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

Final Report
Part II
Arsenic

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Fabiana Dias, Yujun Yin, Herbert E. Allen and C.P. Huang
Department of Civil and Environmental Engineering
University of Delaware
Newark, DE 19716

Project Manager
Paul F. Sanders, Ph. D.
Division of Science and Research
New Jersey Department of Environmental Protection and Energy
Trenton, NJ 08625

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ABSTRACT

Arsenic is a toxic heavy metal. Besides causing skin cancer, arsenic is also known to cause liver, lung, kidney and bladder cancer (Edwards, 1994). Therefore, its maximum permitted concentration in water and soil environments must be considered carefully.

A major problem in the remediation of metal comtaminated sites is the lack of appropriate criteria for some contaminants in soils, including arsenic. Few standards are available for toxic metals and trace elements in soils. Sorption, fate and transport of arsenic must be assessed before the establishment of valid standards. In this project, the behavior of two arsenic species were evaluated in fifteen New Jersey soils.

Having this in mind, the results obtained were used to determine adsorption constants that were incorporated in models to predict adsorption of arsenic as a function of several soil parameters including organic matter, iron oxide content, and soil surface area.

In order to accomplish this, Langmuir and Freundlich adsorption isotherms were obtained for each of the soils at natural pH. Also, the arsenic adsorption behavior as a function of pH was studied for all the soils at two initial As(III) and As(V) concentrations. These adsorption edges provided a picture of what happens when arsenic is adsorbed by different types of soils. Basically the maximum arsenic adsorption is reached around the same pH for all soils, but the amount of adsorption is significantly changed depending upon the soil characteristics. Maximum As(III) adsorption occurred around pH 6 to 9, while the maximum As(V) adsorption occurred in a pH range of 4 to 5.

In addition, desorption experiments were conducted in order to determine the amount of arsenic(III) and arsenic(V) that would be available for desorption after the adsorption process. It was observed that As(V) was strongly retained in the soil than was

As(III). As(III) was oxidized to As(V) during the desorption process. The oxidation reaction would reduce the toxicity of arsenic in soil since As(V) is known to be less toxic than As(III).

The kinetics of arsenic adsorption was investigated to help understand the adsorption and desorption process. These experiments clearly showed that both adsorption and the desorption equilibrium was reached in the 48 hours.

Chapter 1

INTRODUCTION

Human and animal toxicity of arsenic species has been extensively studied. Since arsenic can accumulate in plants entering the animal and human food chain, the problem of arsenic toxicity becomes critical. Chronic arsenicism from water is a result of low intake levels of this contaminant (Huang and Liaw, 1979). Areas of high geothermal activity propitiate the release of arsenic species naturally found in soils to surface water and groundwater (Ghosh and Yuan, 1987). In addition, the oxidation of arsenopyrite found in ores containing gold through weathering or during mineral processing can release significant amounts of arsenic into the nearby environment (Bowell et al., 1994).

Due to the extensive use of arsenic compounds, there have been many studies of its species behavior with several adsorbents. The mobility of arsenic species in soils is dependent upon the speciation and type of soil. Arsenic can be metabolized by naturally occurring soil bacteria, as all organoarsenicals forms are believed to form arsenate through demethylation. Biomethylation and demethylation are dependent on the microorganisms present as well as the arsenic species present (Bowell, 1994). In addition, it seems that biomagnification of arsenic along the food chain is not a problem (Ghosh and Yuan, 1987).

Interestingly, scientists from MIT verified that a previously unknown bacteria makes use of arsenic in order to metabolize its food (Nadis, 1995). The bacteria, named MIT-13, uses arsenic present in lakes and streams, converting arsenic into As(III), the most toxic species. This is the first microorganism found to derive energy from arsenic, and tolerate high concentrations of this contaminant. Researchers also think that this bacteria may be capable of dissolving arsenic locked up in sediments.

Arsenic organic forms are characterized by sigma-bonded organometallic species (Hasegawa et al., 1994). The toxicity of arsenic compounds obey the following order: arsine> arsenite> arsenate> alkyl arsenic.

Frost and Griffin (1977) studied adsorption of arsenic and selenium, an element that shows similar behavior, in clay minerals, like montmorillonite and kaolinite. Huang and Liaw (1979) studied the adsorption of arsenite by lake sediments. They reported that the retention of arsenic by active components present in sediments, like carbonates and sesquioxides, could suppress the levels of arsenic in drinking water and restrain its movement in the food chain.

Drinking water standards for arsenic indicate that the concentration of this contaminant should not exceed 0.05 mg/L (Ghosh and Yuan, 1987). Its concentration in drinking water is regulated by the US Environmental Protection Agency (USEPA). This maximum contaminant level (MCL) may be lowered based on epidemiological studies showing that arsenic causes increase in the risk of skin and lung cancer when inhaled (Cheng et al., 1994). The USEPA estimates that exposure to arsenic at the MCL concentration of 0.05 mg/L can cause an increase of 31 excess skin cancers per 1,000 people.

The amount of arsenic that can get into surface water and groundwater depends on its retention and release by soils and other adsorbents. This study addressed the important factors that affect the behavior of two arsenic species in soils. This was done by determining adsorption edges or adsorption envelopes, adsorption isotherms, and adsorption kinetics and desorption kinetics of arsenic for fifteen New Jersey soils.

Chapter 2

LITERATURE REVIEW

2.1 Origin of arsenic in soils

Arsenic is a naturally ubiquitous element, being found primarily in sedimentary rocks. It ranks as the 53rd element in abundance in the earth's crust (CWQG, 1995). Normal soils are known to have arsenic levels below 40 mg/L (Woolson, 1983). The concentration in contaminated soils depends on the nature of the contamination, the proximity to the source and time since deposition. Major sources of contamination are releases due to geochemical processes, the use of pesticides and herbicides containing arsenic, wood preservatives disposal, glass industry wastes, and petroleum refining industry wastes. In addition, high purity arsenic is used in manufacturing of semiconductors (CWQG, 1995). In soils, arsenic is mainly found as oxysalts or combined with sulfur in anaerobic soils (Bowell et al., 1994). Arsenate is predominant in aerobic soils and arsenite is predominant in anaerobic soils.

Sadler et al. (1994), analysed arsenic contamination levels in soil, seepage water, groundwater and soil leachates on a site in Australia. They reported that there is no significant decrease in soil arsenic concentrations up to 1 meter depth. They concluded that during the experiment arsenic levels were not affected by depth, even though no further experiments were repeated in order to determine the arsenic contamination in the soil profile. Their results show, however, that remediation of contaminated sites would involve at least the removal of soil up to 1 m depth, which makes the arsenic contamination a problem with practical limitations and elevated cost. Bowell et al. (1994), observed the decrease of arsenic species with depth in contaminated aerobic soils. One factor that can cause this decrease in concentration with depth is groundwater leaching.

In sediments arsenic can be found in relatively high concentrations, around 100 to 300 μg/g (Brannon and Patrick, 1987). Arsenic mobility and speciation in this matrix is not known, but probably As(III) is the predominant species since sediments are characterized by anaerobic conditions, which facilitate reduction.

As mentioned by Chunguo and Zihui (1988), the study of arsenic distribution among several solid phases, suspended solids and surface sediments is important for the understanding of deposition and transport of this contaminant in the environment.

2.2 Arsenic toxicity

The organo arsenic species are less toxic than the inorganic compounds. Methylation of arsenic species is thus considered a detoxification process (Gupta and Chen, 1978). Several metals and metalloids are known to be biomethylated, including As, Hg, Sn, Se, Te, Pd, Pt, Au, Tl and Pb. Some of them, like Hg in its methylated form, are poisonous to the central nervous system of higher organisms. This is an example of an increase in biological availability of a metal in toxic concentrations through chemical transformation by the environment (Stumm and Morgan, 1981).

Arsenic, besides being a carcinogen, is also a factor that can cause Haff's disease (Gupta and Chen, 1978). Since arsenic is chemically similar to phosphorus and sulfur, its toxicity effects are related to the replacement of these elements in essential metabolic processes (Burton et al., 1987).

Daphnia magna has been used as an indicator of aquatic toxicity, and several methods are still being developed for acute toxicity testing (Burton et al., 1987). They reported that the presence of sediments increased the D. magna survival when the microorganism was initially exposed to arsenite. This results confirm the fact that river sediments, as well as other adsorbents, are responsible for sorption of arsenic species, leaving less arsenic in solution and thus decreasing arsenic exposure to live organisms.

2.3 Aqueous Speciation

Speciation is primarily studied in order to predict the nature of the contaminant interaction within several environments. Also, important biochemical cycles are understood using speciation knowledge.

Biological availability of metals as well as their effects are dependent upon speciation (Stumm and Morgan, 1981).

In aquatic systems the adsorption of arsenic by sediments is the most important factor controlling this species availability (Pierce and Moore, 1982). In natural waters this contaminant occurs in inorganic and organic forms, the inorganic forms are predominantly the result of dissolution from solid phases, for example, arsenolite (As_2O_3), arsenic oxide (As_2O_5), and realgar (As_2S_2) (Ferguson and Davis, 1972). When sulfide is present in excess, orpiment (As_2S_3) can also occur (Gupta and Chen, 1978).

Four oxidation states are known for arsenic species: +V, +III, 0, and -III (Ghosh and Yuan, 1987). These states are dependent on redox conditions and pH of the medium. For example, in reducing conditions like anaerobic groundwater, arsenite species (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-}) are stable in the pH range of 2 to 9.

In oxidizing conditions arsenate species are found (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}). These forms are predominant at pH range of 7 to 11.5 (Cheng and Liang, 1994).

Arsine can be found at trace levels under extremely reducing conditions, being slightly water soluble. The solubility of arsenic species as well as the rate of oxidation to As(V), and its speciation are processes mainly controlled by Eh and pH of the medium (Bowell, 1994). Arsine is more toxic than As(III), which by its turn, is more toxic than As(V).

In surface waters both arsenate and arsenite forms of arsenic can be found. This may be caused by the slow oxygenation rate of arsenite to arsenate or reduction of arsenate to arsenite by microorganisms at neutral pH in areas of reducing conditions (Gupta and Chen, 1978). The change of arsenic oxidation states is not easily accomplished, therefore the thermodynamic calculation of arsenic proportions doesn't always predict the actual results (O'Neill, 1990).

Reduction of arsenate to arsenite is a process chemically controlled in aerobic and anaerobic soil profiles while the methylation of arsenic species is controlled by microbial activity (Bowell et al., 1994).

Brannon and Patrick (1987) suggested that As(V) was reduced to As(III) under anaerobic conditions in several saline and freshwater sediments. Similar results were also observed in sewage sludge. These authors believe that As(III) can be released into the water in areas where anaerobic sediment is in contact with anaerobic water. This would happen in reservoirs and lakes during periods of temperature stratification or in areas with low water circulation and high oxygen demand. Some of their correlation results indicate that aluminum and iron, present in the reducible phase, wer influencing the adsorption of arsenic species by sediments.

The pK_a values at ambient temperature of 25°C, are 2.2, 6.98, and 11.5 for arsenate acid species, and 9.22, 12.13, and 13.4 for arsenous acid species. Therefor at normal pH conditions, As(III) exists as a neutral species (H_3AsO_3), being no available for adsorption based on ionic interaction. The pH range of optimun adsorption becomes thus really narrow (Maeda et al., 1992).

The dissociation equations are given below.

Arsenate acid species:

$$H_3AsO_4 \rightarrow H_2AsO_4^- + H^+$$

$$H_2AsO_4^- \rightarrow HAsO_4^{2-} + H^+$$

$$HAsO_4^{2-} \rightarrow AsO_4^{3-} + H^+$$

Arsenous acid species:

$$H_3AsO_3 \rightarrow H_2AsO_3^- + H^+$$

$$H_2AsO_3^- \rightarrow HAsO_3^{2-} + H^+$$

$$HAsO_3^{2-} \rightarrow AsO_3^{3-} + H^+$$

As mentioned previously, arsenic acid is a triprotic acid. Its dissociatio constants are very similar to those of phosphoric acid. Therefore, since both anion adsorb via ligand exchange, the same adsorption behavior can be expected from them (Goldberg, 1986). Thus, phosphate interference can occur and the analytical method used to detect arsenic must account for this factor. Some researchers even reported that the presence of phosphate significatively reduced arsenate adsorption in soil systems.

Some important processes used to remove arsenic from water sources are complexation with polyvalent metal species (for example ferric iron), adsorption into a coagulant floc, lime softening, and sulfide precipitation (Gupta and Chen, 1978).

Table 2.1 shown below, gives the arsenic concentration range found in aqueous environments.

Table 2.1 Arsenic in aqueous systems (Gupta and Chen, 1978)

Source	Total As (mg/L)	As(III) (mg/L)	As(V) (mg/L)
Surface waters	0.002-0.21	N. A. *	N. A. *
Groundwater	0.01-4.0	N. A. *	N. A. *
Geothermal water	0.03-3.0	0.01-2.4	0.006-0.5
Seawater	0.002-0.014	0.0005-0.003	0.0005-0.004
Industrial wastewater	0.003-600	N. A. *	N. A. *

* N. A.: Not available.

2.4 Sorption and transformation of arsenic species in waters and soils

Iron hydroxides, as well as chromium and aluminum can adsorb or form insoluble precipitates with arsenic species, which can affect the concentration of this contaminant in natural waters and in soils (Ghosh and Yuan, 1987). Its species can also form solids with calcium, magnesium and nickel. However, compounds of arsenic except for As_2S_3, generally have solubilities above 0.05 mg/L (Gupta and Chen, 1978).

Acid-base reactions involving arsenic species can occur instantaneously while redox reactions require indeterminate periods of time. It is known, however, that there are no proper conditions to favor efficient reduction of As(V). The reduction in the absence of oxygen is extremely slow and might just occur in the presence of microorganisms.

On the other hand, in aqueous oxygenated environments the oxidation of As(III) to As(V) is dynamically favored, but there is no specific time for oxidation, i.e., its oxidation depends on several ambient conditions. Factors like the presence of copper salts, carbon, and catalysts, and higher temperatures can increase the rate of oxidation. Some other parameters like natural manganese oxides, permanganate and chlorine can favor oxidation in the absence of oxygen. As a result of these observations, a correlation between redox conditions and arsenic speciation is hardly determined (Edwards, 1994).

Also, iron and manganese are responsible for arsenic speciation conditions in the soil environment. This contaminant can become immobile through adsorption-coprecipitation with iron and manganese hydroxides. It is mobile when these hydroxides are dissolved under reducing conditions, or released from the oxides surface under the presence of some components like organic matter (Edwards, 1994).

Chapter 3

EFFECT OF pH ON THE SORPTION OF ARSENIC BY SOIL

3.1 Introduction

The solution pH is a master variable when studying the interactions of metals or anions with soil particles. The pH of an environment is responsible for changes in the surface charge of adsorbents, the degree of ionization of the adsorbate and the speciation of the adsorbent as well (Stumm and Morgan, 1981).

Soil pH values are useful in determining the solubility of minerals, predicting the mobility of ions in the soil, and assessing the viability of the soil-plant environment. Higher pH values for some soils indicate the presence of alkaline material in the soil that might have a stronger buffering capacity (Fox, 1989).

Bowell (1994), studied the sorption of arsenic by oxides and oxyhydroxides in soils. The sorption appeared to be controlled by Eh and pH of the suspension containing the adsorbent. It was also influenced by potential sorbents like organic acids, particularly humic acid. These observations are important in disposing of arsenic wastes, like mine tailings, where reducing conditions can lead to an excess of As(III). This species is not greatly adsorbed and consequently leaching of arsenic increases. Their experimental results indicate that in soils with high organic matter content, there is competition for binding sites in the mineral surfaces between organic acids and arsenic species, maybe lowering the adsorption of arsenic in oxides and oxyhydroxides. Also, for all species studied, higher arsenic concentrations were associated with higher adsorption on goethite at pH of 7.

Gupta and Chen (1978) reported that arsenic removal was significantly affected by the pH. They observed this effect in solutions of different chemical composition, like activated bauxite, activated alumina, and activated carbon. The proposed adsorption of As(III) occurred by negatively charged surface group of solids through hydrogen bonding and adsorption increased with increase of negatively charged surface group as pH increased.

Several soil parameters and properties must be considered when evaluating the adsorption behavior of arsenic species. Brannon and Patrick (1987), based on their results, suggested that aluminum and iron present in the reducible phase were influencing the adsorption of arsenic species by sediments. Goldberg (1986), mentioned that arsenic was preferentially adsorbed by the oxalate-extractable amorphous aluminum and iron oxides. The mechanism of specific arsenate adsorption would be ligand exchange with hydroxyl groups as well as surface aquo-groups found in the adsorbent surface.

In addition, small colloidal particles as well as clay and silt size particulates are most likely involved in the sorption because they are characterized by large surface areas.

Some researchers also studied the temperature influence in arsenic adsorption. It seems that adsorption is favored by lower temperatures and the rate of adsorption is not appreciably affected at temperatures of 20°C or higher.

Adsorption experiments should be conducted in a soil/solution suspension adjusted with regard to ionic strength. This is especially important due to the influence of ionic strength in metal ion activities in solution, surface charge of the soil particles, and double-layer capacitance of the hydrated particles. It is obvious tha

ionic strength will affect the metal binding to some extent (Sparks, 1995).

Hydride generation atomic absorption spectrometry is a simple method to analyze aqueous inorganic arsenic in the µg/L range (Glaubig and Goldberg, 1988). This analysis is possible by determining total arsenic, as As(III) plus As(V). Arsenic forms the hydride from the pentavalent oxidation state, although the reaction is accomplished at a much slower rate than from the trivalent oxidation state. As(V) can be determined by reducing it to As(III) prior to hydride generation using a proper reducing reagent in an acidic medium.

The hydride generation system is employed for determinations of mercury and hydride forming elements. The sodium borohydride reducing agent liberates hydrogen when in contact with acids. The reaction mechanism involved in the reduction of metal ions is complicated and takes place via the formation of intermediate radicals. For arsenic the following reaction represents a simplification of the reduction process:

$$8\,H^+ + AsO_3^{3-} + 3\,BH_4^- \longrightarrow AsH_3 + H_2 + B_3H_9 + 3\,H_2O$$

The volatile hydride is then reduced:

$2AsH_3\ (900\ ^\circ C) \longrightarrow 2\ As + 3\ H_2$

For arsenic, the sample solution is first treated so that arsenic is present in ionic form in the acidic solution. The reductant is added to the sample solution where it reacts acid to liberate hydrogen. This in turn reduces the metal ions to the volatile hydride. The hydrogen stream flushes the hydride helped by a stream of inert gas into the heated quartz cell (at about 900°C) where the hydride is decomposed. The absorption due to elemental As is measured at a wavelength of 193.7 nm. This method can detect As at concentrations as low as 1 μg/L. The hydride generation system was optimized for arsenic analysis.

3.2 Materials and methods

3.2.1 Materials

In order to minimize contamination problems, a relatively dust-free environment was necessary. All reagents were prepared with distilled, deionized water. All glass, polypropylene reaction flasks and plastic containers used were cleaned by soaking in 10% HNO_3 for 24 hours and then washed with distilled water followed by DI water.

The residue produced after hydride generation was carefully discarded in one special container and labeled as hazardous material. The reaction flask was rinsed with tap water followed by distilled water before and after its utilization to remove all traces of analyte from the walls of the hydride generation chamber. The reaction flask was never removed or replaced by another flask during determination because an explosive mixture of air-hydrogen could be formed.

A 1000 mg/L As(III) stock solution was prepared by dissolving 1.73 g of $NaAsO_2$ salt in 1000 ml of 0.3 M HCl solution prepared with type I water (distilled and deionized water obtained using a NANOpure ultrapure water system). A 1000 mg/L As(V) stock solution was prepared by dissolving 4.16 g of $NaHAsO_4 \cdot 7\ H_2O$ salt in 1000 ml of 0.3 M HCl solution. A series of standards of 2, 5, 10 and 15 µg/L were prepared by dilution from more concentrated As(III) and As(V) standard solutions.

Potassium iodide reagent used in the As(V) prereduction reaction was prepared by dissolving 40.00 g of KI salt in 100 ml of type I water. This reagent was prepared fresh for use.

Sodium borohydride solution in 0.1 M sodium hydroxide used as the hydride forming reagent was prepared by dissolving 25.00 g of $NaBH_4$ salt and 3.33 g of NaOH in 833 ml of type I water. This reagent was prepared on a weekly basis and kept in a refrigerator while not being used to avoid decomposition to H_2. Although the presence of hydrogen bubbles in the solution during the decomposition of borohydride don't interfere with the hydride generation system. The reagent flask was also kept protected from direct sunlight.

