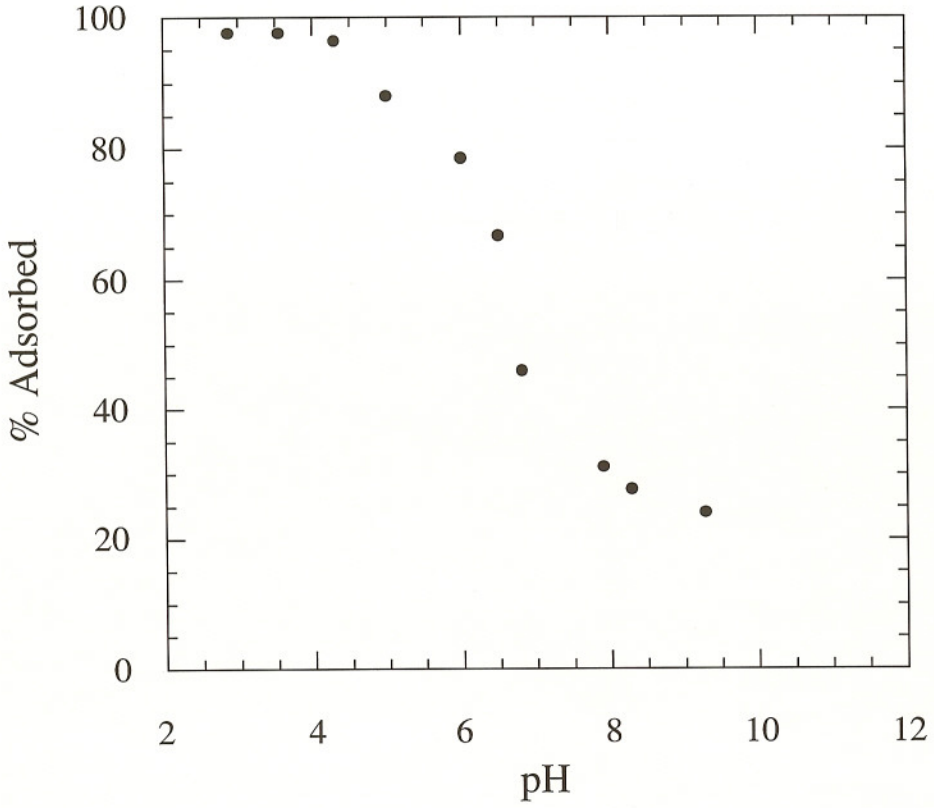

Fig. 20 Adsorption of 1 x 10^{-7} M Hg(II) onto Booyon loam (Bergen County). Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

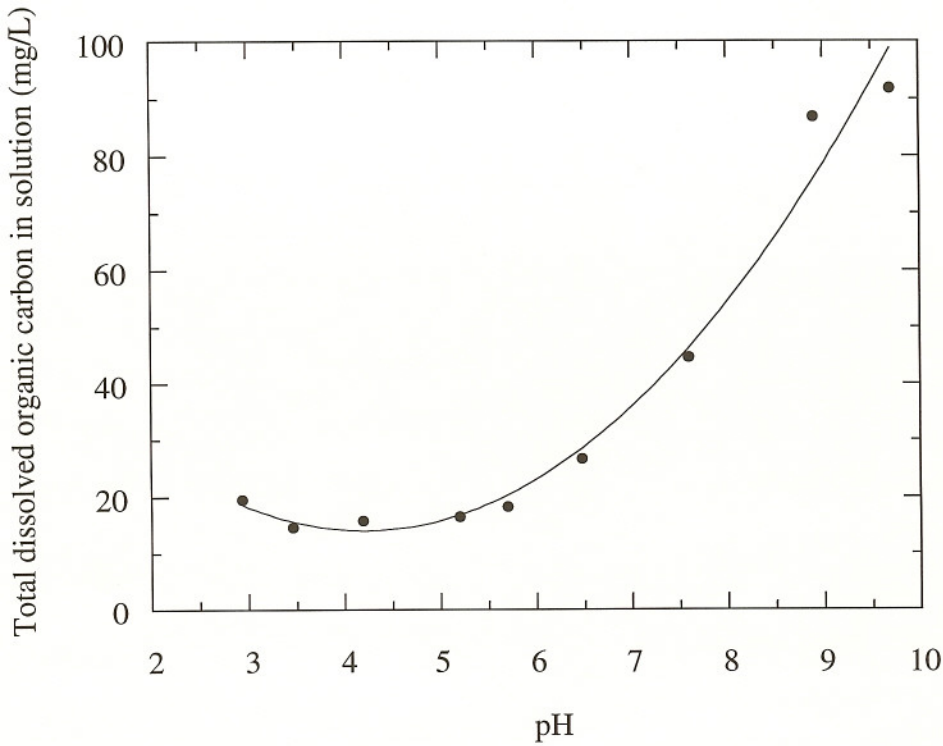

Fig. 21 Desorption of organic matter as a function of solution pH for Freehold subsurface sandy loam. Soil:solution = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