3.2.2 Sorption methods

Sorption experiments were performed using a batch technique, as shown in Figure 3.2. Briefly, 1 ml of 1 M $NaNO_3$ and 0.75 ml of a 100 mg/L arsenic standard solution or 1.0 ml of a 10 mg/L arsenic standard solution, to give a final concentration around 0.75 mg/L or 0.1 mg/L, respectively, were added to 10 plastic flasks of 125 ml containing a soil solution ratio of 1.0 g ± 0.01 g per 100 ml DI water. The pH was adjusted using NaOH or HNO_3 to cover a range of pH 3 to 10. The suspensions were shaken for 48 hours at a room temperature of about 25°C (± 3°C) at a rate of 100 rpm on a rotatory shaker (Lab-Line Orbit shaker, No. 3590). After equilibration, the suspensions were filtered using a 20 cc plastic syringe and a 0.45 µm Nuclepore membrane filter placed on a filter holder. The syringe was washed previously with the suspension and the first 20 ml of filtrate was discarded. The pH of each sample was then determined using a pH meter.

Backgrounds for all soils were prepared in the same way, for low, medium and high pH. Instead of adding arsenic solutions to the backgrounds, 0.3 M HCl was added.

An aliquot of each filtrate was used to determine the concentration of total arsenic in solution. In some cases the analysis was done in duplicate. The amount adsorbed was then obtained by difference between the initial amount of arsenic added and the amount of arsenic in solution after 48 hours of equilibration time.

3.2.3 Calibration Curves

Standards of 0.2, 0.5, 1.0, 1.5, and 2.5 mg/L were prepared from 10 and 100 mg/L arsenic(III) and arsenic(V) stock solutions. 0.1 ml of each standard was added to a 30 ml plastic flask containing 10 ml of DI water, to obtain standards of 2, 5, 10, 15, and 25 µg/L respectively.

5 ml of concentrated hydrochloric acid and 1 ml of 40% w/v of KI were added to prereduce the arsenic. 30 minutes were allowed for the reduction process. The sample was transferred to a reaction flask and then the hydride formation reagent was added.

Calibration curves were obtained daily due to fluctuations in the sensitivity of the absorption spectrophotometer, especially related to the lamp energy.

The correlation coefficients were greater than 0.99 and a triplicate of the curve wa obtained to verify the precision of the method. Figures 3.3 and 3.4 show typica calibration curves for As(III) and As(V) respectively.

Figure 3.5 shows that the hydride generation method is suitable fo determination of total arsenic in solution after reduction of the initial arsenic adde The same procedure described above was employed. All three curves were obtaine simultaneously. As(III), As(V) and standards of mixed As(III) and As(V) wer prepared.

3.2.4 Arsenic analysis

In this study, we used a commercial hydride generation system, th MHS-10 system from Perkin Elmer pictured in Figure 3.1. This system was couple with a Perkin Elmer Atomic Absorption Spectrophotometer (Model 5000) for A determination. The standard operating procedure is described in Appendix A.

A quartz cell placed in the light path of the spectrophotometer wa electrically heated by a 4 meter nickel-chromium wire wrapped around the cell using a electrically isolated material (with braided ceramic sleeving). The use of this cel provided sensitive determination of arsenic by eliminating background interferenc associated with the argon-air-hydrogen flame, which is normally used. A Varia transformer and a thermocouple from Omega Engineering were used to control the cel temperature; the thermocouple was specifically employed to determine the external cel temperature. Graphite cooling rings at the cell ends prevented the ignition of th hydrogen liberated during the analytical determination. In the unlikely event o hydrogen ignition, a flashback arrestor was placed in the transfer hose to prevent a flashback into the reaction flask.

3% $NaBH_4$ in 0.1 M of NaOH was used as reductant. 1 ml of this solution in the presence of H^+ produces about 80 ml of hydrogen. N_2 gas was also employed as the AsH_3 vapor carrier.

An aliquot of the sample solution was used to determine the amount of arsenic in solution. The sample was diluted for better analytical determination and placed in a 30-ml plastic reaction flask. 5 ml of concentrated hydrochloric acid, to promote digestion, and 1 ml of 40% w/v of KI were added to prereduce the arsenic. 30 minutes were allowed for the reduction process. The sample was transferred to a reaction flask located in the commercial hydride generation system and then the hydride formation reagent was added. A violent reaction takes place with the liberation of hydrogen and the release of the volatile hydride, arsine.

Absorbance was measured after the decomposition of arsine to elemental arsenic using a hollow arsenic cathode lamp with adjusted lamp energy of approximately 39 to 42. Lamp current was set to approximately 16 mA, the slit to 0.7 nm and the absorbance measurements were taken each 0.5 seconds in the continuous absorption mode. When the maximum absorbance signal was achieved, the addition of reducing reagent was discontinued.

As(III) adsorption edges at an initial arsenic concentration of 1.33×10^{-6} M (0.1 mg/L) were prepared in triplicate to determine the precision of the sorption. The results shown in Figures 3.6 and 3.7 indicate a good precision. The range of deviations is from 0.83 to 9.05% of the percentage adsorbed, with a mean of 4.50% for Figure 3.6.

The range of deviations is from 1.77 to 28.05% of the percentage adsorbed, with a mean of 10.24% for Figure 3.7.

A standard addition method was used to test the accuracy of the hydride generation method with soil extracts as matrices using arsenic(III) and arsenic(V) as the source of arsenic. The recoveries of added arsenic were determined for three different soils: Lakewood sand (0.5% organic matter), Hazen gravelly loam (3.1% OM) and Boonton Union County (8.6% OM). Three soil extracts were prepared at different pHs, low (around pH 4), medium (natural pH) and high (around pH 9) for each soil. As shown in Tables 3.1 and 3.2 the amount of total arsenic recovered as As(III) and As(V) is always more than 90% for all soil extracts at the different pH values using the method described above.

Table 3.1 Recovery for added arsenic(III)

Soil Name	% recovered As(III) added: 0.2451 μg	sample pH
Lakewood sand	89.92	3.27
	93.09	4.35
	91.11	10.10
	99.24	3.39
	101.42	4.54
	97.50	10.24
	93.39	3.29
	95.80	4.46
	98.22	10.01
Hazen Gravelly Loam	93.48	5.12
	94.67	6.44
	95.46	9.55
	108.82	5.12
	112.74	6.44
	109.26	9.55
Boonton Union County soil	90.31	4.13
	93.48	5.09
	96.26	8.07
	91.41	4.38
	98.37	5.23
	92.28	9.76
	100.63	4.00
	110.29	4.89
	93.39	7.62

Table 3.2 Recovery for added arsenic(V)

Soil Name	% recovered As(V) added: 0.2451 μg	sample pH
Lakewood sand	103.79	3.27
	103.42	4.35
	95.21	10.10
	105.46	3.29
	93.39	4.46
	112.71	10.01
Hazen Gravelly Loam	105.28	5.12
	98.19	6.44
	105.28	9.55
Boonton Union County soil	101.55	4.13
	91.85	5.09
	100.06	8.07
	103.05	4.00
	93.39	4.89
	98.22	7.62

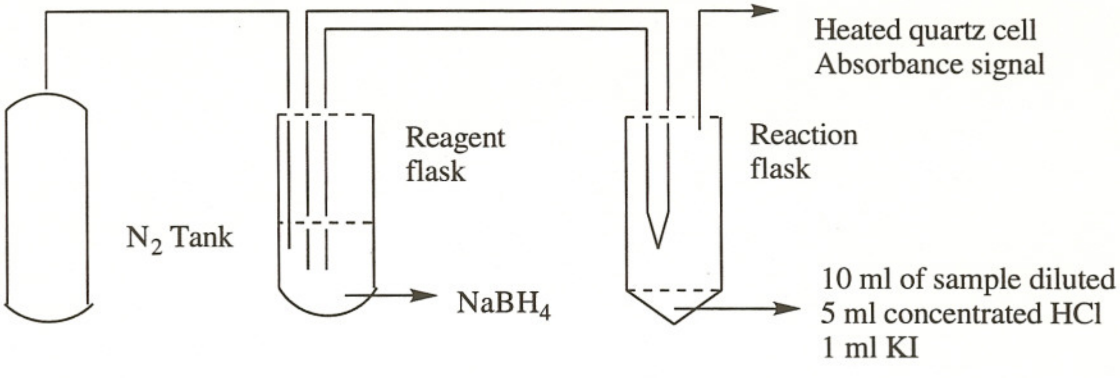

Figure 3.1 Schematic of the hydride generation system.

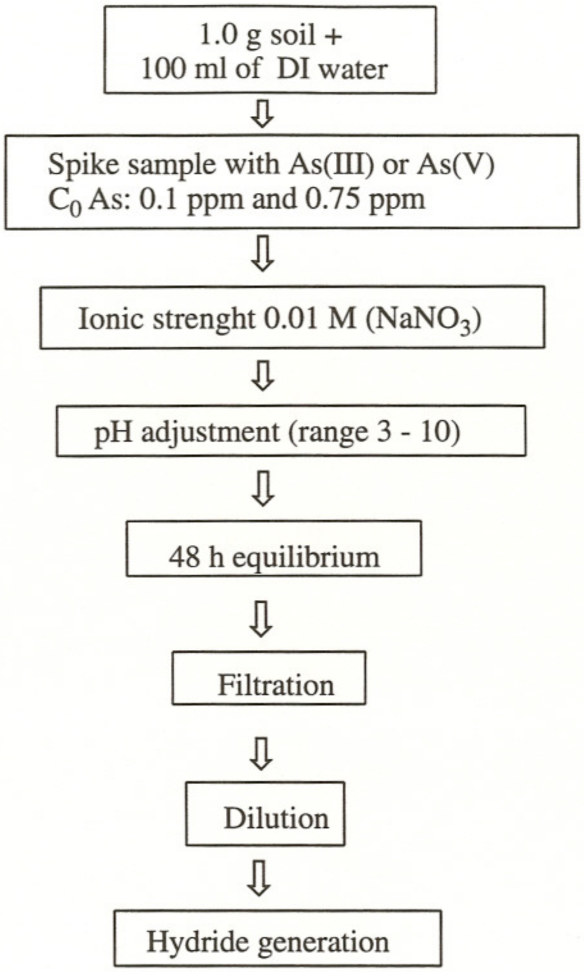

Figure 3.2 Schematic for adsorption edge batch experiment procedure.

3.3 Adsorption edges

3.3.1 Arsenic (III)

Adsorption edges were plotted as the amount of arsenic adsorbed versus the pH of the filtered suspension. The edges are shown in Figures 3.8 to 3.27. The pH value at which adsorption increases abruptly is called the pH of adsorption edge (Huang et al., 1987).

Adsorption edge measurements were performed for fifteen soils using As(III) at an initial concentration of 1.0×10^{-5} M (0.75 mg/L). The maximum adsorption was reached around pH 7 to 9. At pH less than 9 the solution contains predominantly neutral As(III) in the form of arsenious acid H_3AsO_3. These species are adsorbed by negatively charged surface groups on soil particles. Therefore, the amount of adsorbed As(III) increased with increase of negatively charged surface groups as pH increased. At pH greater than 9 the adsorption decreased due to the presence of negatively charged As(III) species in solution.

Adsorption edges were also performed using As(III) at an initial concentration of 1.33×10^{-6} M (0.1 mg/L) for all fifteen soils. The results are very similar to the results obtained using 0.75 mg/L As(III). However, due to the saturation of the adsorption sites, the observed amount of arsenic adsorbed was significantly less at the higher arsenic initial concentration.

In addition, adsorption edge experiments were performed using 1.0×10^{-4} M (7.5 mg/L) As(III) initial concentration. At this concentration, the soil surface sites are saturated after the equilibration time, leaving most of the arsenic in solution, making the amount of As(III) adsorbed analytically difficult to determine. Therefore, measurements of adsorption edges were conducted at 1.0×10^{-5} M (0.75 mg/L) and 1.33×10^{-6} M (0.1 mg/L) initial As(III) concentrations.

3.3.2 Arsenic(V)

Adsorption edge experiments were performed for all fifteen New Jersey soils. As(V) was more strongly adsorbed than was As(III). The maximum adsorption of As(V) was reached around pH 4 to 5. The main As(V) species in solution are $H_2AsO_4^-$ and $HAsO_4^{2-}$. These species are adsorbed by positively charged surfaces. New Jersey soils are negatively charged over a wide range of pH. However, since soils are a very heterogeneous system some soil components like oxides bear positive charges that can be responsible for adsorption of arsenic(V) at low pHs. This explains also why when pH is above 7 As(V) adsorption decreases.

3.4 Soils characterization

Soils used during this study were collected in fifteen sites in New Jersey. They were all characterized according to standard procedures (Allen et al., 1994). These soils ranged from sand to loam, which is an important distinction providing different types of soils when studying adsorption and desorption.

Before their use, all soils were ground to pass a 2 mm sieve and were air dried during a week. The characteristics of these fifteen soils are given in Tables 3.3 to 3.9 (Allen et al., 1994).

Table 3.3 Particle size distribution

Soil Name	Soil Number *	< 2 mm (g)	> 2 mm (g)	> 2 mm (%)
Birdsboro silt loam	13	20203.0	10555.5	34.32
Boonton Bergen County soil	15	16571.0	3745.5	18.44
Boonton Union County soil	11	20611.6	9034.6	30.47
Downer loamy sand	10	16115.5	13132.0	44.90
Dunellen sandy loam	12	24062.0	6129.0	20.30
Fill materials from Delaware River	9	38273.5	770.0	1.97
Freehold sandy loam (surface)	7	32294.5	2518.0	7.23
Freehold sandy loam (subsurface)	6	29394.5	2242.0	7.09
Hazen gravelly loam	14	21928.2	8262.8	27.37
Lakewood sand	2	18777.5	137.6	0.70
Penn silt loam	3	21666.5	3372.2	15.60
Rockaway stony loam	8	15188.5	5902.0	27.98
Sassafras sandy loam	1	25501.7	761.2	3.00
Washington loam	5	14807.9	4379.4	29.60
Whippany silty clay loam	4	18370.8	3946.3	21.50

* Soil number 1, 6, 7, 10, 12, and 13 are Typic Hapludults; number 2 is a Spodic Quartzipsamments; number 3 and 5 are Ultic Hapludalfs; number 4 is a Aquic Hapludalfs; number 8, 11, and 15 are Typic Fragiudalfs; number 9 is a loamy sand dredged from Delaware River; number 14 is a Mollic Hapludalfs.

Table 3.4 Analysis of particle size distribution, and soil pH

Soil Name	Soil No.	Particle Size Distribution			pH*	
		Sand %	Silt %	Clay %	In water	In $CaCl_2$
Birdsboro silt loam	13	50	32	18	5.69	5.24
Boonton Bergen County soil	15	60	27	13	5.12	4.31
Boonton Union County soil	11	49	35	16	5.14	4.70
Downer loamy sand	10	87	5	8	4.74	3.74
Dunellen sandy loam	12	56	30	14	5.57	4.93
Fill materials from Delaware River	9	85	5	10	4.77	4.09
Freehold sandy loam (subsurface)	7	37	42	21	6.44	5.72
Freehold sandy loam (surface)	6	92	2	6	5.22	4.87
Hazen gravelly loam	14	39	38	23	6.02	5.77
Lakewood sand	2	91	3	6	4.18	3.65
Penn silt loam	3	25	48	27	4.67	4.13
Rockaway stony loam	8	54	30	16	4.69	4.23
Sassafras sandy loam	1	45	37	18	5.78	5.31
Washington loam	5	20	49	31	6.03	5.80
Whippany silty clay loam	4	49	16	37	6.17	5.72

* soil pH was determined after 30 minutes stirring, and then 1 hour standing in 1:1 soil/water suspension.

Table 3.5 Analysis of soil cation exchange capacity, organic carbon and soil organic matter

Soil Name	K	Mg	Ca	ECEC	Organic Matter	Organic Carbon
	(meq/100g)				(%)	(g/Kg)
Birdsboro silt loam	0.47	1.37	3.30	5.30	2.2	12.8
Boonton Bergen County soil	0.02	0.60	2.59	4.20	5.3	30.7
Boonton Union County soil	0.19	0.42	1.58	4.20	8.6	49.9
Downer loamy sand	0.21	0.43	1.10	2.30	0.8	4.6
Dunellen sandy loam	0.13	1.06	2.71	4.20	1.9	11.0
Fill materials from Delaware River	0.21	0.43	1.10	2.30	1.2	7.0
Freehold sandy loam (subsurface)	0.33	0.91	2.84	4.30	2.4	13.9
Freehold sandy loam (surface)	0.07	0.21	0.46	0.80	0.2	1.2
Hazen gravelly loam	0.81	1.90	6.53	9.30	3.1	18.0
Lakewood sand	0.01	0.02	0.05	0.90	0.5	2.9
Penn silt loam	0.14	0.42	1.25	3.80	1.3	7.5
Rockaway stony loam	0.15	0.14	0.59	2.70	4.9	28.4
Sassafras sandy loam	0.14	0.69	2.06	3.10	0.6	3.5
Washington loam	0.65	1.63	6.59	8.90	2.9	16.8
Whippany silty clay loam	0.05	2.52	6.87	9.50	2.3	13.3

Organic carbon content determined by the Walkley-Black wet combustion method (Sims and Heckerdorn, 1991).

Table 3.6 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 soil	3.859	4.541	0.057
Boonton Union County soil	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 Delaware 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 3.7 Amorphous and crystalline Fe, Al, and Mn oxides extracted by sodium dithionite-citrate-bicarbonate solutions.

Soil Name	Fe_2O_3 (%)	Al_2O_3 (%)	MnO_2 (%)
Birdsboro silt loam	1.600	0.744	0.119
Boonton Bergen County soil	2.080	0.661	0.076
Boonton Union County soil	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 Delaware 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 3.8 Amorphous Fe, Al, and Mn oxides extracted by ammonium oxalate

Soil Name	Fe_2O_3 (%)	Al_2O_3 (%)	MnO_2 (%)
Birdsboro silt loam	1.035	0.714	0.025
Boonton Bergen County soil	1.563	1.321	0.013
Boonton Union County soil	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 Delaware 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 3.9 BET specific surface area and surface acidity of soils

Soil Name	$A_{sp}{}^2$ (m^2/g)	pH_{zpc}	pK_{a1}	pK_{a2}
Birdsboro silt loam	7.06	3.40	2.50	4.30
Boonton Bergen County soil	7.20	3.00	2.10	3.90
Boonton Union County soil	6.45	2.80	1.80	3.80
Downer loamy sand	1.15	3.40	2.54	4.26
Dunellen sandy loam	5.21	3.20	1.95	4.45
Fill materials from Delaware River	2.37	3.20	2.07	4.33
Freehold sandy loam (subsurface)	9.01	3.60	2.74	4.46
Freehold sandy loam (surface)	2.04	2.90	1.70	4.10
Hazen gravelly loam	5.90	3.10	2.08	4.12
Lakewood sand	1.10	3.60	2.90	4.30
Penn silt loam	8.04	3.30	2.12	4.48
Rockaway stony loam	8.62	2.80	1.48	4.12
Sassafras sandy loam	5.31	3.40	2.26	4.54
Washington loam	11.59	2.85	1.40	4.30
Whippany silty clay loam	5.98	3.00	1.80	4.20

3.5 Results and discussion

The effect of pH on arsenic sorption by the fifteen New Jersey soils was examined to better understand the partitioning of this contaminant to soils under environmental conditions.

The surface of soil particle is negatively charged over a wide pH range. At the natural soil pH, all of the fifteen New Jersey soils are negatively charged.

The maximum sorption ranged from 40% to 100% of the added arsenic in a pH range of 6 to 9 for arsenic(III) and in a pH range of 4 to 5 for arsenic(V). Adsorption of arsenic(III) decreased abruptly with increasing pH above 8 due to the repulsion between the negatively charged surface groups in the soil particles and the negatively charged arsenic species.

Adsorption of arsenic(V) was characterized by a adsorption plateau from pH 4 to 5. This behavior can be better understood by knowing that the main arsenic(V) species in solution being adsorbed is negatively charged and thus adsorbed by positively charged surface groups in the soil components, like oxide surfaces when $pH < pH_{zpc}$. For example, goethite (pH_{zpc} of 7.6-8.1) and hematite (pH_{zpc} of 6.5-8.6), are known to be positively charged at low pH and negatively charged at high pH (Bowell, 1994).

According to Bowell (1994), the sorption of As(III) is less dependent on pH than is As(V), because the arsenic(III) species being adsorbed in solution is a neutral species.

The presence of organic matter also had an important effect on arsenic adsorption. It was observed that generally soils with high organic matter content were responsible for higher amounts of adsorbed arsenic. This behavior was observed for low and high initial arsenic concentrations in solution.

The adsorption edges obtained were plotted as the percent of arsenic adsorbed versus the pH of the filtered suspension. As expected, the adsorption of arsenic in soils is pH dependent. The maximum adsorption peak occurs at different pH ranges for As(III) and As(V) due to the existence of negatively or positively charged ions in solution. Basically, the adsorption of arsenic(V) occurs at a lower pH than does the adsorption of arsenic(III).

It was observed that adsorption was a function of available sites for arsenic binding. Experiments using higher initial concentrations of As(III) and As(V) (0.75 mg/L) showed that the adsorption decreases when compared to adsorption edges using an initial arsenic concentration of 0.1 mg/L, probably due to the saturation of surface sites present on the soil surface.

For As(III) some form of specific adsorption, like hydrogen bonding, is the most likely mechanism for adsorption. For As(V), the adsorption occurs through electrostatic interactions between this species and positively charged mineral surfaces.

The partition coefficient (K) is defined as the metal or arsenic concentration in soil divided by the arsenic concentration in solution. No relationship between K and solution pH was found for either arsenic species studied.

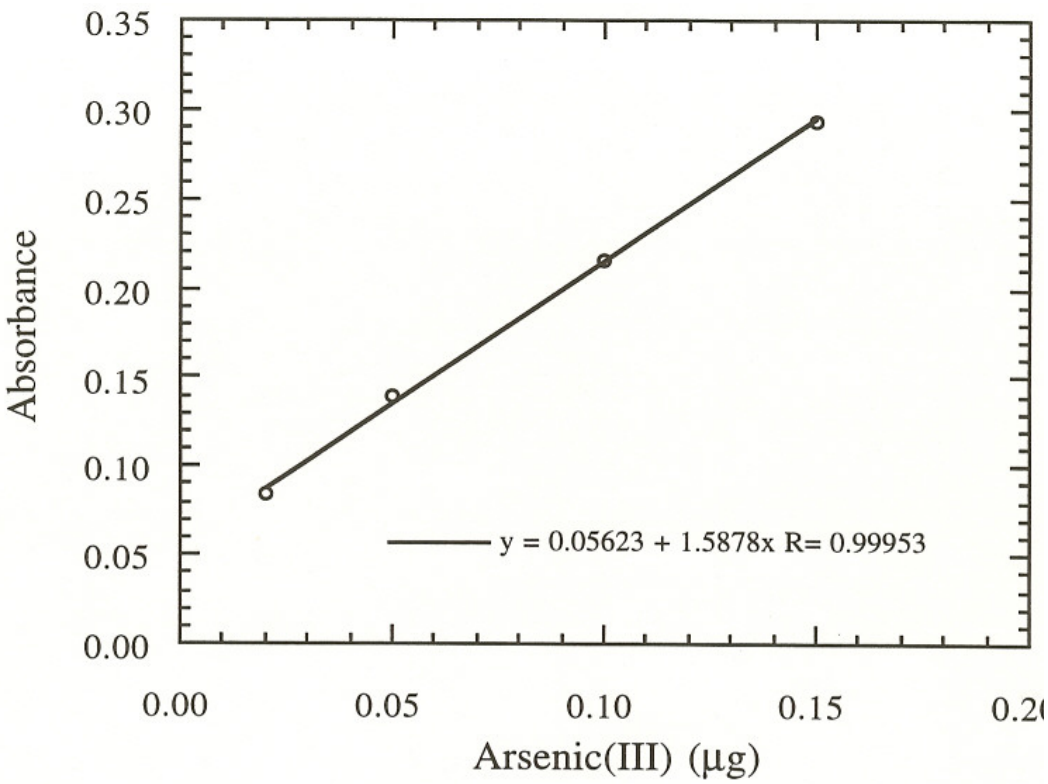

Figure 3.3 Calibration curve for arsenic(III) by the hydride generation metho

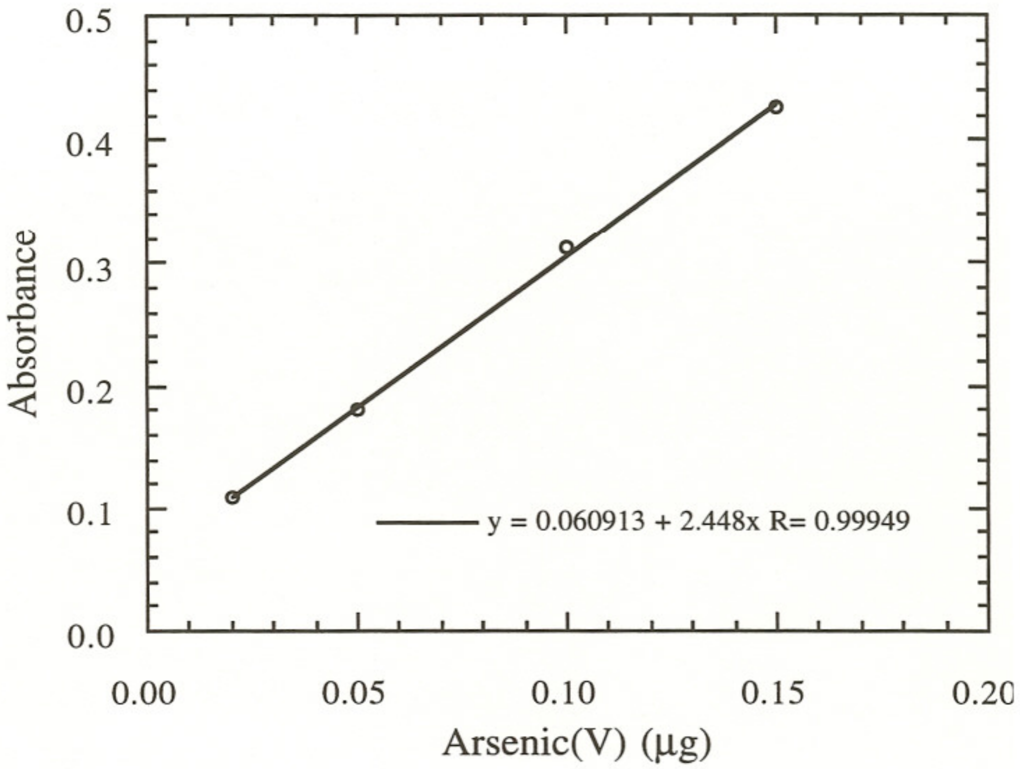

Figure 3.4 Calibration curve for arsenic(V) by the hydride generation method

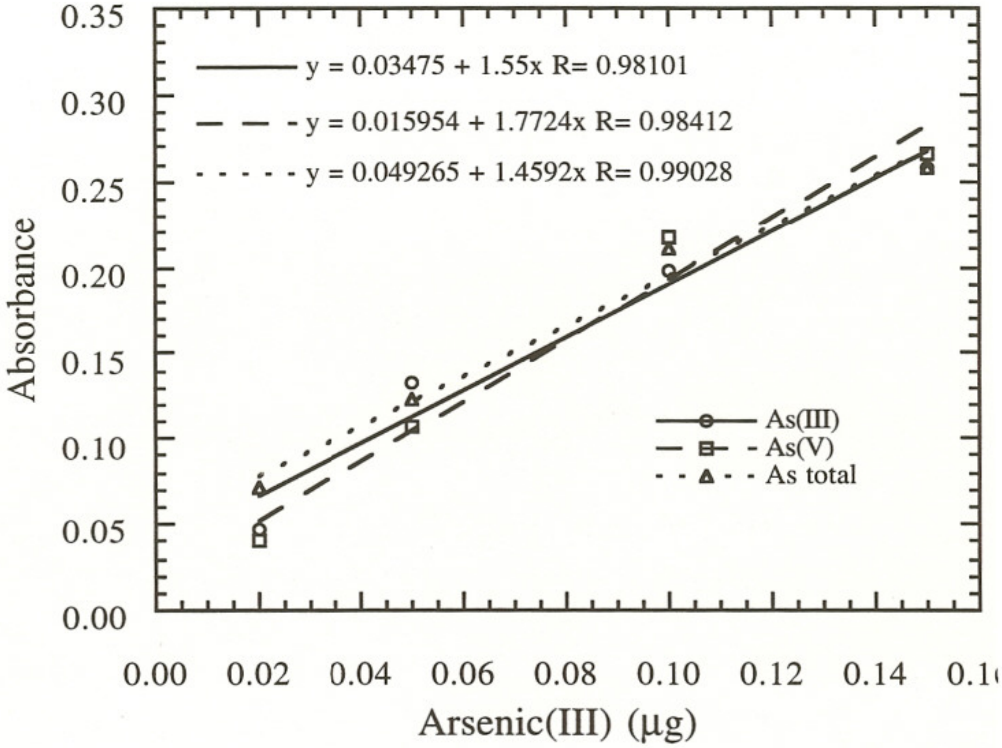

Figure 3.5 Calibration curves for As(III), As(V), and total As obtained simultaneously.

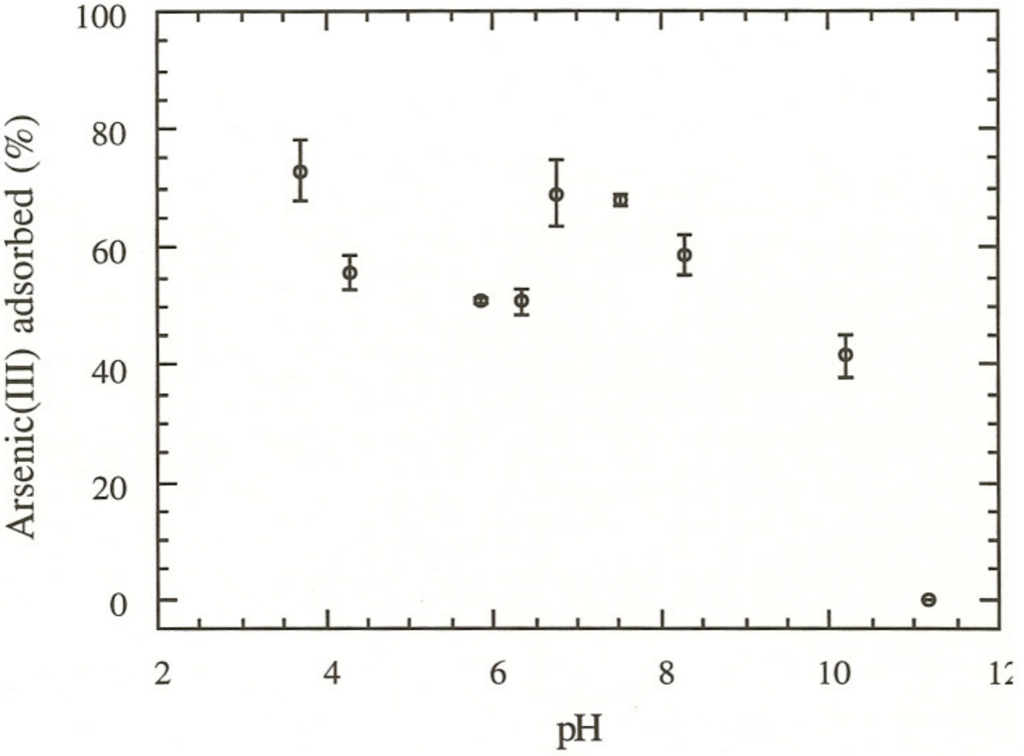

Figure 3.6 As(III) adsorption edge for Washington loam. Initial As(III) concentration = 1.33×10^{-6} M (0.1 mg/L).

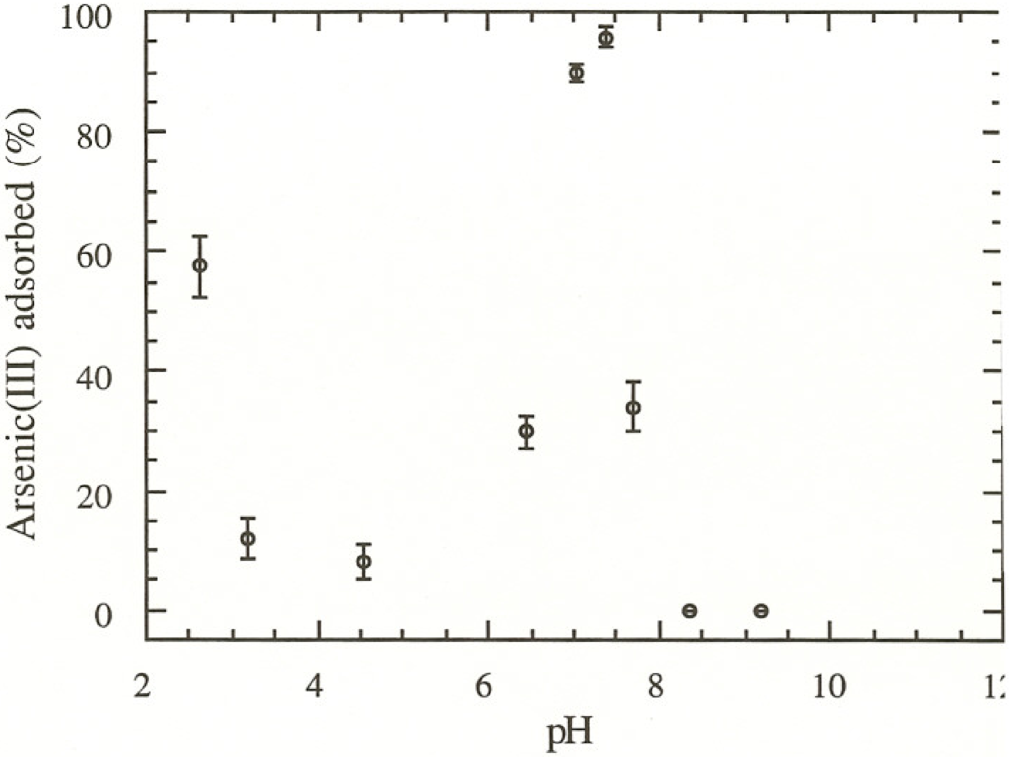

Figure 3.7 As(III) adsorption edge for Sassafras sand loam. Initial As(III) concentration = 1.33×10^{-6} M (0.1 mg/L).

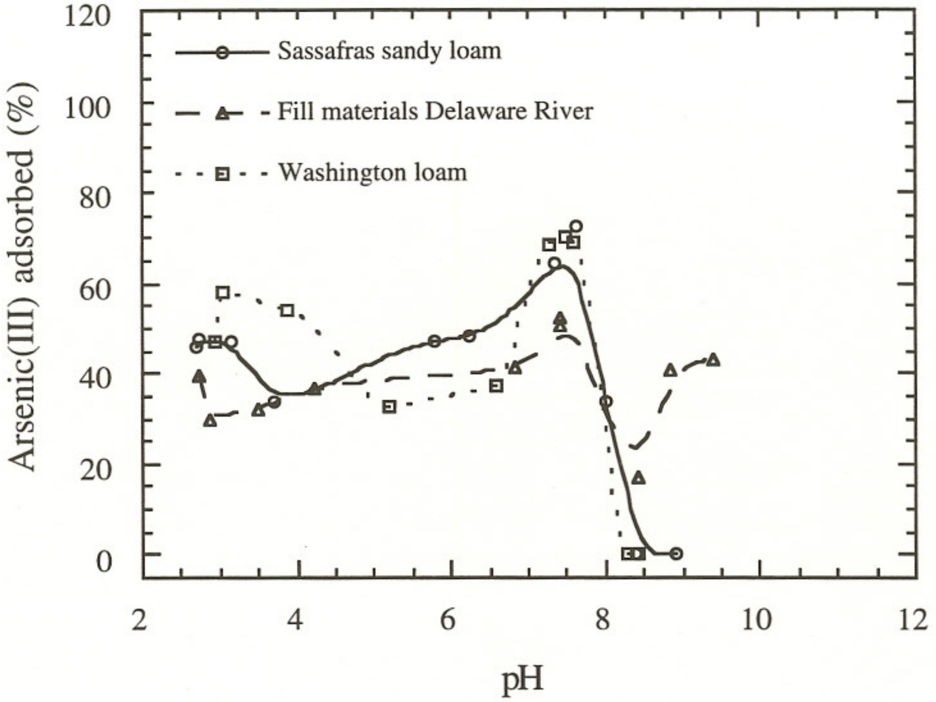

Figure 3.8 As(III) adsorption edge for Sassafras sandy loam, Fill materials from Delaware River, and Washington loam. Initial As(III) concentration = 1.00×10^{-5} M (0.75 mg/L).

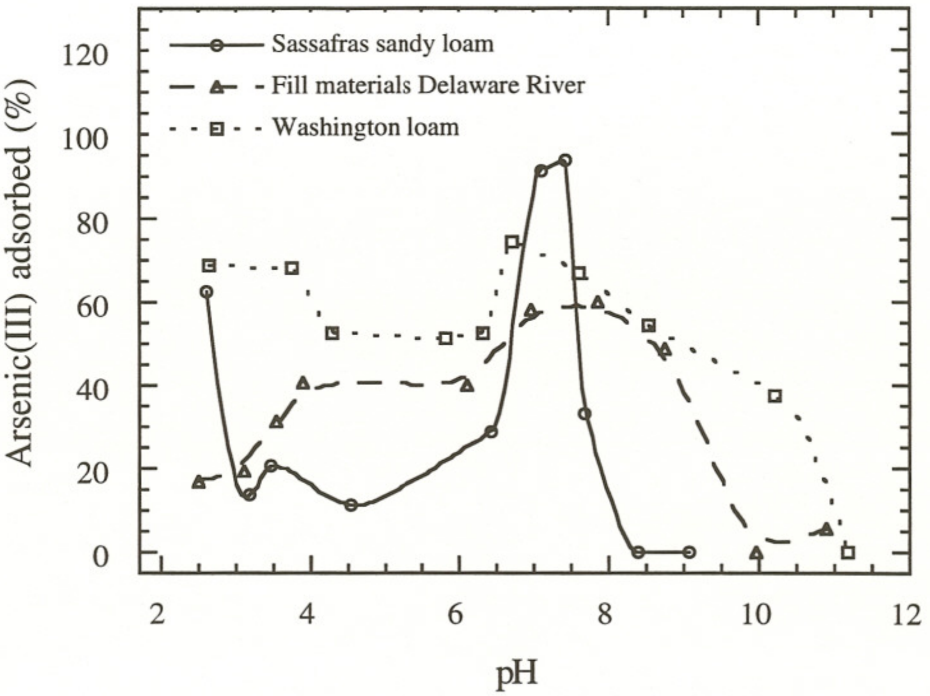

Figure 3.9 As(III) adsorption edge for Sassafras sandy loam, Fill materials fro Delaware River, and Washington loam. Initial As(III) concentration 1.33 × 10^{-6} M (0.1 mg/L).

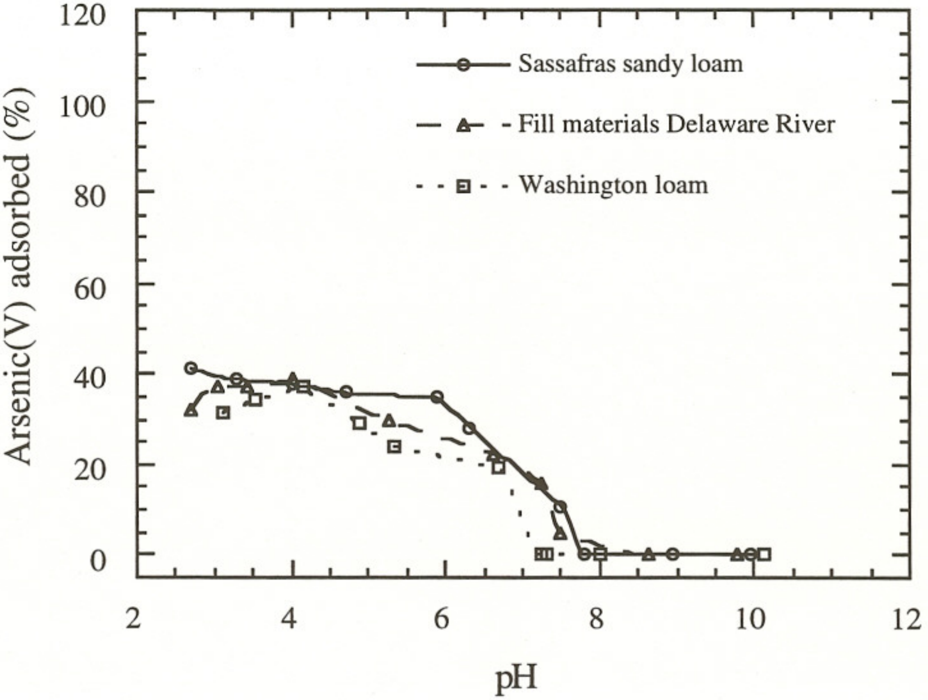

Figure 3.10 As(V) adsorption edge for Sassafras sandy loam, Fill materials fror Delaware River, and Washington loam. Initial As(V) concentration 1.00×10^{-5} M (0.75 mg/L).