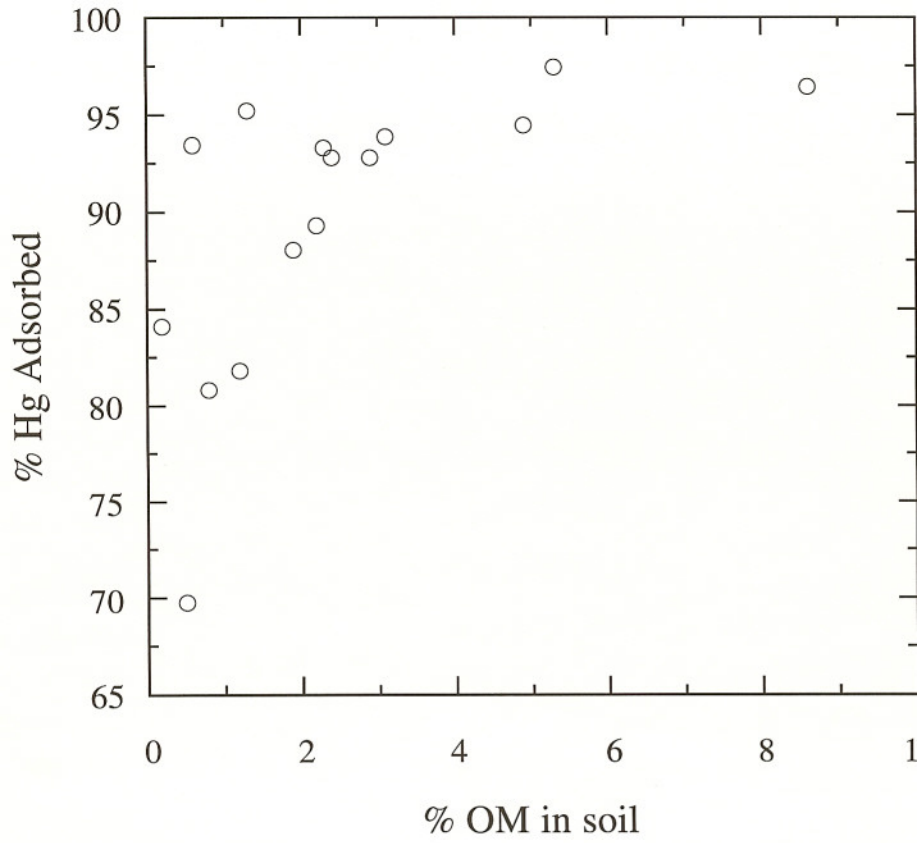

Fig. 22 Correlation between percent Hg(II) adsorption and soil organic matter content.

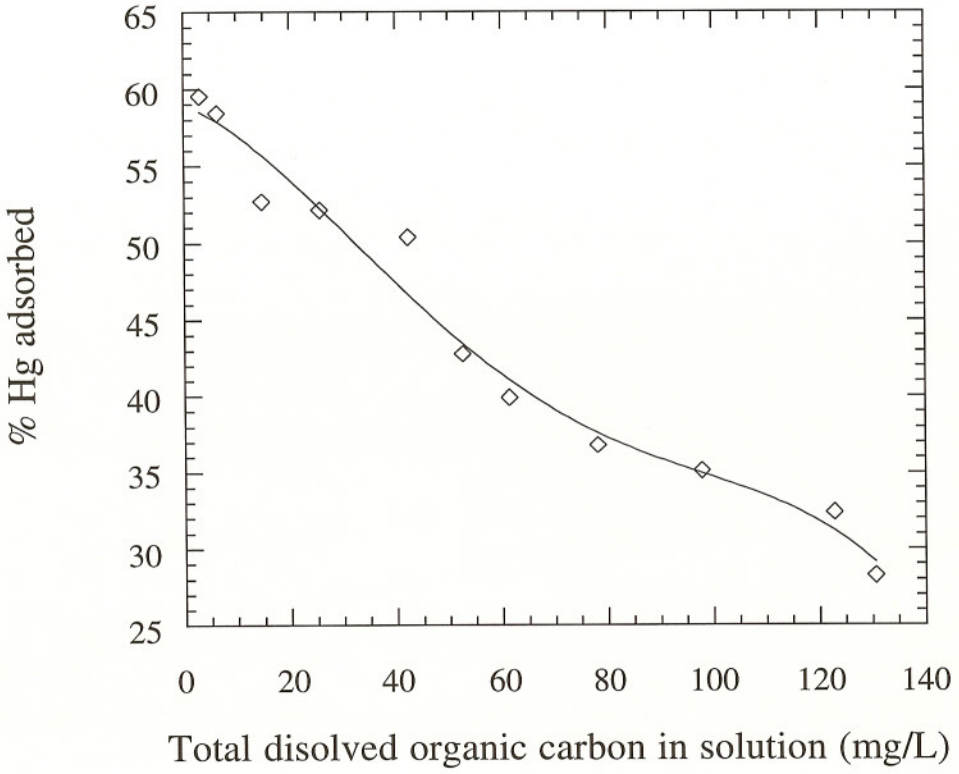

Fig. 23 Hg Adsorption as a function of dissolved organic matter in solution. Soil:water = 1 g/100 ml; I = 0.01 M $NaNO_3$; T = 25°C.