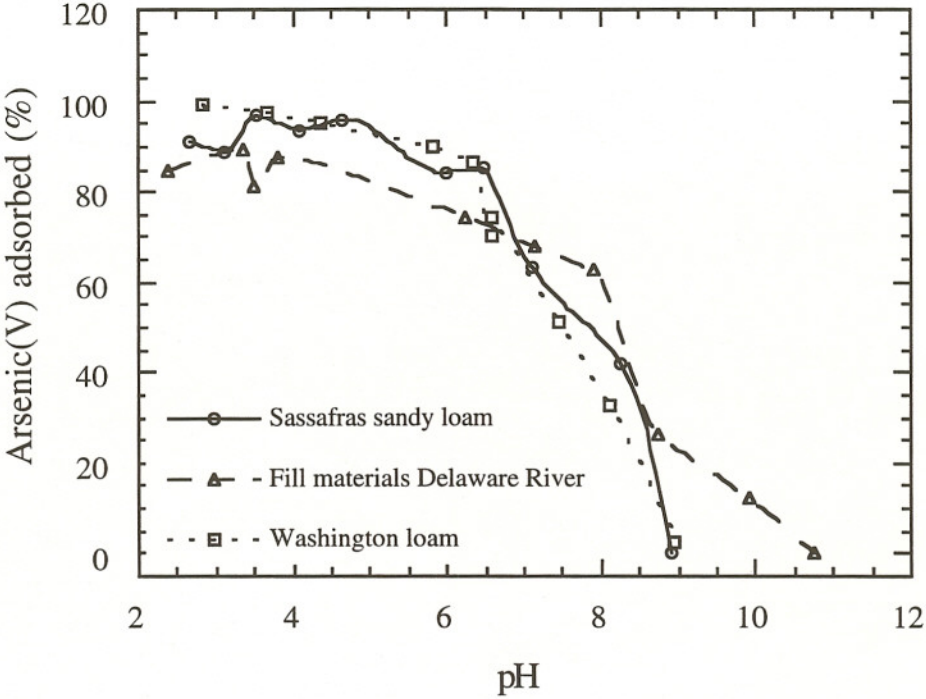

Figure 3.11 As(V) adsorption edge for Sassafras sandy loam, Fill materials fron Delaware River, and Washington loam. Initial As(V) concentration = 1.33×10^{-6} M (0.1 mg/L).

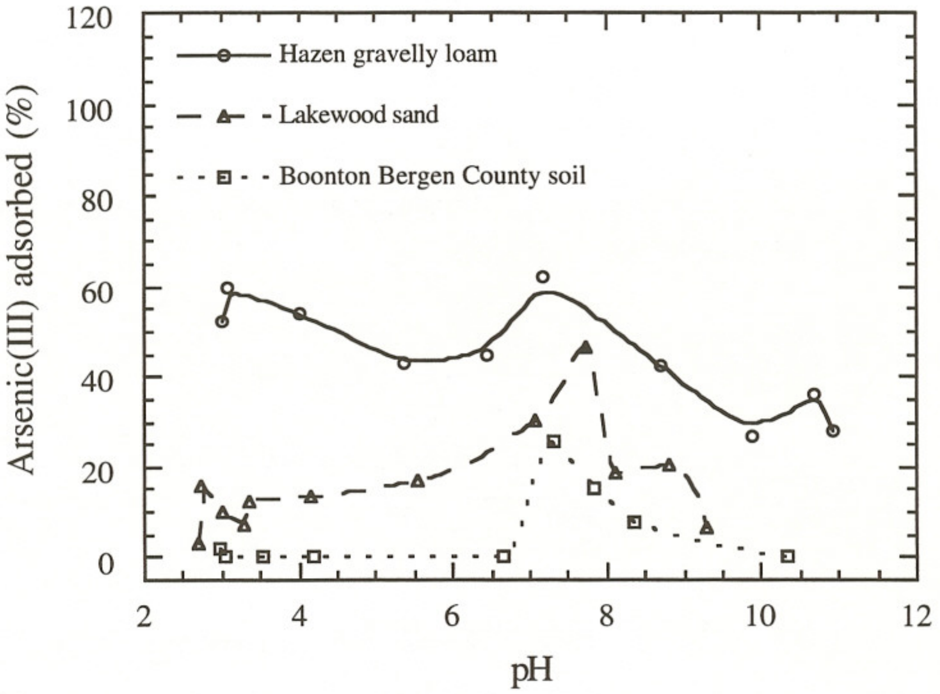

Figure 3.12 As(III) adsorption edge for Hazen gravelly loam, Lakewood sand, and Boonton Bergen County soil. Initial As(III) concentration = 1.00×10^{-5} M (0.75 mg/L).

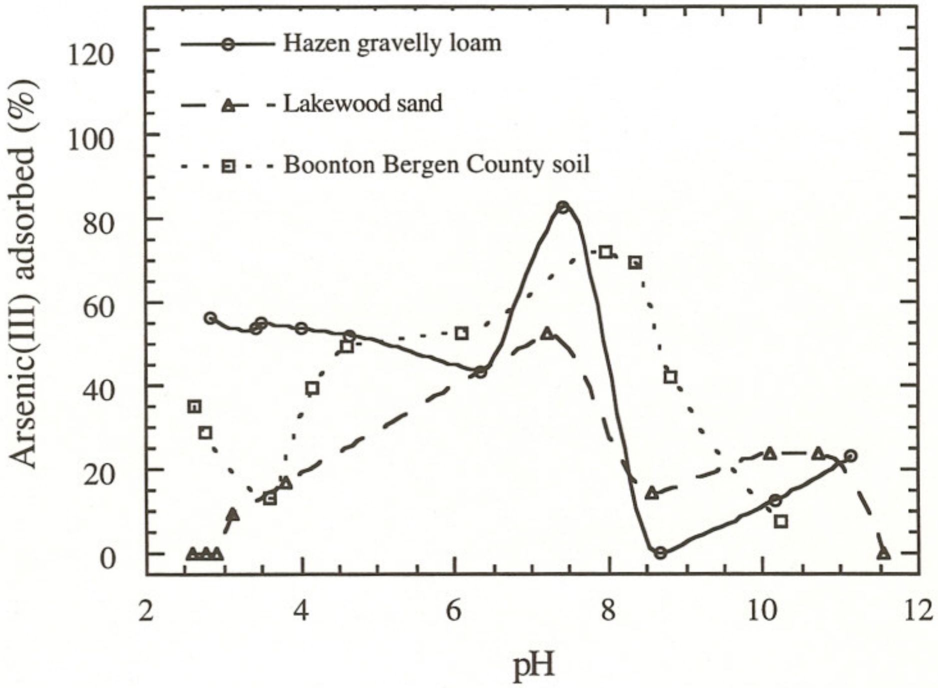

Figure 3.13 As(III) adsorption edge for Hazen gravelly loam, Lakewood sand, and Boonton Bergen County soil. Initial As(III) concentration = 1.33×10^{-6} M (0.1 mg/L).

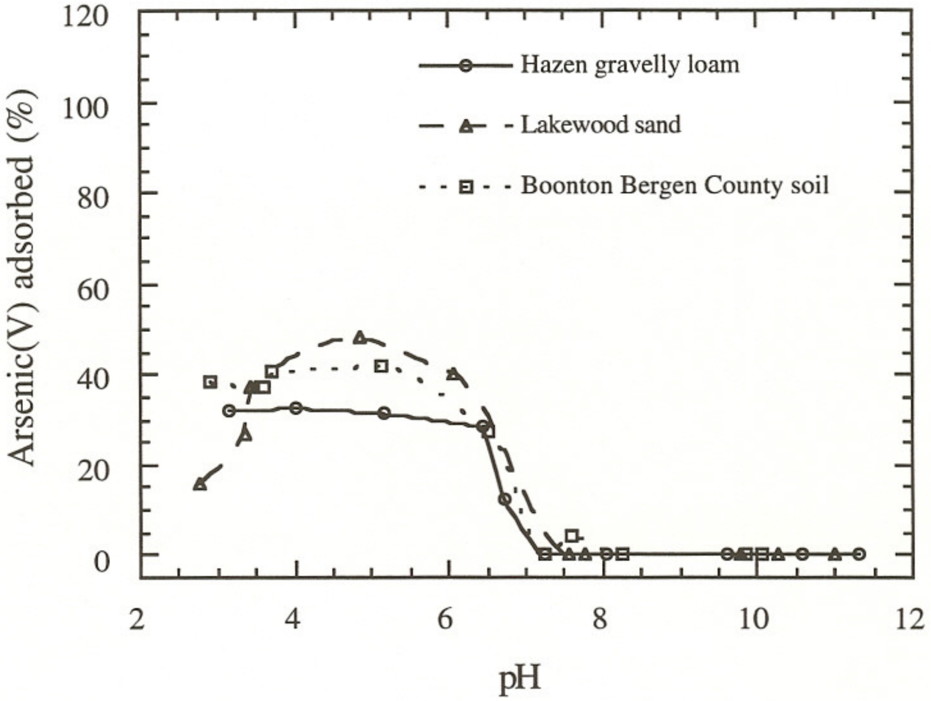

Figure 3.14 As(V) adsorption edge for Hazen gravelly loam, Lakewood sand, and Boonton Bergen County soil. Initial As(V) concentration = 1.00×10^{-5} M (0.75 mg/L).

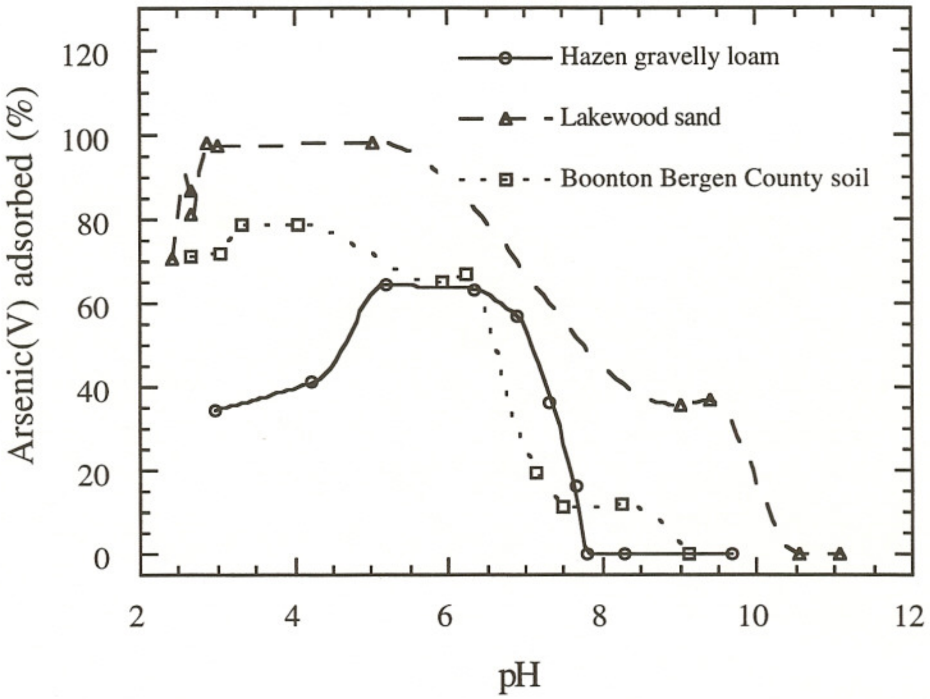

Figure 3.15 As(V) adsorption edge for Hazen gravelly loam, Lakewood sand, and Boonton Bergen County soil. Initial As(V) concentration = 1.33×10^{-6} M (0.1 mg/L).

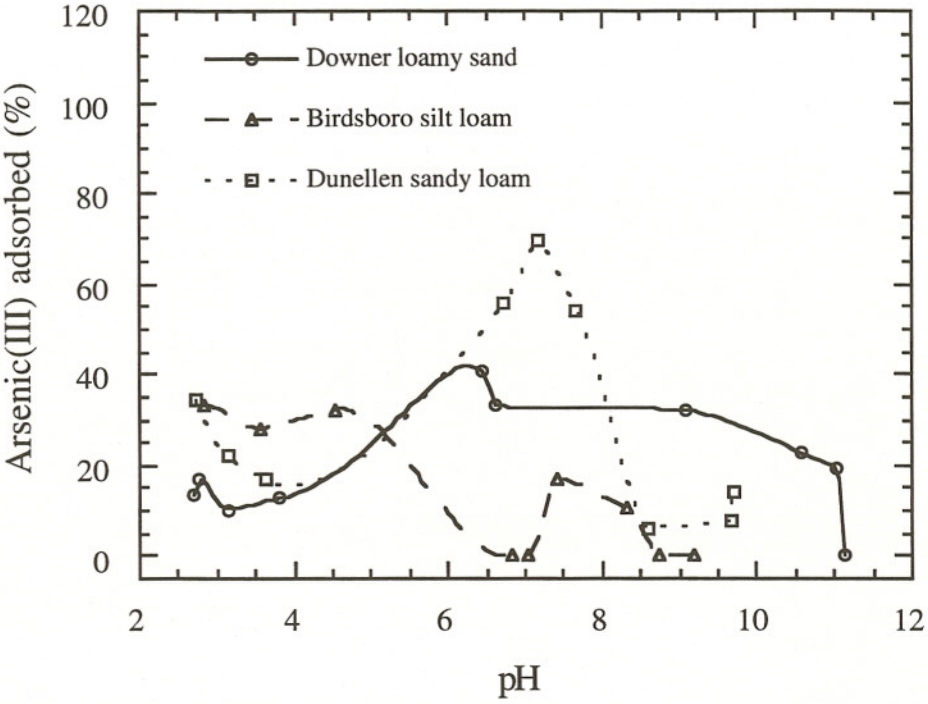

Figure 3.16 As(III) adsorption edge for Downer loamy sand, Birdsboro silt loam, and Dunellen sandy loam. Initial As(III) concentration = 1.00×10^{-5} M (0.75 mg/L).

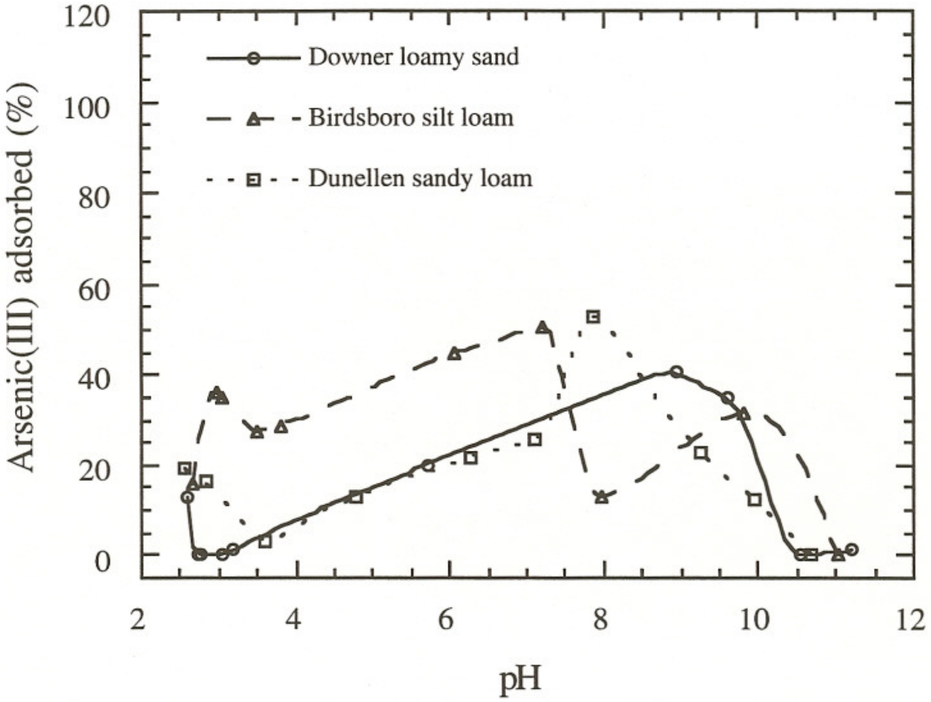

Figure 3.17 As(III) adsorption edge for Downer loamy sand, Birdsboro silt loam, and Dunellen sandy loam. Initial As(III) concentration = 1.33 × 10^{-6} M (0.1 mg/L).

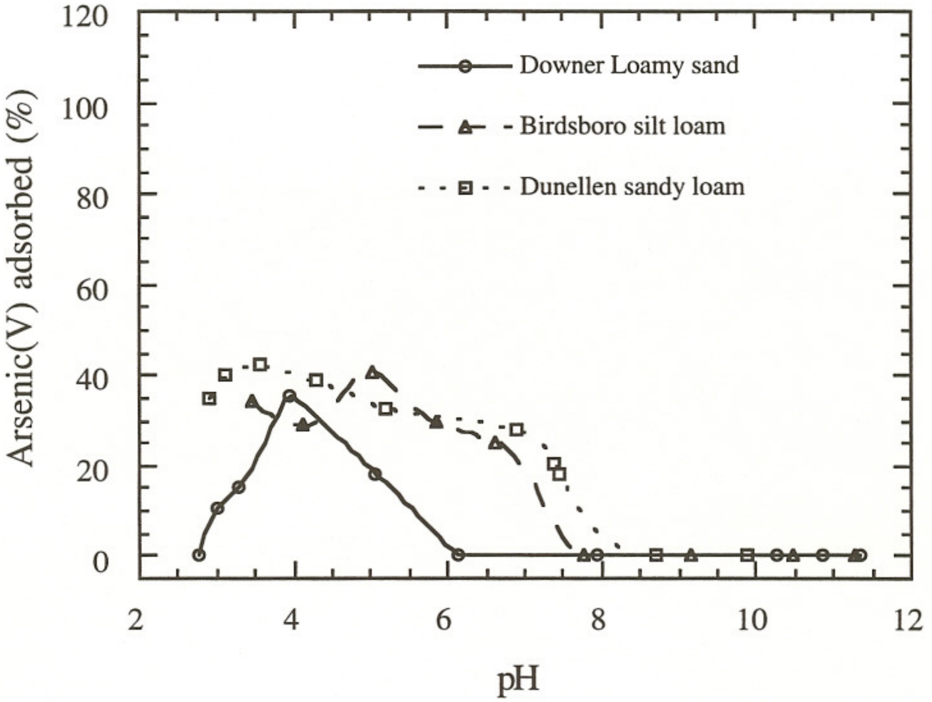

Figure 3.18 As(V) adsorption edge for Downer loamy sand, Birdsboro silt loam, and Dunellen sandy loam. Initial As(V) concentration = 1.00×10^{-5} M (0.75 mg/L).

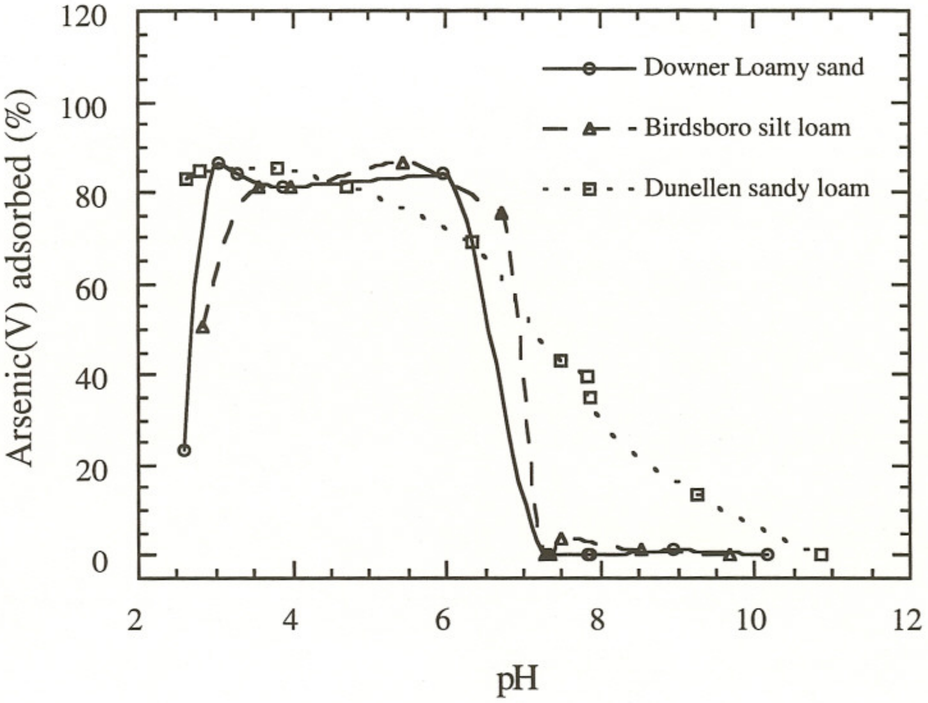

Figure 3.19 As(V) adsorption edge for Downer loamy sand, Birdsboro silt loam, and Dunellen sandy loam. Initial As(V) concentration = 1.33×10^{-6} M (0.1 mg/L).