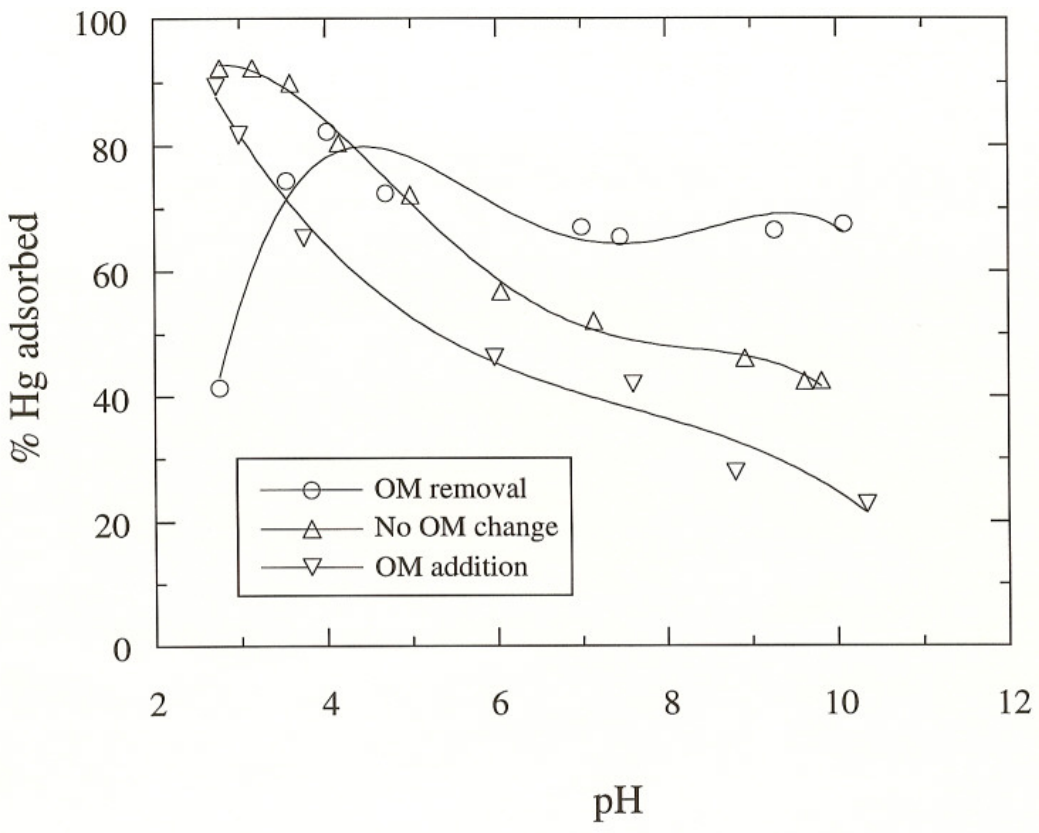

Fig. 24 Adsorption of Hg(II) by Freehold surface sandy loam witl organic matter removal, addition, and no change.

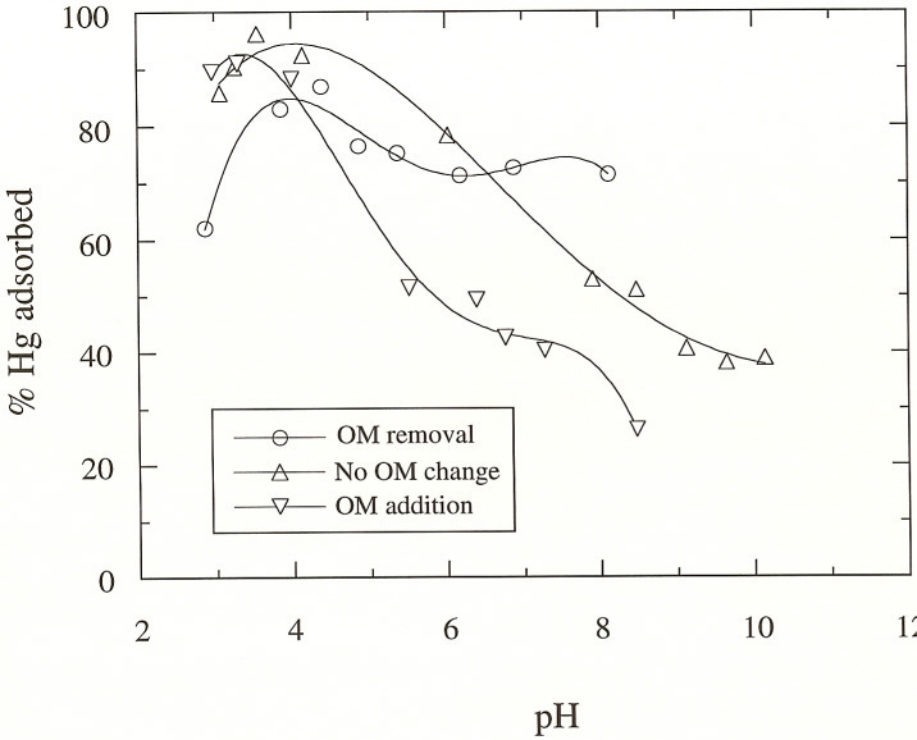

Fig. 25 Adsorption of Hg(II) by Rockaway sandy loam with organic matter removal, addition, and no change.

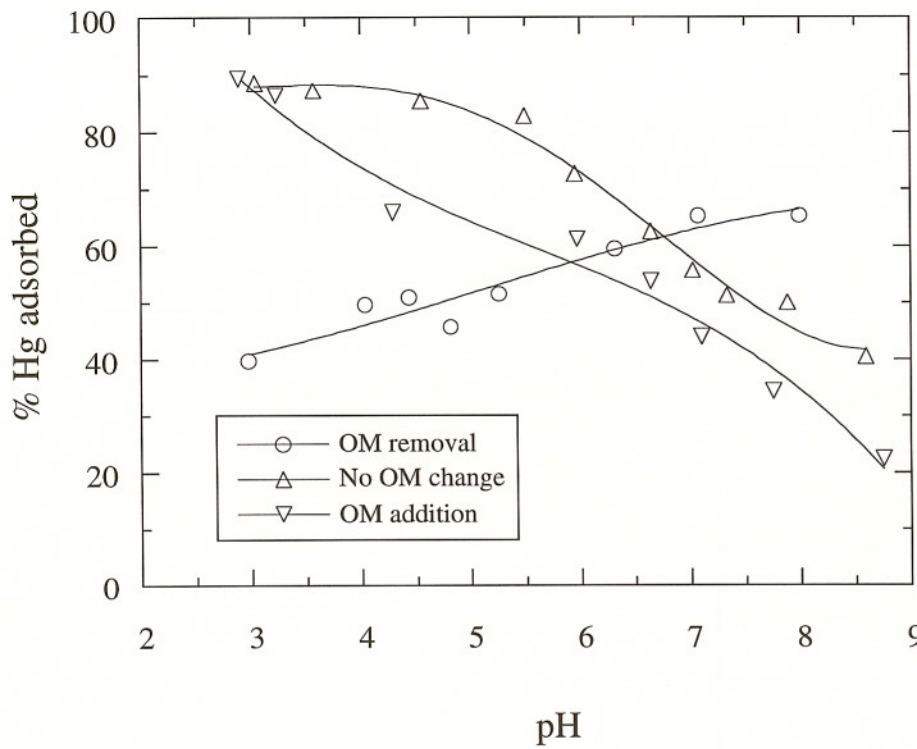

Fig. 26 Adsorption of Hg(II) by Dunellen sandy loam with organic matter removal, addition, and no change.

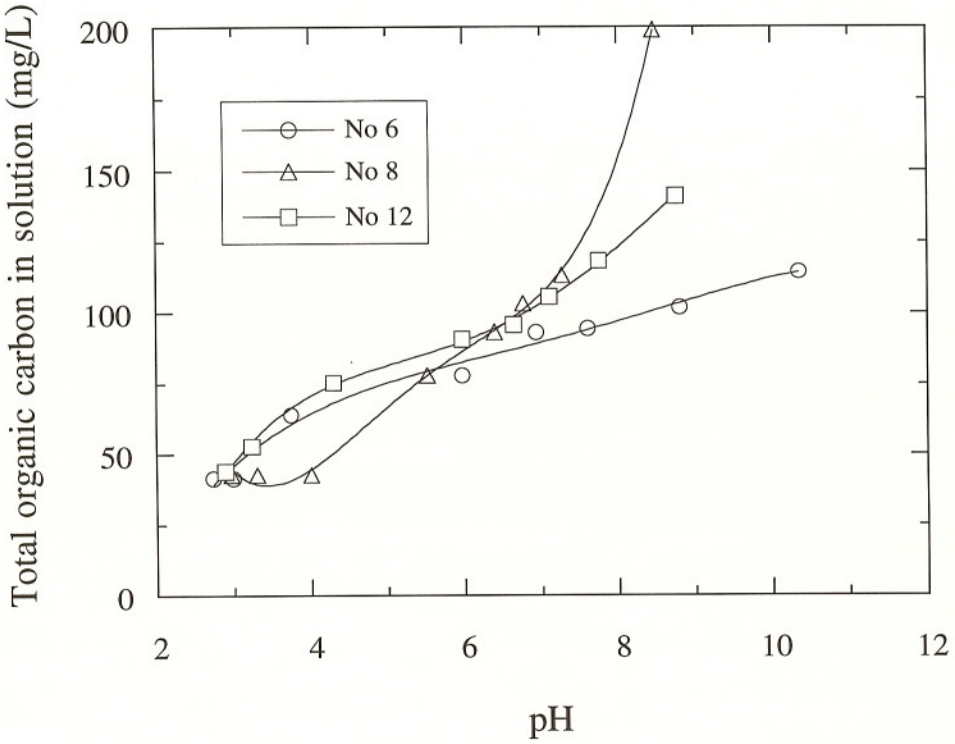

Fig. 27 Total organic carbon in solution at equilibrium as a function of solution pH. Concentration of added organic matter = 93 mg/L; No 6 = Freehold surface sandy loam; No 8 = Rockaway sandy loam; No 12 = Dunellen sandy loam.