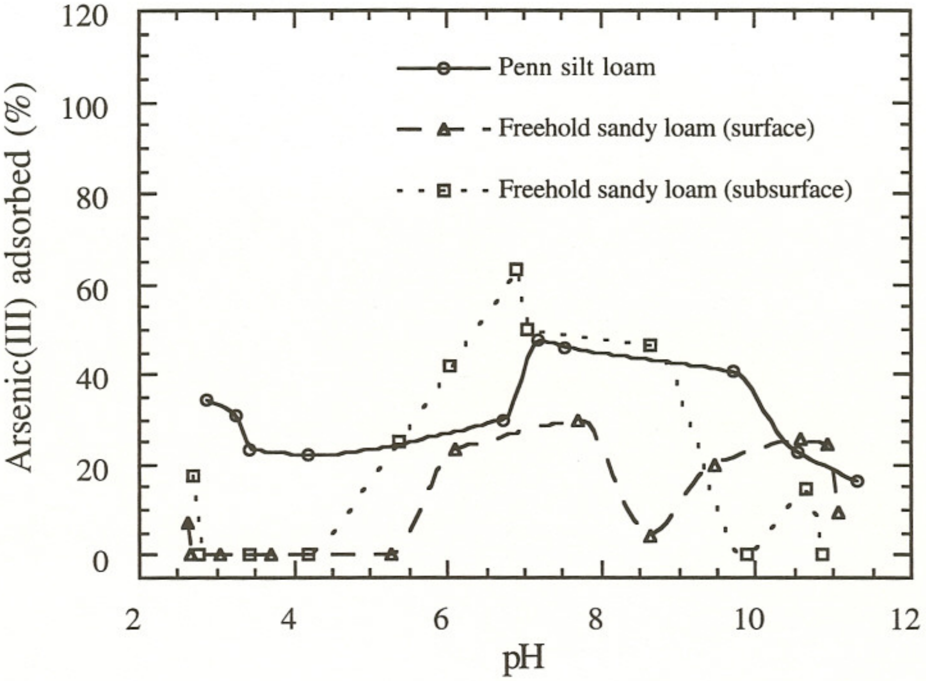

Figure 3.20 As(III) adsorption edge for Penn silt loam, Freehold sandy loam (surface), and Freehold sandy loam (subsurface). Initial As(III) concentration = 1.00×10^{-5} M (0.75 mg/L).

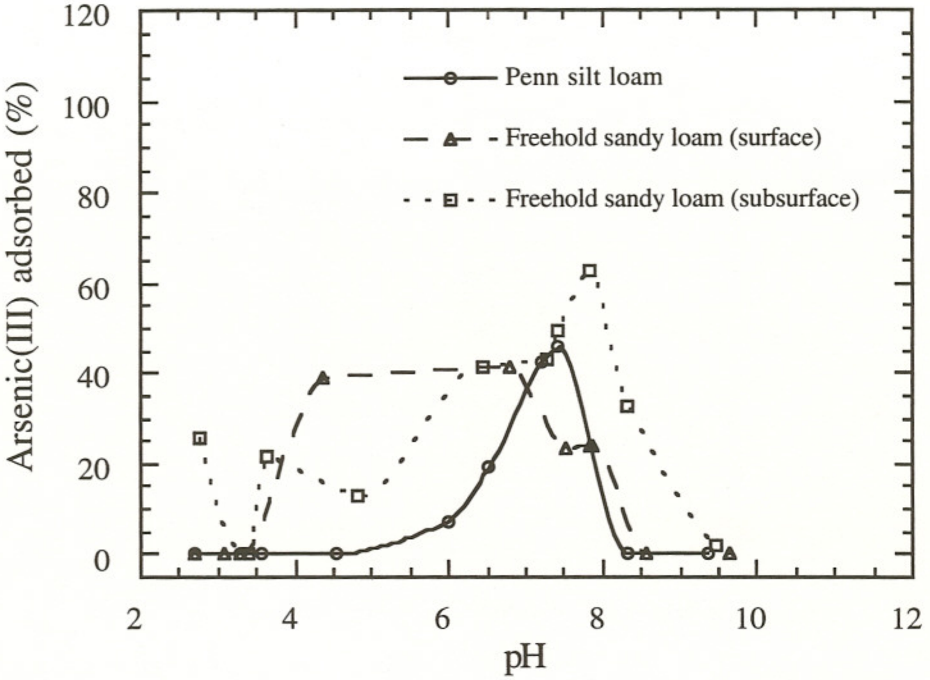

Figure 3.21 As(III) adsorption edge for Penn silt loam, Freehold sandy loam (surface), and Freehold sandy loam (subsurface). Initial As(III) concentration = 1.33×10^{-6} M (0.1 mg/L).

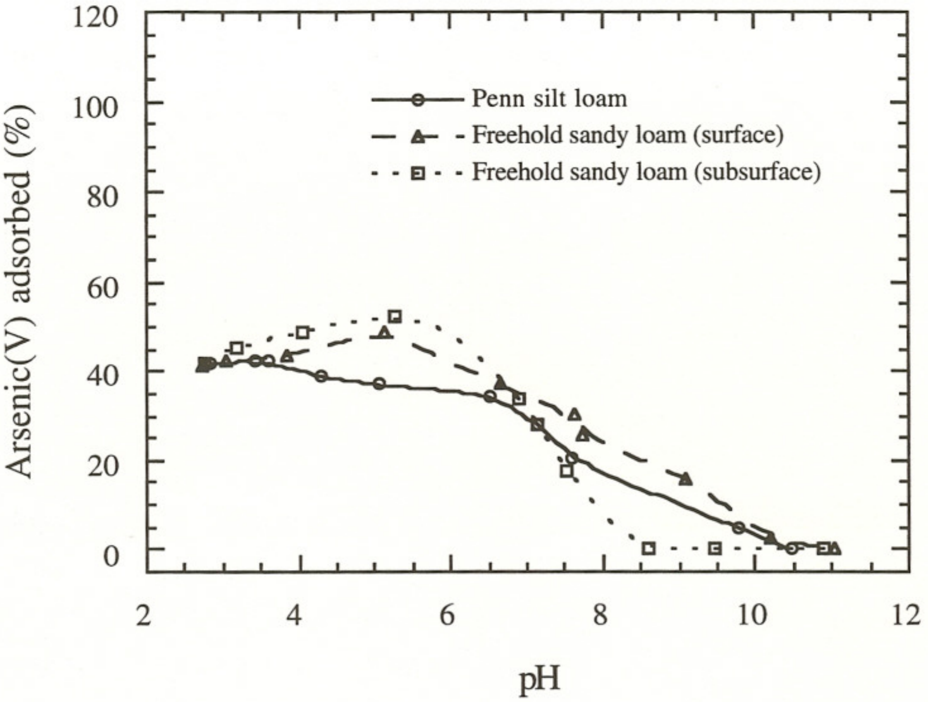

Figure 3.22 As(V) adsorption edge for Penn silt loam, Freehold sandy loam (surface) and Freehold sandy loam (subsurface). Initial As(V) concentration = 1.0 $\times 10^{-5}$ M (0.75 mg/L).

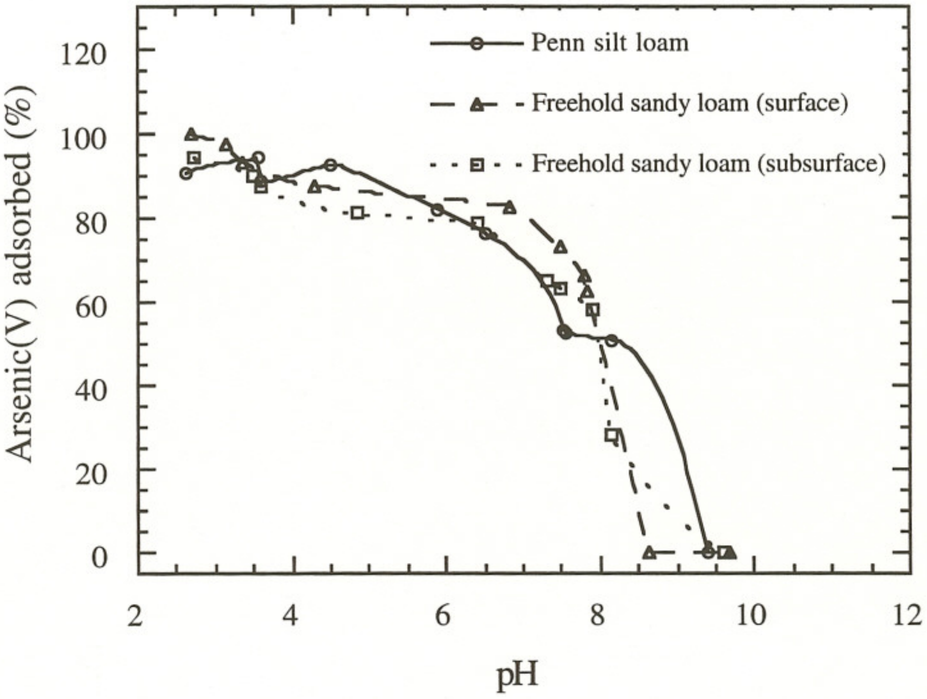

Figure 3.23 As(V) adsorption edge for Penn silt loam, Freehold sandy loam (surface), and Freehold sandy loam (subsurface). Initial As(V) concentration = 1.33 $\times 10^{-6}$ M (0.1 mg/L).

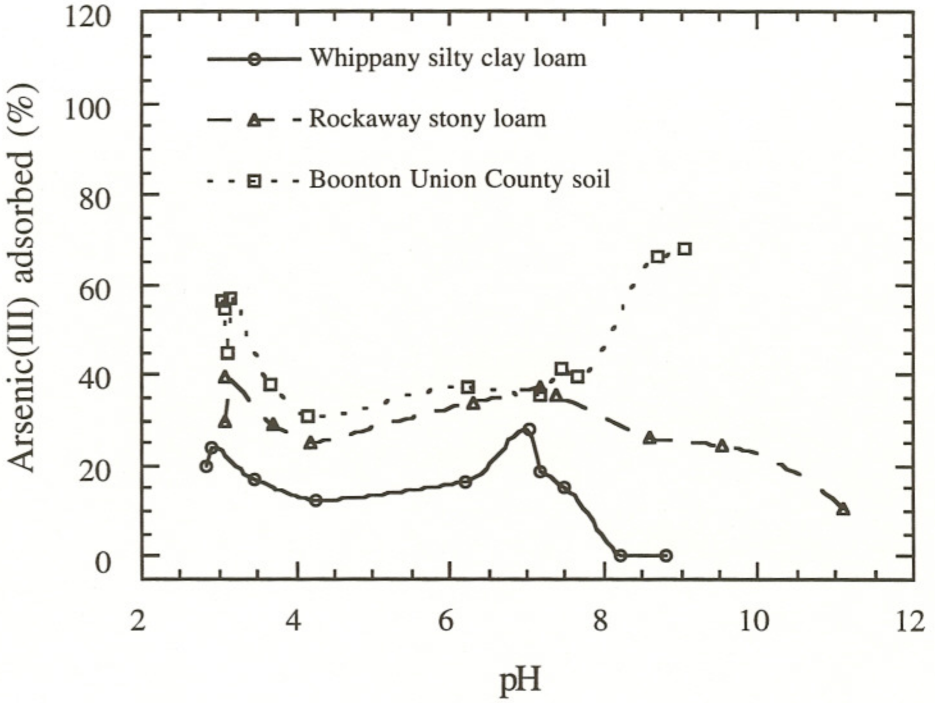

Figure 3.24 As(III) adsorption edge for Whippany silty clay loam, Rockaway stony loam, and Boonton Union County soil. Initial As(III) concentration = 1.00×10^{-5} M (0.75 mg/L).

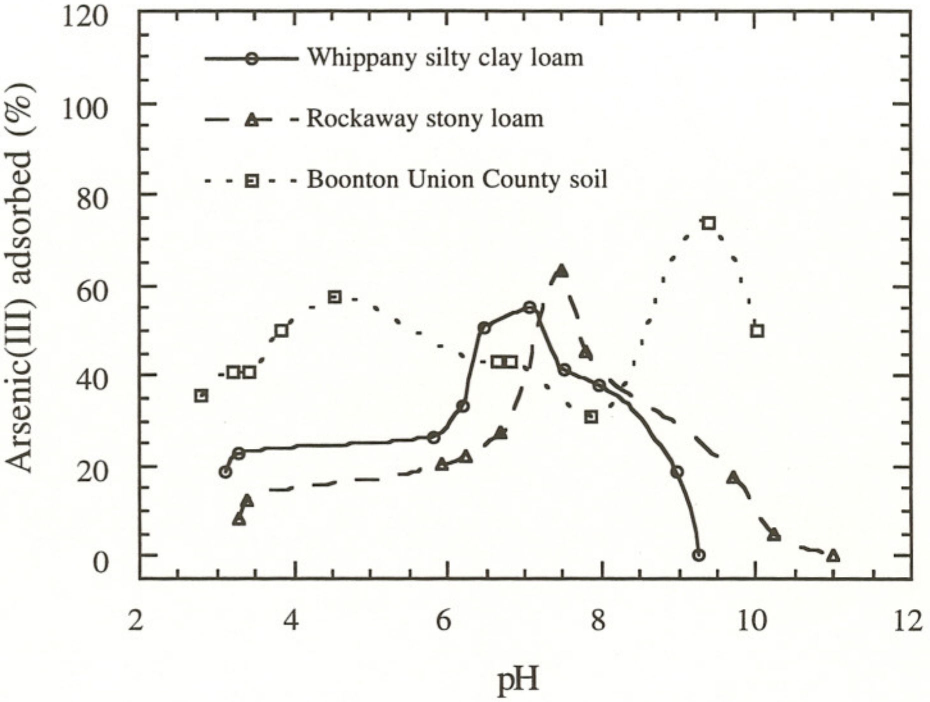

Figure 3.25 As(III) adsorption edge for Whippany silty clay loam, Rockaway stony loam, and Boonton Union County soil. Initial As(III) concentration = 1.33×10^{-6} M (0.1 mg/L).

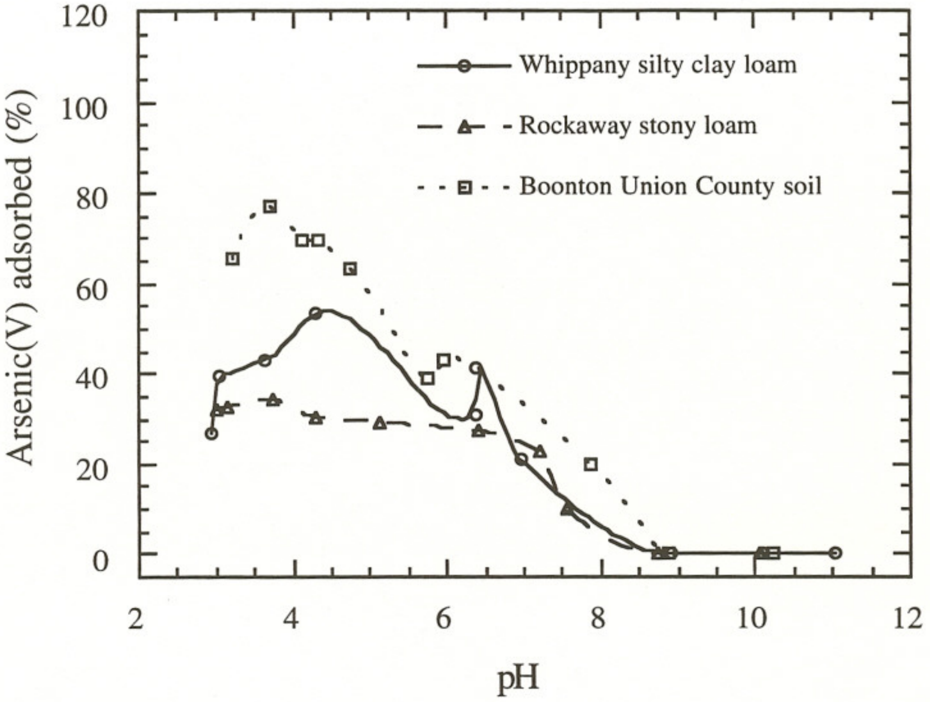

Figure 3.26 As(V) adsorption edge for Whippany silty clay loam, Rockaway stony loam, and Boonton Union County soil. Initial As(V) concentration = 1.00 × 10^{-5} M (0.75 mg/L).

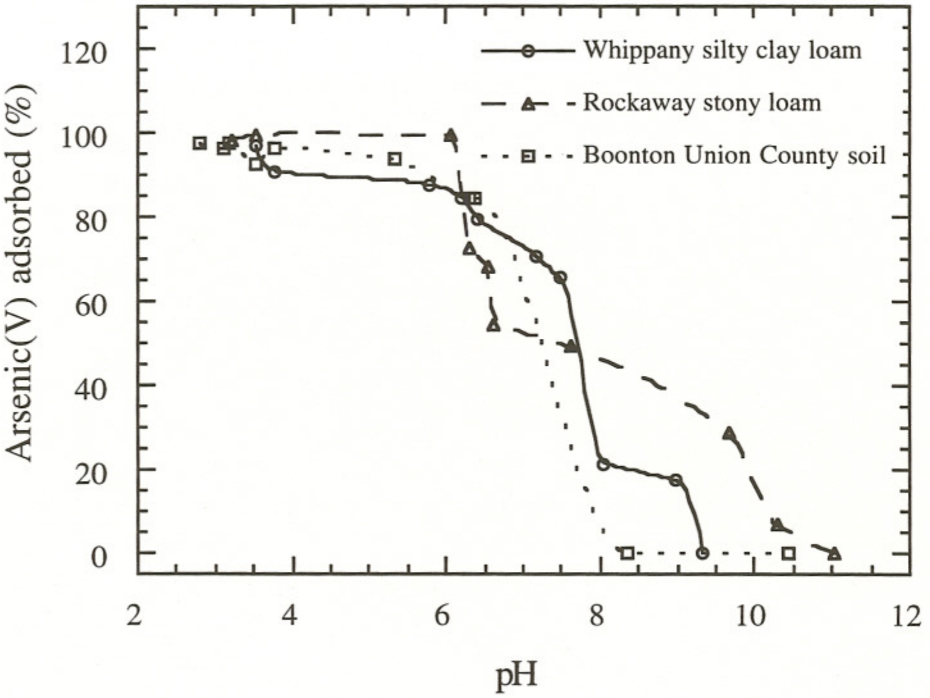

Figure 3.27 As(V) adsorption edge for Whippany silty clay loam, Rockaway stony loam, and Boonton Union County soil. Initial As(V) concentration = 1.33 × 10^{-6} M (0.1 mg/L).

Chapter 4

SORPTION AND DESORPTION OF ARSENIC BY SOILS: ISOTHERMS

4.1 Introduction

Adsorption isotherms are obtained in order to assess adsorption strengt and the maximum adsorption capacity of an adsorbent. Pierce and Moore (1982 studied the adsorption of As(III) and As(V) on amorphous iron hydroxide. The observed that at low initial concentrations of arsenic, all isotherms followed th Langmuir type. At higher concentrations, the isotherms were linear, which indicate th existence of more than one type of adsorption site. Also, the adsorption was dependen on pH.

Huang et al. (1979) reported that the adsorption of arsenite on river sediments was linearly dependent on concentration while arsenate adsorption followed the Langmuir isotherm. They studied arsenic in the range of 0.75 to 7.5 mg/L.

The desorption process is also extremely important, especially for soils already contaminated. Desorption studies are necessary to predict the fate and mobility of a contaminant as well as to develop remediation techniques and strategies. Contaminants that are strongly bound in soil particles, for example, wouldn't offer a serious problem of movement into the groundwater, so remediation can be addressed just to potential dangerous contaminants. However, the persistence of the contaminant can be a problem when considering the use of the contaminated site for crop production or home construction (Sparks, 1995).

It is also proven that in most cases the desorption process is more difficult than is adsorption, and not all the contaminant is desorbed, suggesting that the reaction is irreversible. This is known as hysteresis. A number of factors such a microbial transformations can help to explain why hysteresis occurs.

Some factors that can alter desorption making it slow are diffusion precipitation and ligand exchange. Unfortunately, many parameters such as partitio coefficients used to assess the retention of contaminants are obtained through short-ter experiments that don't account for factors that can alter desorption (Sparks, 1995).

In this study, desorption of two arsenic species was studied in order to examine the reversibility of the adsorption/desorption process.

Arsenic is considered analytically difficult to measure. A colorimetric method developed by Johnson (1971) and Johnson and Pilson (1972) was used for quantitative determination of arsenic in solution. The colorimetric method was described as efficient in natural water systems. This method is simple to operate and allows simultaneous determination of both As(V) and As(III). However, during this adsorption study only the determination of total arsenic in solution was necessary.

A mixed reagent containing ammonium molybdate, sulfuric acid, ascorbic acid and potassium antimonyl-tartrate was used to develop color by complexation of As(V) to form a molybdenum blue compound. The absorbances of the solutions were subsequently determined using a spectrophotometer at the wavelength maximum absorbance, 865 nm. This maximized the sensitivity for arsenate determination and only slightly reduced the sensitivity for phosphate, a known interferent in arsenic determinations using spectrophotometric methods. Maeda et al. (1992), found that in the aqueous phase only phosphate interfered with arsenic analysis; other anions like sulfate, nitrate and acetate hardly influenced the adsorption behavior of arsenic species. Therefore, in order to obtain better results, it was necessary to be careful about the minimum detectable arsenic concentration in which phosphate interference was negligible.

4.2 Materials and methods

4.2.1 Materials

1000 mg/L As(III) and As(V) stock solutions were prepared from $NaAsO_2$ and $NaHAsO_4 \cdot 7\ H_2O$ salts in 0.3 M HCl solution. A series of standards of 0.025, 0.05, 0.1, 0.25, 0.5, 1.0, 2.5, 5.0, and 7.5 mg/L were prepared by dilution from more concentrated As(III) and As(V) standard solutions.