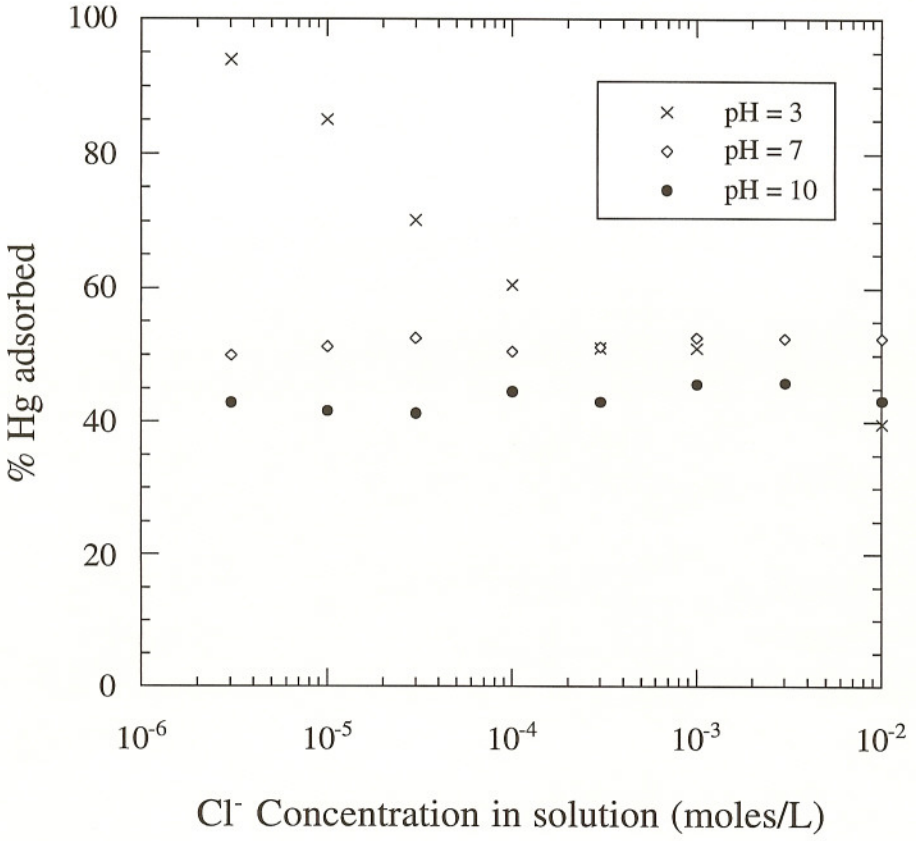

Fig. 28 Hg(II) adsorption on Freehold sandy soil (A horizon) as a function of Cl^- concentration in solution (organic matter content = 0.2%)

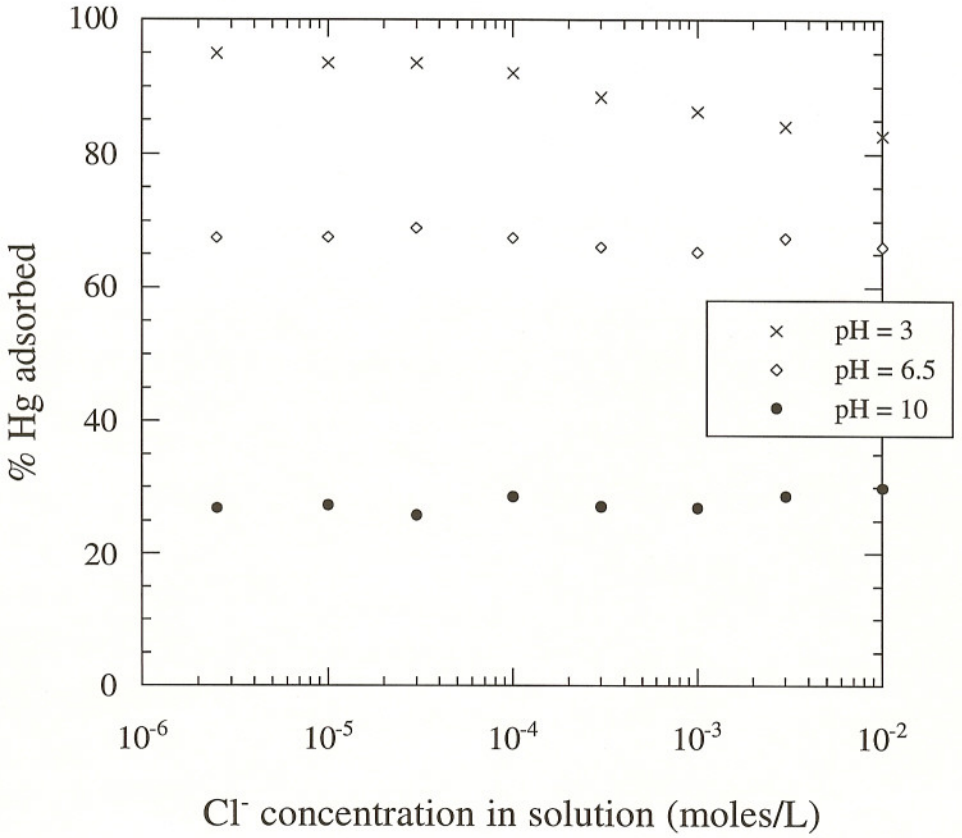

Fig. 29 Hg(II) adsorption on Dunellen sandy loam as a function of Cl^- concentration in solution (organic matter content = 1.9%)

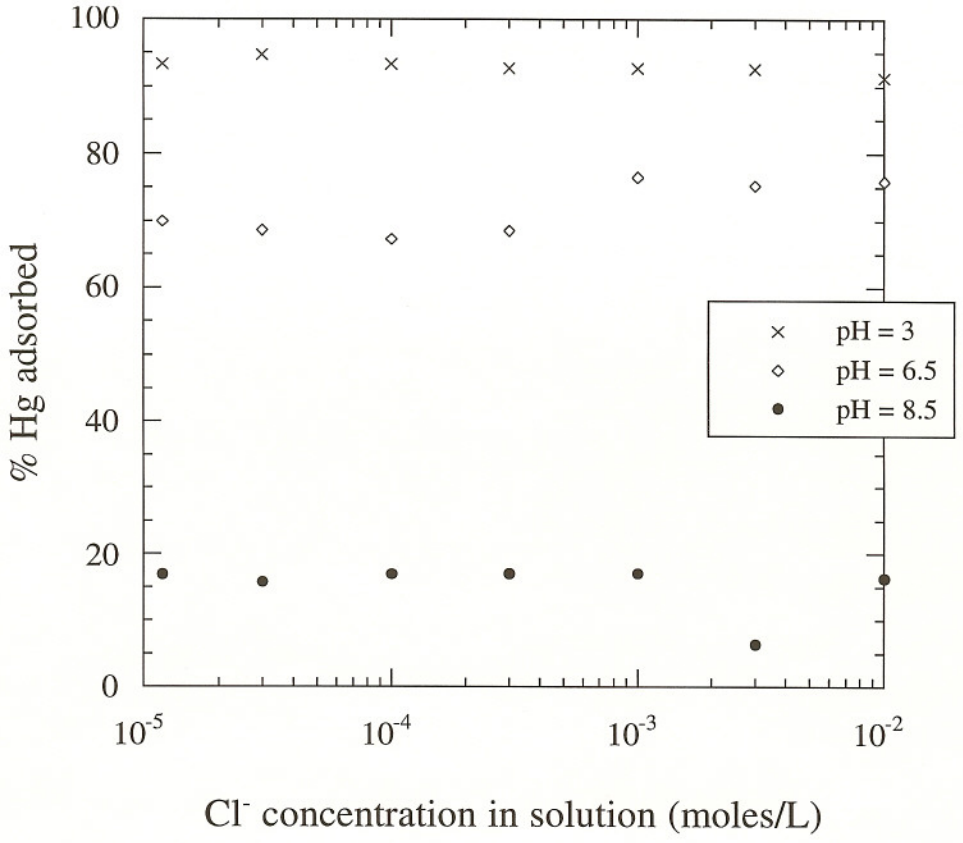

Fig. 30 Hg(II) adsorption on Booton loam (Union County) as a function of Cl^- concentration in solution (organic matter content = 8.6%)

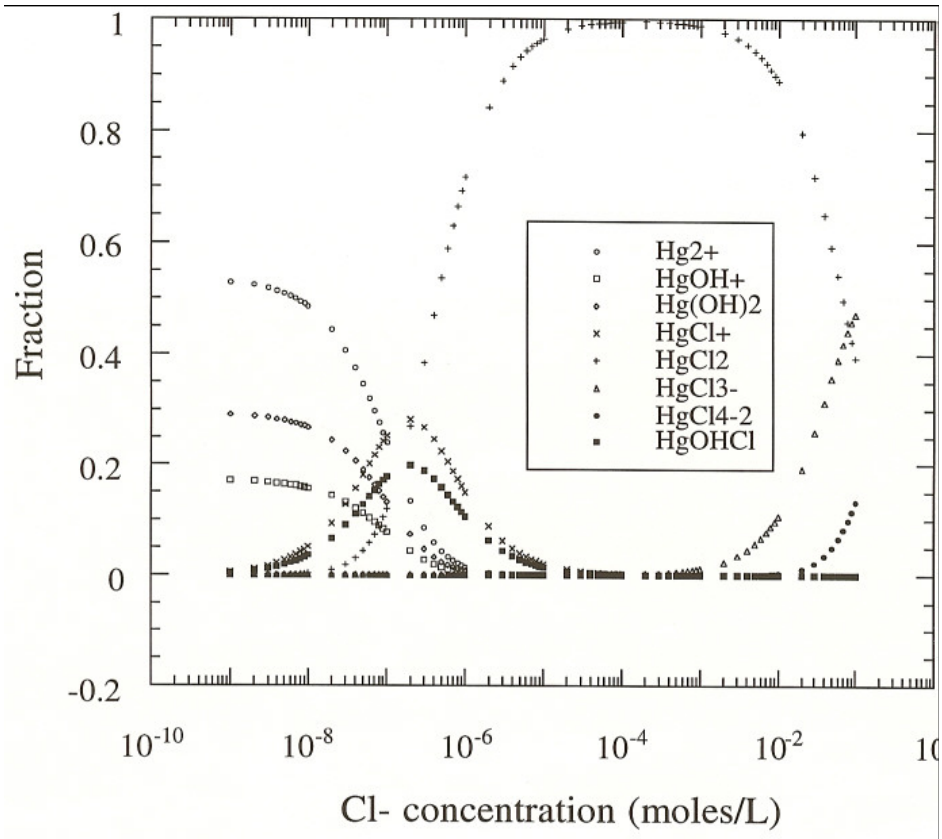

Fig. 31 Hg speciation diagram (pH = 3).