The mixed reagent was prepared by mixing 0.024 M ammonium molybdate, 3.5 N sulfuric acid, 0.3 M ascorbic acid, and 0.0042 M potassium antimonyl-tartrate solutions with a ratio of 2:5:2:1, respectively. The mixed reagent was prepared fresh daily for use.

The reducing reagent was prepared by mixing 0.074 M sodium metabisulfite, 0.056 M sodium thiosulfate, and 3.5 N sulfuric acid solutions with a ratio of 2:2:1, respectively. The sulfuric acid solution was carefully added to the sodium metabisulfite solution to avoid excessive bubbling caused by liberation of SO_2. Then the sodium thiosulfate solution was added. This reagent is stable for up to 24 hours when refrigerated.

Potassium iodate, 0.04 M KIO_3, was used as the oxidizing reagent.

4.2.2 Calibration curves

8 ml of each standard was taken and put into a 10 ml test vial. 0.2 ml of 3.5 N HCl and 0.2 ml of 0.04 M potassium iodate solution, which corresponds to 100 μM of iodate, were subsequently added to each vial to oxidize As(III) to As(V). In the

case of As(V) this procedure was also followed to ensure that all As was in the +5 oxidation state, the state in which the arsenic containing complex absorbs light at 865 nm. The solutions were allowed to react for 30 minutes to complete the oxidation. 1 ml of mixed reagent was then added to each vial and 2 hours, which was found to be adequate for the completion of the reaction, were allowed to develop color. The absorbance of each standard was determined using a DR/2000 spectrophotometer at a wavelength of 865 nm.

As expected, the calibration curves for As(III) and As(V) are almost identical as is shown in Figure 4.1 and Figure 4.2, respectively. The correlation coefficients were greater than 0.999. The linear range extends to 10 mg/L.

4.2.3 Sorption methods

Sorption experiments were performed using a batch technique.

1 ml of 1 M $NaNO_3$, to adjust the ionic strength to 0.01 M, and more concentrated arsenic standard solutions were added, to obtain spiked samples in the range of 0.75 to 200 mg/L, in ten 125 ml plastic flasks containing a soil solution ratio of 1.0 g ± 0.01 g per 100 ml DI water. The pH was adjusted using NaOH in order to obtain samples at natural pH, i.e. 0.3 M NaOH was added to neutralize the hydrochloric acid contained in the arsenic standard solutions. The suspensions were shaken for 48 hours at a room temperature of 25 °C (± 3 °C) at a rate of 100 rpm on a rotatory shaker. After equilibration, the suspensions were filtered using a plastic syringe and a 0.45 µm membrane filter placed on a filter holder. The syringe was washed previously with the suspension and the first 20 ml of filtrate was discarded. The pH of each sample was then determined using a pH meter.

An aliquot of each filtrate was used to determine the amount of total arsenic in solution, in some cases the analysis was done in duplicate. The amount adsorbed was then obtained by difference between the initial amount of arsenic added and the amount of arsenic in solution after 48 hours of equilibration time.

4.2.4 Desorption methods

Desorption experiments were performed using five different soils, Penn silt loam, Washington loam, Boonton Bergen County soil, Freehold sandy loam (subsurface), and Dunellen sandy loam. Initial concentrations of 5 mg/L of As(III) and As(V) were used.

The samples were equilibrated for 48 hours to ensure arsenic adsorption. At the end of the adsorption process, 75 ml of the supernatant was withdrawn from the reaction flask and replaced with the same amount of background electrolyte, 0.01 M $NaNO_3$ at pH 6. The new suspension was placed on the rotatory shaker for an additional 24 hours. This procedure was repeated 3 times and the supernatants were analyzed for total arsenic in solution using the colorimetric method and the results were corrected for dilution. In addition, the samples were analyzed for As(V) in solution, and As(III) was obtained by difference between total arsenic and As(V).

4.2.5 Arsenic analysis

By adding 0.4 ml of reducing reagent to an aliquot of 8 ml of the sample all arsenic in solution is converted to As(III), which is not determined by the colorimetric reaction. By adding oxidizing reagent to a sample all arsenic in solution is converted to As(V). This species forms a blue complex that absorbs light. Therefore, by subtracting the absorbance values of reduced sample from the oxidized sample, total arsenic in solution is obtained. Absorbance from untreated samples, 8 ml of sample plus 0.4 ml of DI water, are equivalent to the amount of As(V) in solution; thus As(III) is obtained by subtracting As(V) from total As in solution.

A standard addition method was used to test the accuracy of the colorimetric method with soil extracts as matrices using arsenic(V) as the source of arsenic. The recoveries of added arsenic were determined for three different soils: Lakewood sand (0.5% organic matter), Hazen loam (3.1% organic matter) and Boonton Union County soil (8.6% organic matter). Three soil extracts were prepared at different pHs, low (around pH 4), medium (ambient pH) and high (around pH 9) for each soil. As shown in Table 4.1, the recoveries of arsenic(V) were greater than 90% for all soil extracts at the different pH values.

The method of standard additions was used to test the accuracy of the colorimetric method for the determination of As(III). The recovery of arsenic was determined to be around 70% when the initial As(III) concentration was below 0.5 mg/L and the soil had a high organic matter content, like Boonton Union County soil (8.6% organic matter). However, recovery was above 90% for higher As(III) concentrations. Therefore, the adsorption isotherms were obtained respecting this limitation. Recoveries of arsenic(III) are shown in Table 4.2.

Based on recovery experiments it was concluded that the colorimetric method is suitable for the determination of adsorption isotherms. The interaction of organic matter is only significative when high organic matter soils are studied using low arsenic concentrations. Also, results indicate that pH has no influence on recovery of arsenic species.

Following arsenic adsorption, the colorimetric method was cross-checked with the hydride generation method for the two lowest initial arsenic concentrations used, 0.75 and 1.0 mg/L, using all fifteen New Jersey soils. The results are shown in Figure 4.3. Both methods agreed when arsenic(III) and arsenic(V) were used as the initial source of arsenic. Equilibrium concentrations of As(III) and As(V) in solution, in mg/L, obtained using these methods were plotted and the correlation coefficients were greater than 0.99, which means that there wasn't any deviation between the methods.

The attainment of maximum absorbance has been interpreted as the point at which the absorbance versus time curve reaches a linear plateau. There was a tendency to believe that increasing the colorimetric reaction time would increase the sensitivity of the method especially for the low concentration standards. Therefore, the stability of the arseno-molybdate complex formed in the colorimetric method was studied. The conclusion is that the complex is stable for up to 4 hours as seen in Figure 4.4. Three different As concentrations were tested, 0.025, 0.05 and 0.1 mg/L. A stabilization time of 2 hours was chosen for practical reasons. Some authors report the use of 4 hours, in order to standardize the formation of the complex in sea water samples (Johnson and Pilson, 1971).

4.3 Results and discussion

4.3.1 Adsorption isotherms

Adsorption isotherms were obtained for the fifteen New Jersey soils, using the colorimetric method for analysis. Both As(III) and As(V) were used, each at different initial concentrations. The Langmuir equation is defined as:

$$q = kCb / (1+kC) \qquad (1)$$

where k is a constant related to the binding strength in L/mg, b is the maximum amount of adsorbate that can be adsorbed for monolayer coverage or simply the adsorption capacity, in mg/g (Sparks, 1995). C is equivalent to the equilibrium or final adsorbate concentration in solution, in mg/L, and q is the amount of adsorption, i.e., adsorbate per unit mass of adsorbent, in mg/g.

The experimental data was fitted to this equation and k and b were determined. The statistical parameters R (correlation coefficient) and Chi square (χ^2), a measure of how much the observed values diverge from the expected values (Moore and McCabe, 1993). If the observed value is very different from the expected value, a large value of χ^2 will be obtained.

The Freundlich equation is defined as:

$$q= K_d\, C^{1/n} \qquad (2)$$

where K_d is a distribution coefficient, in mg/g, and n is a adsorption factor, in L/g. If 1/n is equal to one, the distribution coefficient becomes a partition coefficient, K_p. The disadvantage of this equation is that there is no possibility of predicting a maximum adsorption. However, the Freundlich equation is commonly used to represent adsorption, particularly when there are a variety of adsorption strengths.

Langmuir isotherms for As(III) and As(V) are shown in Figures 4.5 to 4.18. Freundlich isotherms for As(III) and As(V) are shown in Figures 4.19 to 4.32.

The isotherms were plotted as arsenic equilibrium concentration in mg/L versus the amount of arsenic adsorbed in mg/g for the Langmuir isotherms and as logarithm of arsenic equilibrium concentration in mg/L versus the logarithm of the amount of arsenic adsorbed in mg/g for the Freundlich isotherms.

In the arsenic concentration range studied, from 0.75 to 200 mg/L, soils studied had a L-type curve shape for the Langmuir isotherm. This behavior was observed for As(III) and As(V). The L-shaped Langmuir isotherm shows the decreasing of the slope as concentration increases due to the decrease in vacant adsorption sites as the soil becomes saturated, i.e. its sites become covered (Sparks, 1995). A high affinity between arsenic and appropriate soil surface sites is therefore observed at a relatively low arsenic concentration in the soil suspension solution.

In addition, the curve parameters show that the maximum amount of arsenic that can be adsorbed for monolayer coverage is generally higher for As(V) than is for As(III) at natural pH. Based on these same results, the Freundlich adsorption isotherms were also obtained for all fifteen New Jersey soils. The Langmuir and Freundlich parameters are shown in Tables 4.3 and 4.4, and 4.5 and 4.6, respectively.

4.3.2 Desorption isotherms

Five soils were used for the desorption study: Penn silt loam with 1.3% organic matter, Washington loam with 2.9% OM, Boonton Bergen County soil with 5.3% OM, Freehold sandy loam (subsurface) with 2.4% OM, and Dunellen sandy loam with 1.9% OM. As(III) and As(V) were used at an initial concentration of 5 mg/L.

The arsenic concentration retained by the soil after each desorption step was calculated according to the equation below, which accounts for dilution:

$$q_i = q_{i-1} - [C_i - (C_{i-1}/ 4)]/ W \qquad (3)$$

where q_i is the concentration of arsenic remaining in the soil at the end of the ith desorption step (mg/g), q_{i-1} is the concentration remaining in the soil at the end of the i-

1th desorption step, C_i is arsenic concentration in the solution at the end of the ith step (mg/L), and C_{i-1} is the concentration in the solution at the end of the i-1th desorption step. W is the concentration of solids in the suspension (g/L).

The amount of arsenic desorbed in each desorption step was calculated as the amount released in solution as a function of the amount adsorbed.

Results seen in Figures 4.33 to 4.37 obtained for desorption experiments using As(III) as source of arsenic and Figures 4.38 to 4.42, obtained using As(V), are indicative of significant adsorption/desorption hysteresis for all five soils studied.

Exchange reversibility is indicated when the exchange isotherms for the forward and backward exchange reactions coincide (Sparks, 1995). In the case of arsenic adsorption/desorption, there is no coincidence between the isotherms, therefore the process of adsorption is irreversible.

One factor that might be responsible for the hysteresis observed is that the adsorption can occur as an inner sphere process. Small differences in hysteresis among the soils is probably due to different binding behavior of arsenic species to different sites in the soil particles.

Results obtained from redox transformations during the desorption experiments and amount of arsenic desorbed for all five soils are summarized on Table 4.7 when As(III) was used as the source of arsenic, and Table 4.8 when As(V) was used.

Adsorption was significantly higher for As(V) than for As(III) species. For example, 27.5, 40.5, 27.0, 27.9, and 34.4% of the arsenic(III) was adsorbed by Penn silt loam, Washington loam, Boonton Bergen County soil, Freehold sandy loam, and Dunellen sandy loam, respectively. 74.6, 79.2, 86.2, 76.7, and 69.0% of the arsenic(V) was adsorbed by Penn silt loam, Washington loam, Boonton Bergen County soil, Freehold sandy loam, and Dunellen sandy loam, respectively.

The high adsorption of As(III) by Washington loam can be explained based on the fact that this soil is characterized by the highest iron oxide content among the soils used for the desorption experiment. Penn silt loam has 4.85% iron oxide, Washington loam has 5.56%, Boonton Bergen County soil has 3.86%, Freehold sandy loam has 3.54%, and Dunellen sandy loam has 4.92%. Figure 4.43 show that increasing levels of iron oxide are responsible for increasing adsorption, which agrees with the fact that iron oxide is the most important soil parameter involved in As(III) adsorption, even though the correlation coefficient is just 0.8041, the curve pattern is still very significant.

The percentage of arsenic desorbed after 3 desorption steps was calculated considering a dilution factor. For example, after all the desorption steps studied, 80.9% of the adsorbed As(III) was desorbed from Penn silt loam, 62.7% from Washington loam and 76.0% from Boonton Bergen County soil. 30.0% of the adsorbed As(V) was desorbed from Penn silt loam, 26.7% from Washington loam and 19.5% from Boonton Bergen County soil. Such results indicate that As(V) is more strongly retained in the soil matrix than is As(III).

As observed on Tables 4.7 and 4.8, the percentage of arsenic species desorbed reaches equilibrium shortly after the first desorption step, or 24 hours. The desorption increases by 2% at most from the first to the last desorption step. This is observed as plateaus, in Figures 4.34 to 4.42. Since desorption occurs mainly in the first desorption step and very little is desorbed in the next two desorption steps, it can be concluded that the arsenic left is tightly bound to the soil matrix.

In addition, As(V) desorption is dependent on organic matter content, following the pattern shown in Figure 4.44 (correlation coefficient = 0.889). Soils with high organic matter didn't show significant arsenic desorption. Such results suggest that besides chemical and electrostatic binding, arsenic could become entrapped in the soil organic matter, decreasing the desorption of arsenic(V).

Redox transformations during the desorption study, involving arsenic species, were determined using the colorimetric method. Untreated aliquots of samples were reacted with the mixed reagent and the results of arsenic speciation were collected. It was observed from this experiment that the arsenic form detected in solution after adsorption was As(III) when samples were initially spiked with As(III), and As(V) when samples were initially spiked with As(V). However, during desorption steps, As(III) is desorbed as As(V), suggesting that oxidation of As(III) occurs on the soil or during the adsorption/desorption process. In addition, As(V) is not reduced to As(III) during the desorption experiment.

As said before, when samples are initially spiked with As(III), redox reactions occur and they can be better understood by reporting arsenic speciation. For Penn silt loam, 93.9% of As(III) and 6.1% of As(V) are detected after the adsorption step, later during desorption more than 97.0% of the arsenic in solution is As(V). For Washington loam, 39.1% of As(III) and 60.9% of As(V) are detected after the adsorption step, later during desorption more than 94.0% of the arsenic in solution is As(V). For Boonton Bergen County soil, 95.4% of As(III) and 4.6% of As(V) are detected after the adsorption step, later during desorption more than 96.0% of the arsenic in solution is As(V).

The higher As(V) level observed after the adsorption equilibration time for Washington loam can be explained if the manganese oxide content is analyzed. This soil has twice the amount of MnO_2 as do the other soils. Manganese oxide in soils is a source of Mn, an essential plant nutrient, an adsorbent for heavy metals and also a natural oxidant of certain metals such as arsenic and chromium (Sparks, 1995). Not just manganese oxides, but also microbial activity, is known to oxidize As(III).

Arsenic(III) persists in aerated water, even at high pH, but is easily oxidized by manganese dioxide. Manganese dioxide has been shown to be a relative strong oxidant in the environment, controlling the mobility and toxicity of elements such as iron, cobalt, chromium, and arsenic as well as of natural and anthropogenic organics. Also, to a lesser extent, Fe oxides have the ability to directly oxidize metals or to catalyze metal oxidation by O_2 (Wolfgang et al., 1995).

These results are very significant since As(III) is a more toxic form of arsenic. Its release into solution as a less toxic form has many environmental implications.

Results also indicate that As(V) was not reduced during the desorption experiment. Such observation agrees with recent research on As(V) transformations in aqueous solution and in soils (McGeehan et al., 1992).

Based in adsorption data it was possible to develop models that can be used to predict adsorption as a function of soil parameters.

4.4 Sorption equations and mechanisms

A stepwise linear regression procedure was employed in order to develop equations to predict the arsenic adsorption capacity of soils. New Jersey soil parameters were used for the model. Among these parameters, the independent variables are: organic matter content (OM), iron oxide (Fe), manganese oxide (Mn), and aluminum oxide content (Al), cation exchange capacity (CEC), BET surface area, clay, silt, and sand content. Soil pH and pH_{zpc} were at first considered as independent variables but no correlation with soil As(III) and As(V) adsorption capacity were observed. Therefore these two variables were not included in the model. Values of the Langmuir adsorption capacity for each individual soil were used as the dependent variables.

The forward stepwise linear regression procedure picks up the independent variable that has the highest correlation coefficient with the dependent variable as the first regressor (Cody and Smith, 1991).

If the value of probability (P) is as small or smaller than the alpha level, it is said that the data are statistically significant at this level. In other words, if a independent variable has a P value larger than 0.5, it means that this variable won't be incorporated into the model.

In this study it was used the forward stepwise linear regression as the first regression procedure; which means that the best regressor was the first one to be included into the model, followed by the second one, and so on. A cut-off value of 0.5 was used for the forward stepwise linear regression procedure

The equation obtained, using the forward procedure, for arsenic(III) species is shown below. "b" is the adsorption capacity. The R-square for this model is 0.8950.

b= -1.62 +1.59 [Organic matter] -0.63 [CEC] +2.71 [Fe oxide] +0.94 [Al oxide] -52.96 [Mn oxide] -0.98 [BET] -0.04 [Clay]

The equation for As(V) species is:

b= -2110.04 +3.50 [CEC] +3.37 [Fe oxide] -2.20 [BET] +22.51 [silt] +18.47 [Clay] +21.28 [sand]

And the R-square for this model is 0.7806.

From the data obtained from this linear regression procedure, shown in Table 4.9, some conclusions can be reached. For example, parameters are added in the model follow an order of importance. The parameters which bear a high standardized estimate value were added as the first regressors. The greater this estimate, the more important the variable to the model.

Therefore for As(III) adsorption, iron oxide content is the most important soil parameter, followed by organic matter content, aluminum oxide, clay, CEC, BET and manganese oxide.

These results agree with the available literature. For example, Sakata (1987) related adsorption of arsenic(III) to soil properties. He observed that the distribution coefficient for this arsenic species was highly correlated with the dithionite-extractable iron oxide content in the soils ($r = 0.90$). The same behavior for arsenic(III) species was observed, even though Sakata was using the amorphous iron oxide content, and in this thesis research we used the total iron oxide extracted by perchloric and nitric acids (Table 3.6).

The equation for As(III) soil adsorption capacity given above shows that the parameter estimate for manganese oxide is relatively high and negative (-52.96). We cannot offer a good explanation for that. The standardized estimate shows that this is the least relevant parameter added to the model, but its contribution to the equation is large. This parameter was included because its significance level was greater than the 0.5 cut-off value. As discussed before, manganese oxide is not just involved in the adsorption process but also in redox transformations of arsenic.

For As(V) adsorption, the sand, silt, and clay fractions are the most important factors involved in the adsorption process. Because As(V) adsorption occurs via electrostatic mechanisms, these results are very important.

It is known that some anions, like arsenic species in solution, show different affinities for surface sites. This is termed specific adsorption and can happen even when the adsorbent surface is uncharged (Pierce and Moore, 1982). Anion adsorption by clay minerals is usually less than cation adsorption, and some researchers believe that the anion adsorption sites on clay particles are related to exposed octahedral cations on broken clay particle edges (Frost and Griffin, 1977).

Broken edges is considered the main factor to cause charge in some minerals like kaolinite; 100% of the charge on kaolinite, pyrophillites and talc comes from broken edges. The number of broken bonds and hence the exchange capacity would increase as the particle size decreases (Grim, 1953). In addition, clay particles (< 0.002 mm particle diameter) are smaller than silt (0.05-0.002 mm), which is in turn smaller than sand particles (2-0.05 mm). This order doesn't necessarily relate to the adsorption capacity properties of soil particles as can be noticed from experimental results.

Chunguo and Zihui (1988), reported that clay particles present in river sediments are related to high levels of arsenic adsorbed. They determined that the predominant clay mineral in the sediments studied was illite. The edge of this mineral possesses positive charges which are responsible for adsorption of arsenate ions with negative charges.

Other relevant factors for As(V) adsorption are CEC, iron content, and BET, in order of importance.

The CEC is largely related to clay mineral content and organic matter content (Bohn et al., 1985). Therefore, a correlation is observed since clay minerals fractions are the most important parameter in As(V) adsorption, followed by soil CEC.

Yin et al. (1996) also observed that the adsorption of mercury in soils from New Jersey was affected by soil particle size distribution. They observed that for a low organic matter content soil, the adsorption of mercury over the pH range studied was relatively large due to the silt and clay content.