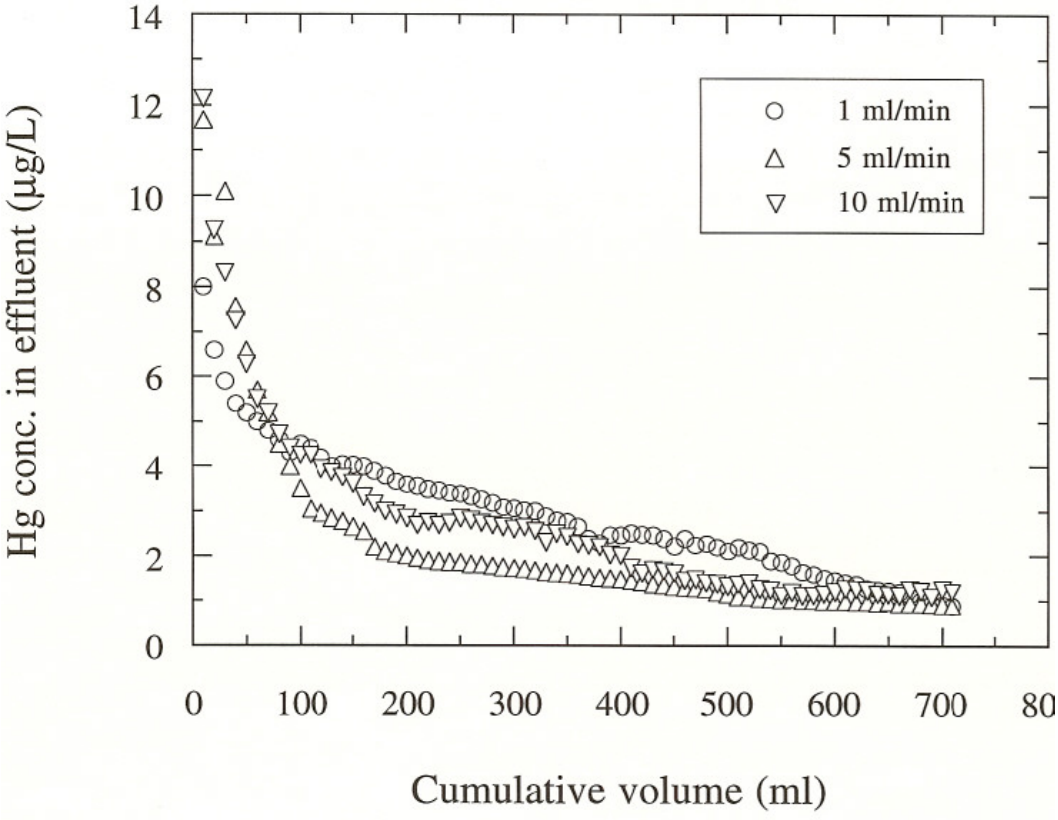

Fig. 32 Column desorption of Hg(II) on Birdsboro silt loam.

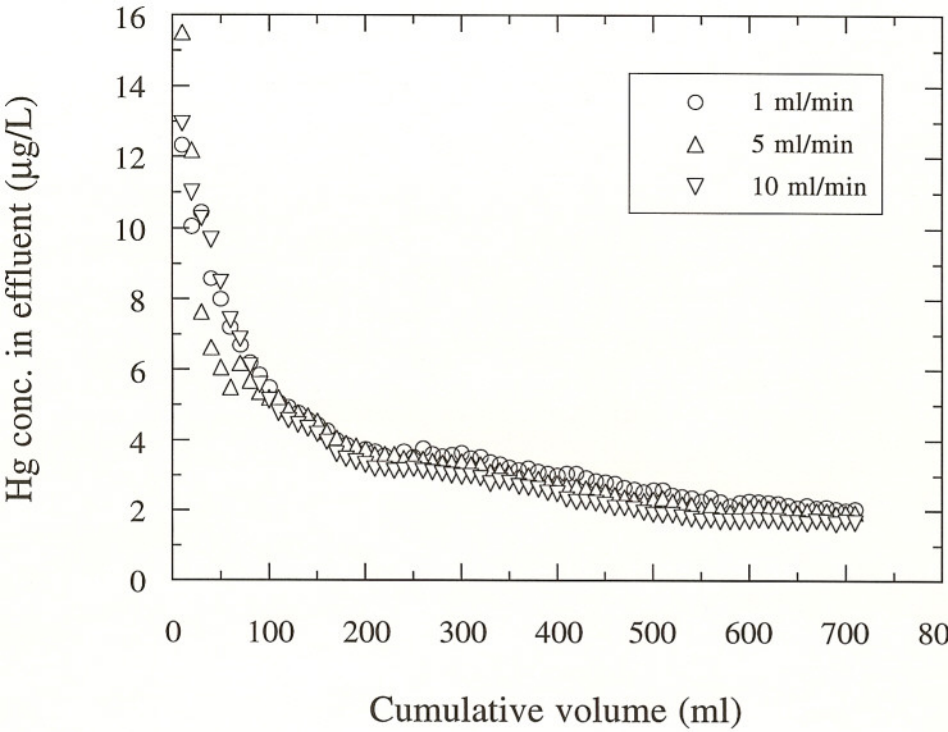

Fig. 33 Column desorption of Hg(II) on Sassafras sandy loam.

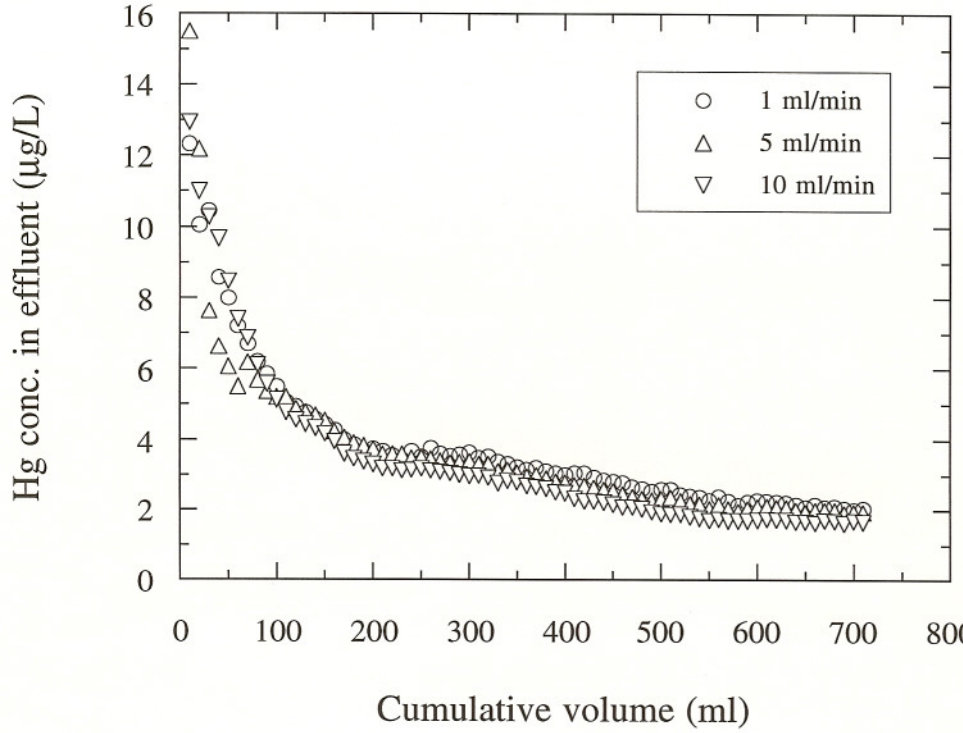

Fig. 34 Column desorption of Hg(II) on Downer loamy sand.