A backward stepwise linear regression procedure was used to confirm the modeling of arsenic(III) and arsenic(V) adsorption. The results are shown in Table 4.10. This procedure enters all the independent variables and keeps removing variables that are not significant for inclusion into the model. All variables left in the model are significant at the 0.1 level, while for the forward procedure the cut-off value was 0.5. For soil As(V) adsorption capacity, iron oxide content and BET were removed from the model due to their high probability values, 0.249 and 0.187, respectively. For soil As(III) adsorption capacity, the variable clay was removed due to its high probability value of 0.730. Even with the removal of these variables, the parameter estimate for each independent variable wasn't altered in a significantly way.

The equation obtained, using the backward procedure, for arsenic(III) species is shown below. "b", as said before is the adsorption capacity. The R-square for this model is 0.8931.

b= -1.75 +1.63 [Organic matter] -0.72 [CEC] +2.77 [Fe oxide] +0.91 [Al oxide] -52.94 [Mn oxide] -1.04 [BET]

The equation for As(V) species is:

b= -2068.79 +4.23 [CEC] +22.02 [silt] +17.85 [Clay] +20.88 [sand]

The R-square for this model is 0.7074. These equations are indicative o agreement between the stepwise linear regression procedures.

Figures 4.45 and 4.46 show the predicted versus the measured value fo soil adsorption capacity of As(III) and As(V). Both models obtained using the forward and backward stepwise linear regression procedure were used. For As(III), the agreement between both models was good, and both correlation coefficients are greater than 0.94. For As(V), the correlations are satisfactory, around 0.88. Also note that the regression lines for As(III) are closer to the line of equality than are those for As(V). However, when both figures are compared, it can be seen that the As(III) and As(V) adsorption models don't deviate too much from the line of equality, which means that the models can be used satisfactorily in order to predict adsorption in soils.

Table 4.11 shows regression models for soil As(III) and As(V) adsorption capacity. The R-square option gives the multiple r-square value for every one, two, three, ... n way combinations of the independent variables (Cody and Smith, 1991). The reported value of r-square was indicative of the best set of independent variables.

The model doesn't consider microorganisms that could play a role in the adsorption and desorption process of arsenic, and also interactions among the individual soil components.

The mechanism for arsenic adsorption wasn't determined or studied during this thesis project, however, hysteresis observed on adsorption isotherms suggest that the process might be inner-sphere. X-ray data for arsenic adsorption would make possible the inference of an adsorption mechanism.

For example, x-ray absorption fine structure spectroscopy data show that selenate is adsorbed as an outer-sphere complex on pure goethite (Hayes et al., 1987).

This was determined by the use of spectroscopic approaches, which is a tool determine the mechanism of adsorption (Sparks, 1995).

Ferguson and Anderson (1974) mentioned that the arsenic adsorptio mechanism on amorphous iron and aluminum hydroxide couldn't be explained in ter of molecule-surface interaction, electrostatic interaction or occlusion.

The mechanism of specific As(V) adsorption on oxides like iron aluminum is considered to be ligand exchange with surface hydroxyls or surface aqu groups (Goldberg, 1986). And according to some researchers, since the main As(II species in solution being adsorbed is a neutral species, hydrogen bonding could als present a major mechanism for adsorption.

Table 4.1 Recovery test for As(V)

Equilibrium pH	Arsenic Added (mg/L)	As(V) Recovered (mg/L)	As(V) Recovered (%)
	Lakewood sand		
3.28	4.24	4.09	96.4
4.74	4.24	4.07	96.0
9.81	4.24	4.09	96.4
	Hazen loam		
4.14	4.24	4.08	96.2
5.90	4.24	3.88	91.5
9.62	4.24	3.89	91.7
	Boonton Union soil		
3.67	4.24	3.97	93.6
4.58	4.24	4.04	95.2
7.31	4.24	4.00	94.3

Table 4.2 Recovery test for As(III) on Boonton Union County soil extract at natural pH

Sample No.	Arsenic(III) Added (mg/L)	As(III) Recovered (mg/L)	As(III) Recovered (%)
1	3.45	3.48	100.8
2	3.45	3.58	103.6
3	3.45	3.43	99.3
4	3.45	3.46	100.1
5	3.45	3.43	99.2
6	3.45	3.49	101.1
Average			100.7

Table 4.3 Langmuir isotherm parameters for As(III) adsorption

Soil Name	k (L/mg)	b (mg/g)	R	Chisq
Birdsboro silt loam	0.234	0.396	0.9966	0.0003
Boonton Bergen County	0.007	8.901	0.9999	0.5216
Boonton Union County	1.386	0.770	0.9825	0.0082
Downer loamy sand	0.026	1.563	0.9949	0.1503
Dunellen sandy loam	0.004	8.697	0.9999	0.2786
Fill materials from Delaware River	0.147	0.739	0.9870	0.0016
Freehold sandy loam (subsurface)	0.131	0.801	0.9977	0.0004
Freehold sandy loam (surface)	0.197	0.589	0.9956	0.0693
Hazen gravelly loam	0.212	0.472	0.9889	0.1481
Lakewood sand	1.396	0.229	0.9800	0.1504
Penn silt loam	0.014	4.407	0.9999	0.4581
Rockaway stony loam	0.018	4.401	0.9996	1.3710
Sassafras sandy loam	0.171	0.450	0.9647	0.0022
Washington loam	0.397	0.447	0.9778	0.0025
Whippany silty clay loam	0.077	1.099	0.9970	0.0003

Table 4.4 Langmuir isotherm parameters for As(V) adsorption

Soil Name	k (L/mg)	b (mg/g)	R	Chisq
Birdsboro silt loam	0.016	18.92	0.9999	0.6705
Boonton Bergen County	0.016	21.43	0.9999	0.1540
Boonton Union County	0.012	27.96	0.9979	0.0949
Downer loamy sand	0.022	13.57	0.9999	0.4196
Dunellen sandy loam	0.005	42.40	0.9995	0.2208
Fill materials from Delaware River	0.030	15.25	0.9969	0.2082
Freehold sandy loam (subsurface)	0.031	17.40	0.9925	0.5669
Freehold sandy loam (surface)	0.454	0.95	0.9921	0.1557
Hazen gravelly loam	0.008	32.54	0.9999	0.2497
Lakewood sand	0.529	0.74	0.9952	0.0910
Penn silt loam	0.047	8.64	0.9991	0.0482
Rockaway stony loam	0.019	18.27	0.9961	0.2080
Sassafras sandy loam	0.012	24.62	0.9998	1.2170
Washington loam	0.019	17.30	0.9999	0.5014
Whippany silty clay loam	0.058	7.58	0.9999	0.0323

Table 4.5 Freundlich isotherm parameters for As(III) adsorption

Soil Name	- Log K_d (mg/g)	1/n (L/g)	R
Birdsboro silt loam	1.146	0.736	0.9914
Boonton Bergen County	1.171	0.876	0.9939
Boonton Union County	0.382	0.540	0.9915
Downer loamy sand	1.392	0.973	0.9795
Dunellen sandy loam	1.392	0.927	0.9934
Fill materials from Del. River	1.058	0.845	0.9803
Freehold sandy loam subsurface	1.048	0.832	0.9905
Freehold sandy loam surface	1.030	0.764	0.9916
Hazen gravelly loam	1.091	0.728	0.9824
Lakewood sand	0.920	0.405	0.8808
Penn silt loam	1.169	0.809	0.9921
Rockaway stony loam	0.968	0.732	0.9412
Sassafras sandy loam	1.196	0.768	0.9542
Washington loam	0.953	0.721	0.9768
Whippany silty clay loam	1.101	0.857	0.9924

Table 4.6 Freundlich isotherm parameters for As(V) adsorption

Soil Name	- Log K_d (mg/g)	1/n (L/g)	R
Birdsboro silt loam	0.487	0.840	0.9973
Boonton Bergen County	0.456	0.871	0.9953
Boonton Union County	0.302	0.776	0.9971
Downer loamy sand	0.538	0.827	0.9981
Dunellen sandy loam	0.547	0.870	0.9919
Fill materials from Del. River	0.389	0.879	0.9916
Freehold sandy loam subsurface	0.246	0.745	0.9801
Freehold sandy loam surface	0.545	0.755	0.9893
Hazen gravelly loam	0.612	0.928	0.9966
Lakewood sand	0.621	0.720	0.9971
Penn silt loam	0.376	0.747	0.9948
Rockaway stony loam	0.180	0.610	0.9882
Sassafras sandy loam	0.484	0.862	0.9961
Washington loam	0.486	0.868	0.9920
Whippany silty clay loam	0.446	0.810	0.9962

Table 4.7 Desorption experiment; C_0 As(III): 5 mg/L

Soil Name	Total As (mg/L)	As(III) (%)	As(V) (%)	Total As (%) Desorbed
Penn silt loam				
Step #1 *	3.9898	93.94	6.06	
Step #2	0.9952	0.27	99.73	79.75
Step #3	0.2873	2.79	97.21	80.52
Step #4	0.0923	2.89	97.11	80.93
Washington Loam				
Step #1 *	2.9747	39.06	60.94	
Step #2	0.8109	2.31	97.69	60.84
Step #3	0.2579	5.18	94.82	61.94
Step #4	0.1003	2.66	97.34	62.66
Booton Union County soil				
Step #1 *	3.6506	95.42	4.58	
Step #2	1.0139	0.26	99.74	75.04
Step #3	0.2526	3.17	96.83	75.02
Step #4	0.1110	2.41	97.59	75.98
Freehold sandy loam (subsurf.)				
Step #1 *	3.6052	96.18	3.82	
Step #2	0.8029	0.33	99.67	70.14
Step #3	0.2900	2.77	97.24	71.92
Step #4	0.0683	3.91	96.09	71.84
Dunellen Sandy loam				
Step #1 *	3.2793	92.30	7.70	
Step #2	0.9765	3.01	97.00	68.72
Step #3	0.2473	1.08	98.92	68.78
Step #4	0.0469	5.70	94.30	68.48

* Step #1 is the adsorption step.

Table 4.8 Desorption experiment; C_0 As(V): 5 mg/L

Soil Name	Total As (mg/L)	As(III) (%)	As(V) (%)	Total As (%) Desorbed
Penn silt loam				
Step #1 *	1.2704	9.46	90.54	
Step #2	0.4209	0.63	99.37	27.47
Step #3	0.1698	3.14	96.85	28.76
Step #4	0.1030	2.59	97.41	29.98
Washington Loam				
Step #1 *	1.0406	5.39	94.61	
Step #2	0.4155	0.64	99.36	23.92
Step #3	0.2045	3.92	96.08	25.93
Step #4	0.0870	6.14	93.86	26.65
Booton Union County soil				
Step #1 *	0.6907	1.16	98.84	
Step #2	0.3060	0.87	99.13	16.48
Step #3	0.1511	3.54	96.46	17.97
Step #4	0.1164	2.30	97.70	19.54
Freehold sandy loam (subsurf.)				
Step #1 *	1.1662	0.46	99.54	
Step #2	0.4636	1.73	98.27	26.77
3Step #3	0.2152	1.24	98.76	28.75
Step #4	0.0870	3.07	96.93	29.42
Dunellen Sandy loam				
Step #1 *	1.5482	2.42	97.58	
Step #2	0.5224	3.58	96.42	33.67
Step #3	0.1911	6.99	93.01	34.88
Step #4	0.0603	4.43	95.57	35.13

* Step #1 is the adsorption step.

Table 4.9 Forward stepwise linear regression data for soil arsenic adsorption capacity

Dependent variable	Independent variable	Standardized estimate	Probability (P)	Standard Error	R-square *
b, As(III)	Organic matter	1.20	0.002	0.33	0.7393
b, As(III)	CEC	-0.60	0.069	0.30	0.8950
b, As(III)	Iron oxide	1.38	0.002	0.55	0.1313
b, As(III)	Aluminum oxide	0.57	0.023	0.32	0.4432
b, As(III)	Manganese oxide	-1.09	0.002	11.28	0.5222
b, As(III)	BET	-1.01	0.017	0.31	0.8259
b, As(III)	Clay	-0.12	0.730	0.11	0.3363
b, As(V)	CEC	0.87	0.037	1.40	0.5026
b, As(V)	Iron oxide	0.45	0.249	2.71	0.2626
b, As(V)	BET	-0.60	0.187	1.52	0.7806
b, As(V)	Silt	32.79	0.059	10.23	0.6000
b, As(V)	Clay	14.83	0.081	9.24	0.3801
b, As(V)	Sand	43.76	0.065	9.94	0.7234

* R-Square values refer to coefficients obtained when the previous important independent variables were included in the model. Order of importance for regressor is determined by high standardized estimate numbers.

Table 4.10 Backward stepwise linear regression data for soil arsenic adsorption capacity

Dependent variable	Independent variable	Standardized estimate	Probability (P)	Standard Error
b, As(III)	Organic matter	1.23	0.001	0.29
b, As(III)	CEC	-0.68	0.003	0.29
b, As(III)	Iron oxide	1.42	0.001	0.49
b, As(III)	Aluminum oxide	0.55	0.016	0.30
b, As(III)	Manganese oxide	-1.09	0.001	10.64
b, As(III)	BET	-1.07	0.003	0.25
b, As(V)	CEC	1.05	0.010	3.18
b, As(V)	Silt	32.08	0.064	2.08
b, As(V)	Clay	14.33	0.091	1.87
b, As(V)	Sand	42.94	0.069	2.04

Table 4.11 Regression models for soil As(III) and As(V) adsorption capacity

R Square	Variables in model for As(III) adsorption capacity
0.1313	Fe
0.3363	Fe, Clay
0.4432	Fe, Clay, Al
0.6351	OM, Fe, Mn, Clay
0.7679	OM, CEC, Fe, Mn, BET
0.8931	OM, CEC, Fe, Al, Mn, BET
0.8950	OM, CEC, Fe, Al, Mn, BET, Clay
0.8951	OM, CEC, Fe, Al, Mn, BET, Clay, Sand
0.8975	OM, CEC, Fe, Al, Mn, BET, Clay, Sand, Silt

R Square	Variables in model for As(V) adsorption capacity
0.2626	Fe
0.3801	Fe, Clay
0.6049	CEC, Silt, Sand
0.7074	CEC, Silt, Sand, Clay
0.7383	CEC, BET, Silt, Sand, Clay
0.7806	CEC, Fe, BET, Silt, Sand, Clay
0.7889	CEC, Fe, Al, BET, Silt, Sand, Clay
0.7924	OM, CEC, Fe, Al, BET, Silt, Sand, Clay
0.7925	OM, CEC, Fe, Al, Mn, BET, Silt, Sand, Clay

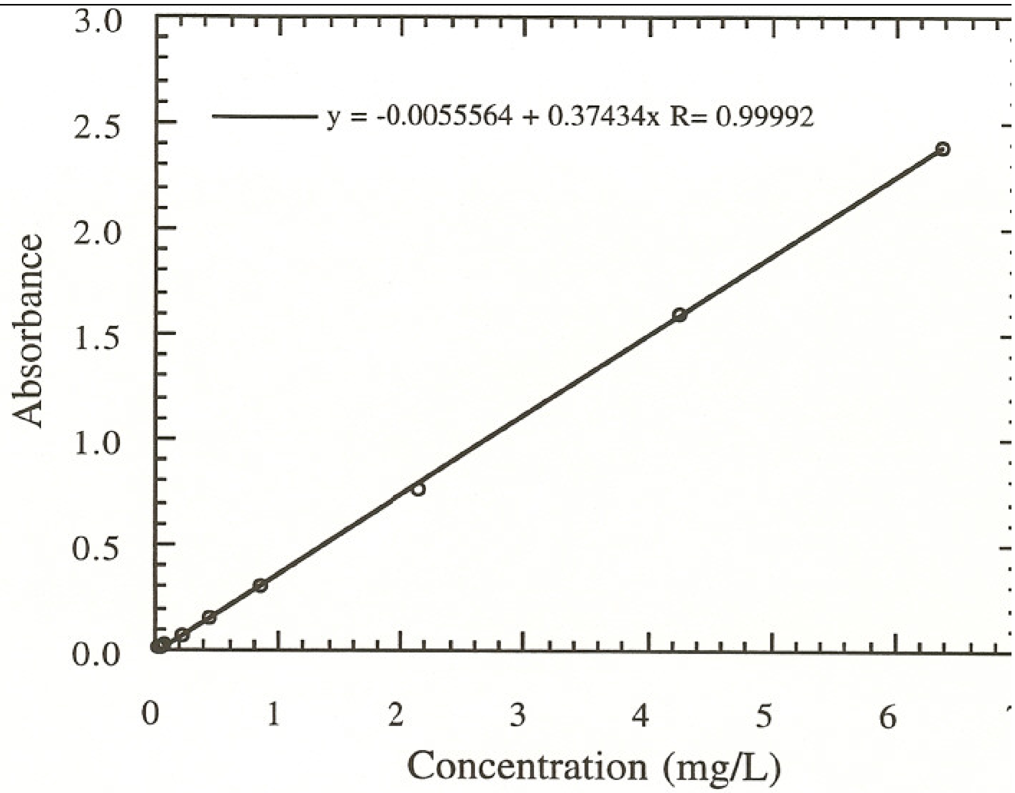

Figure 4.1 Calibration curve for As(III) by the heteropoly blue colorimetric procedure.

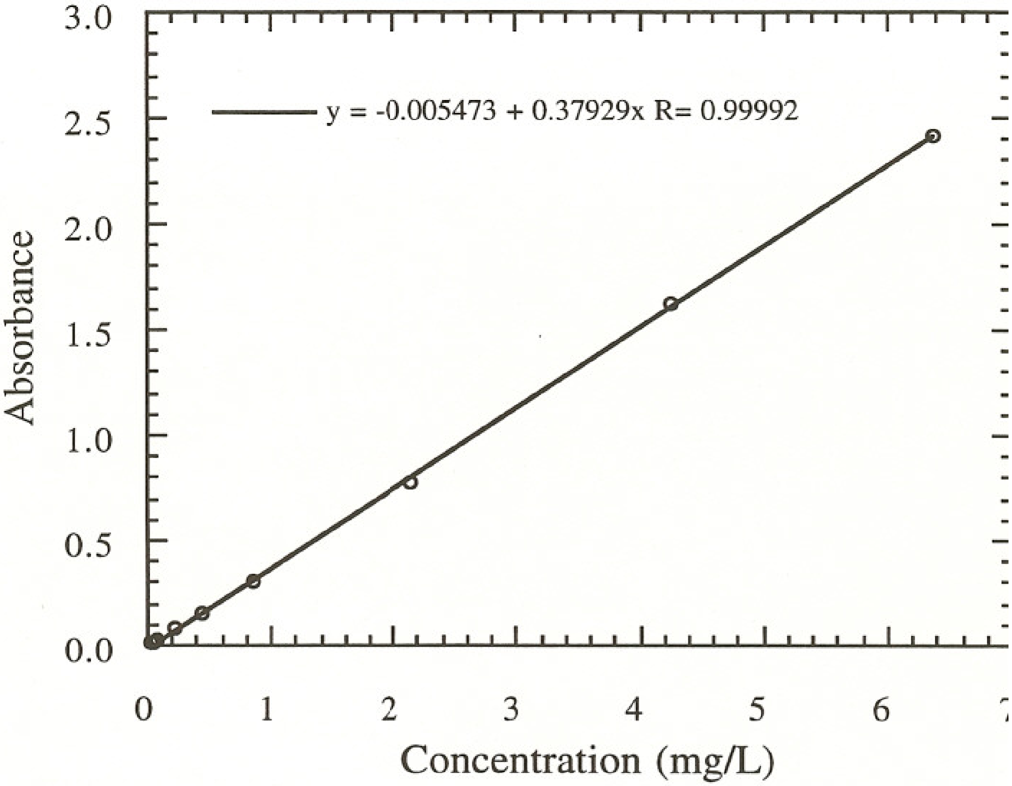

Figure 4.2 Calibration curve for As(V) by the heteropoly blue colorimetric procedure.

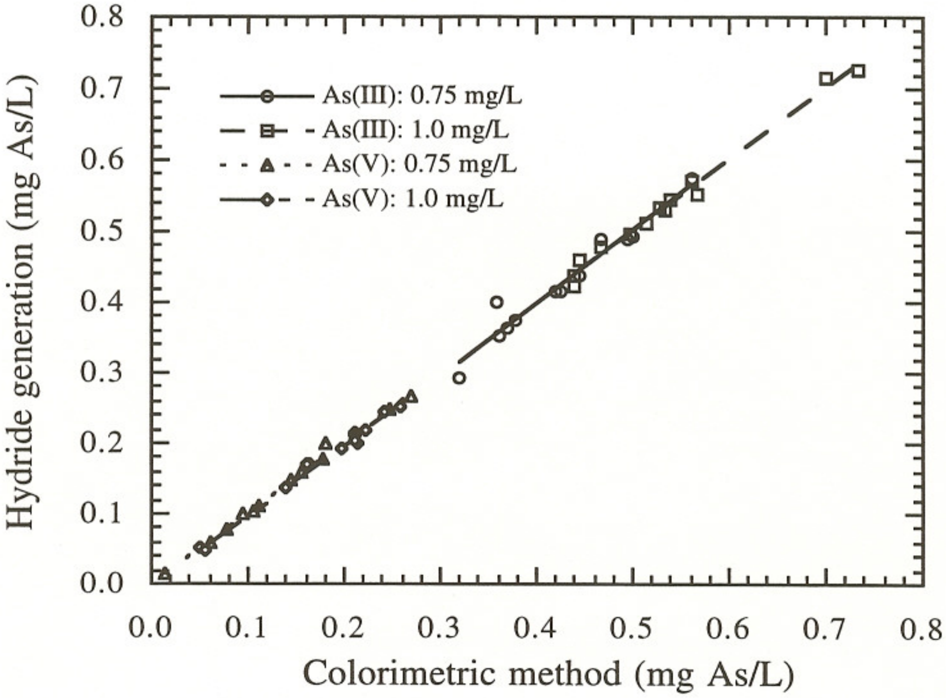

Figure 4.3 Arsenic analysis for hydride generation versus the colorimetric method.