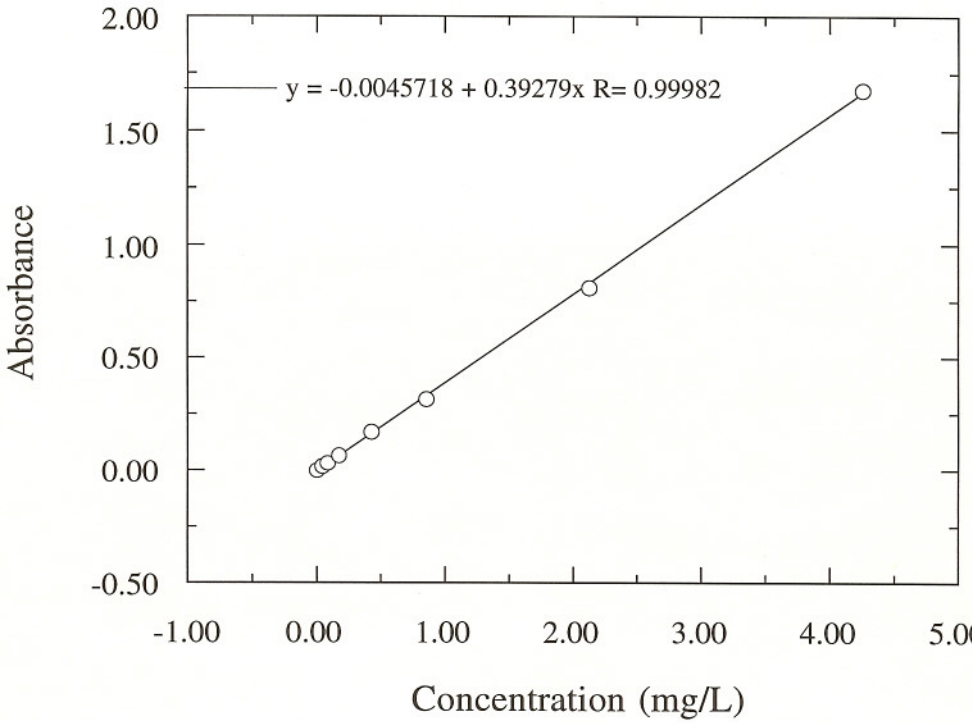

Fig. 35 Arsenic calibration curve.

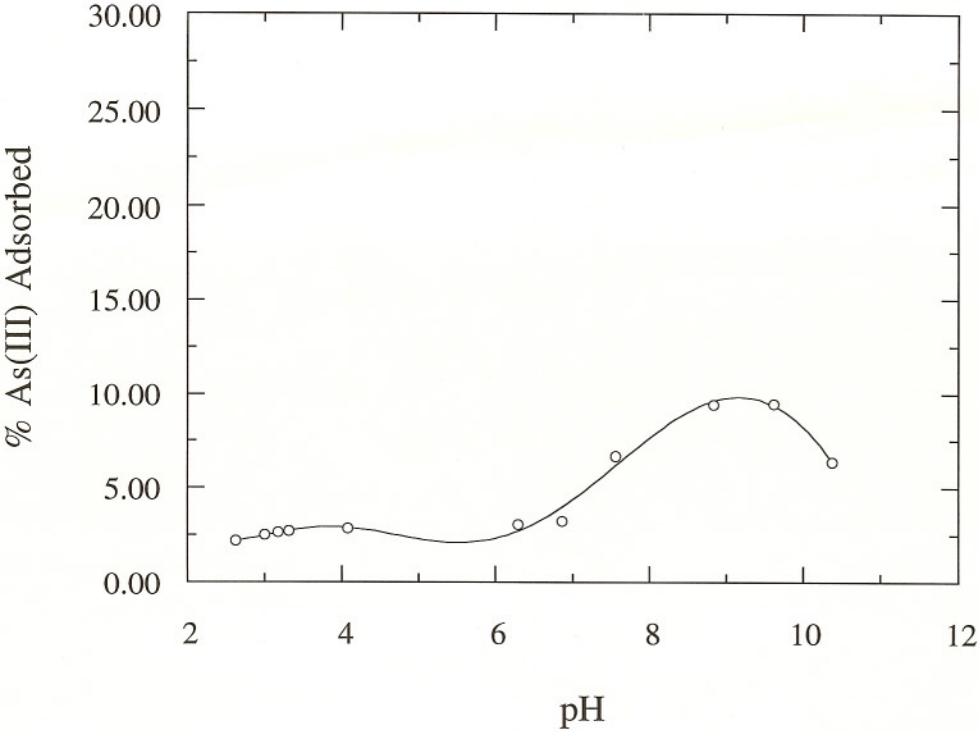

Fig. 36 Adsorption of As(III) on Downer loamy sand as a function of pH
Soil:solution = 0.3 g/30 ml; I = 0.01 M $NaNO_3$; T = 25°C.