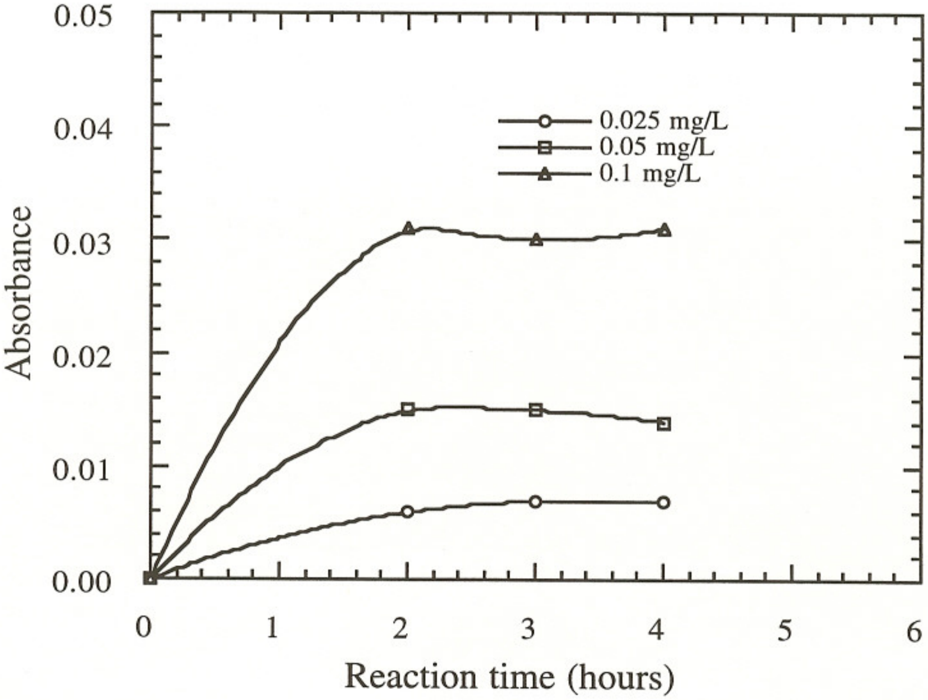

Figure 4.4 Absorbance of arseno-molybdate complex as a function of reaction time.

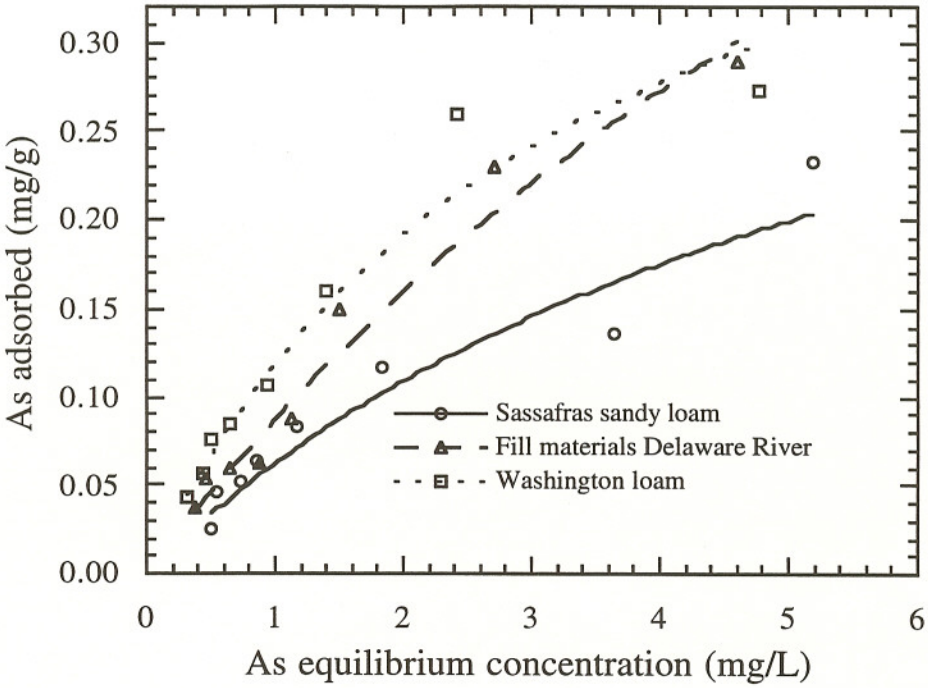

Figure 4.5 Langmuir isotherm of As(III) for Sassafras sandy loam, Fill materials from Delaware River, and Washington loam.

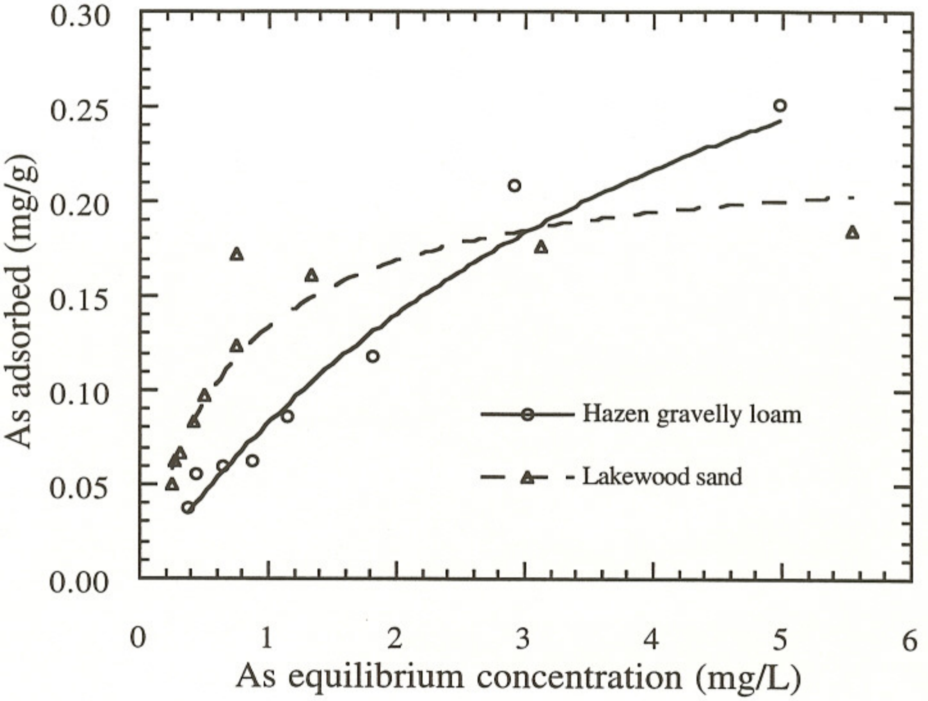

Figure 4.6 Langmuir isotherm of As(III) for Hazen gravelly loam and Lakewood sand.

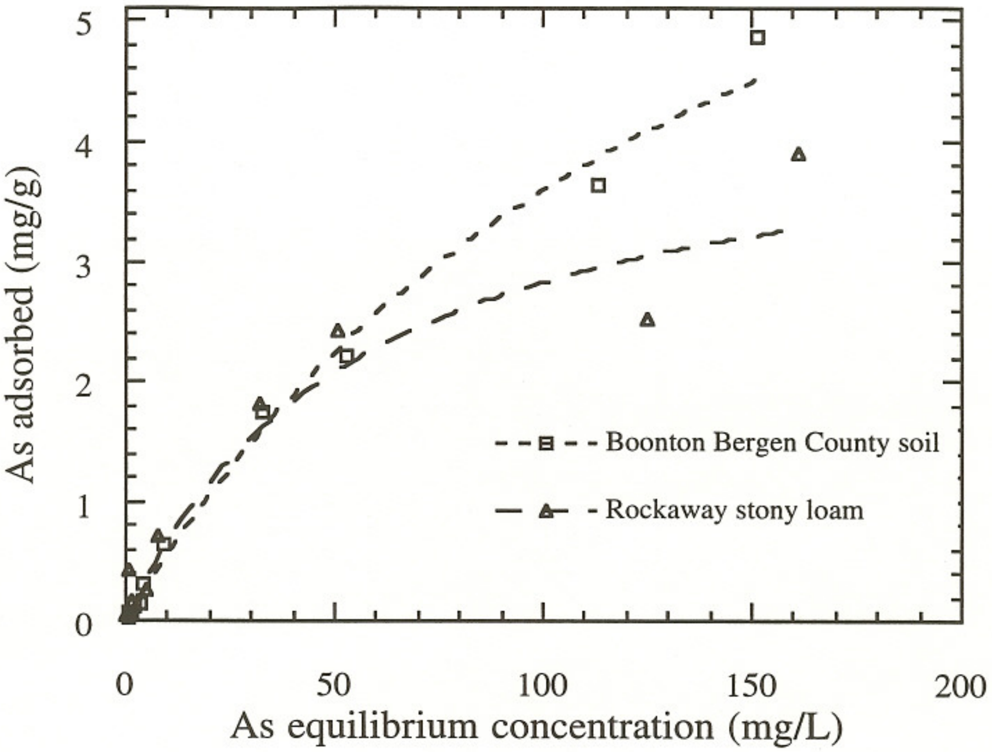

Figure 4.7 Langmuir isotherm of As(III) for Boonton Bergen County soil and Rockaway stony loam.

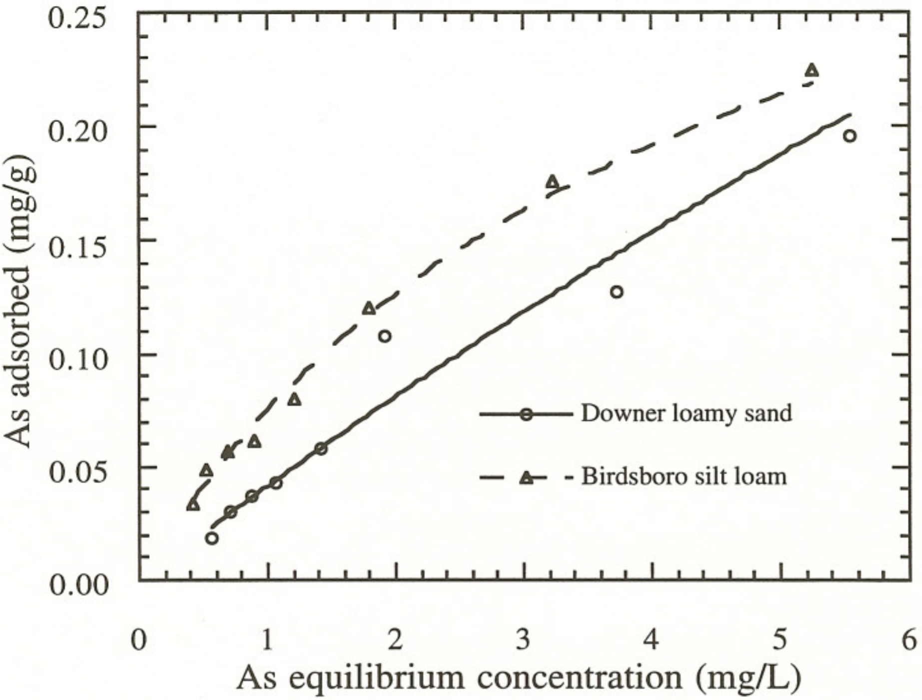

Figure 4.8 Langmuir isotherm of As(III) for Downer loamy sand and Birdsboro sil loam.

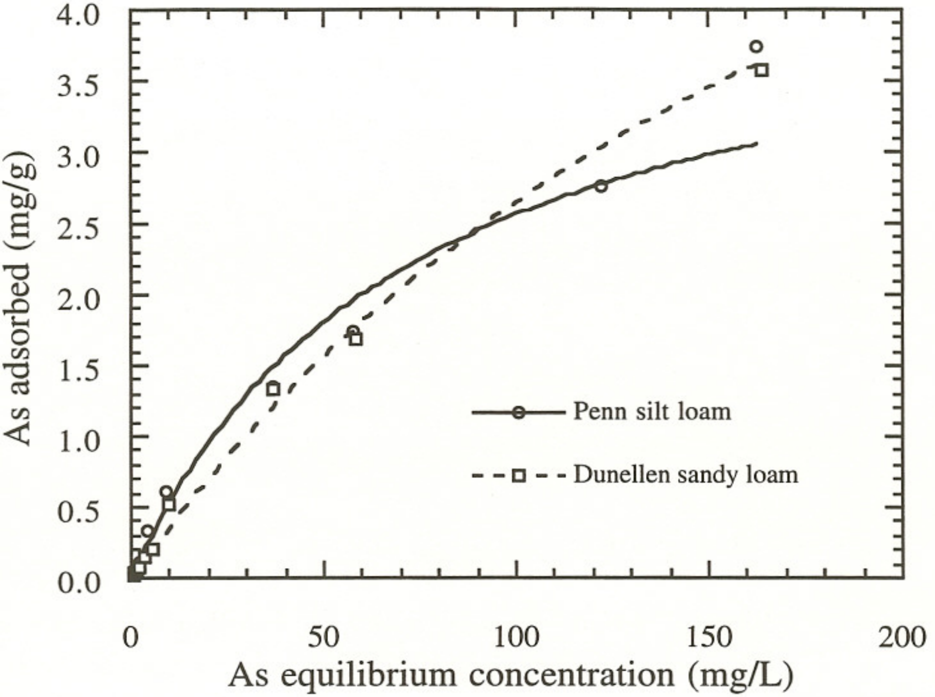

Figure 4.9 Langmuir isotherm of As(III) for Penn silt loam and Dunellen sand loam.

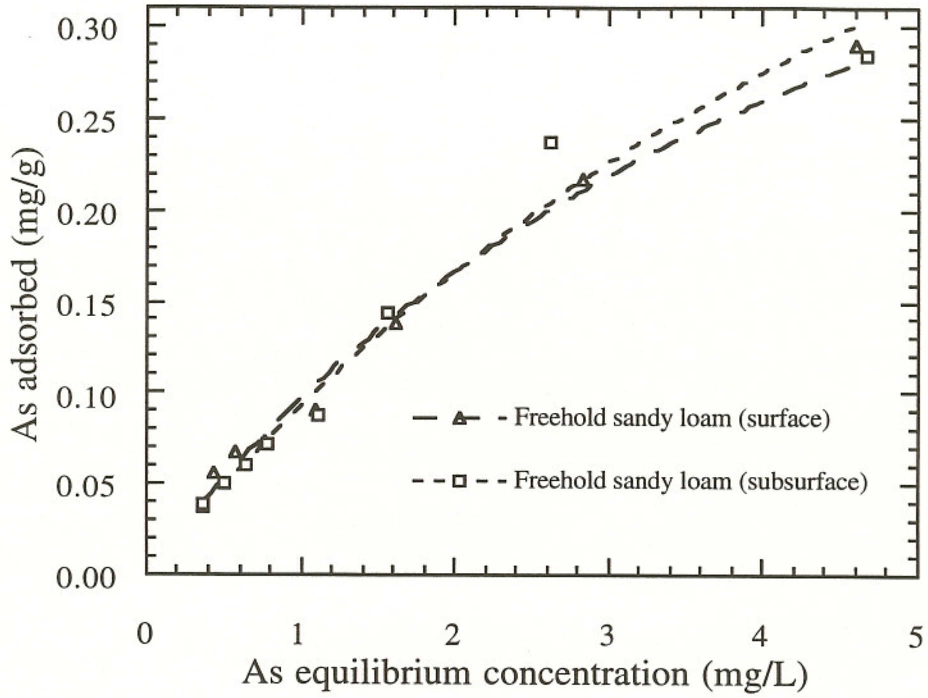

Figure 4.10 Langmuir isotherm of As(III) for Freehold sandy loam (surface) and Freehold sandy loam (subsurface).

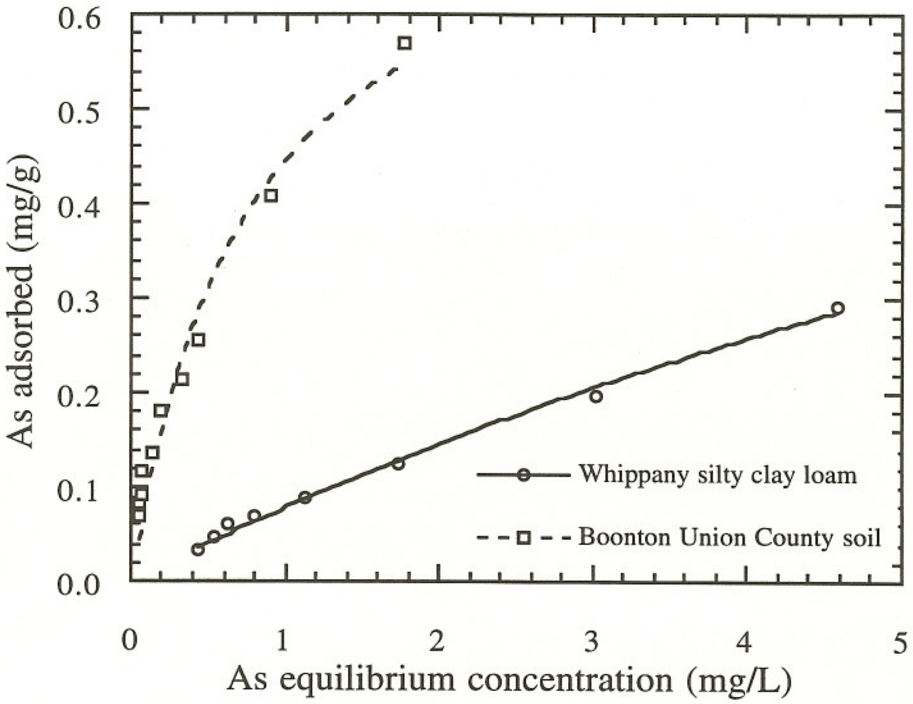

Figure 4.11 Langmuir isotherm of As(III) for Whippany silty clay loam and Boonton Union County soil.

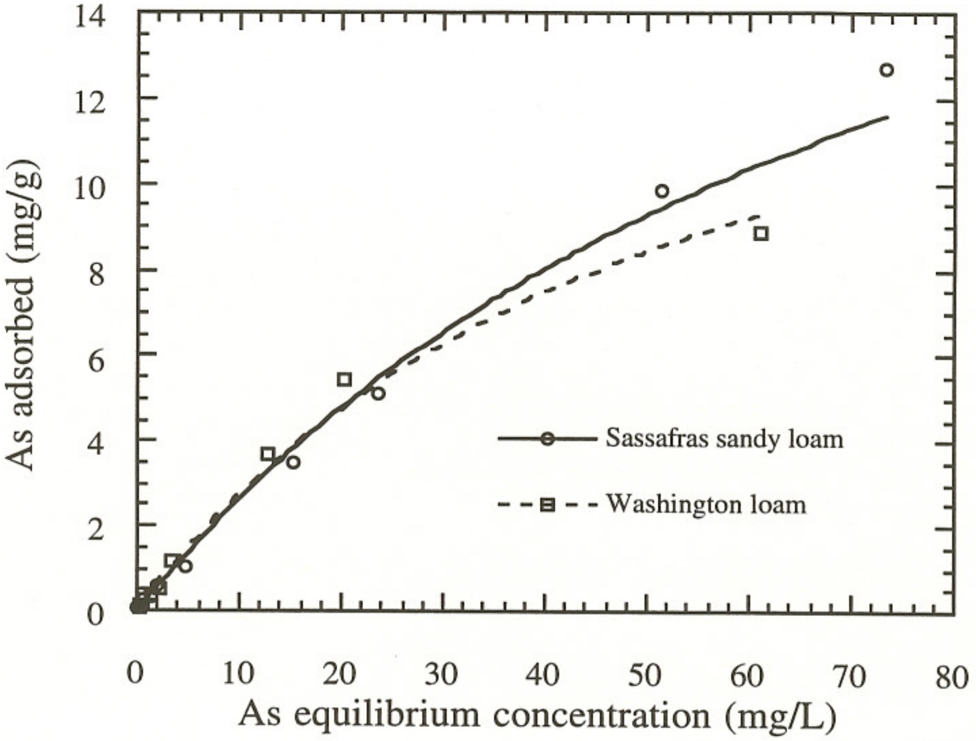

Figure 4.12 Langmuir isotherm of As(V) for Sassafras sandy loam and Washingto loam.

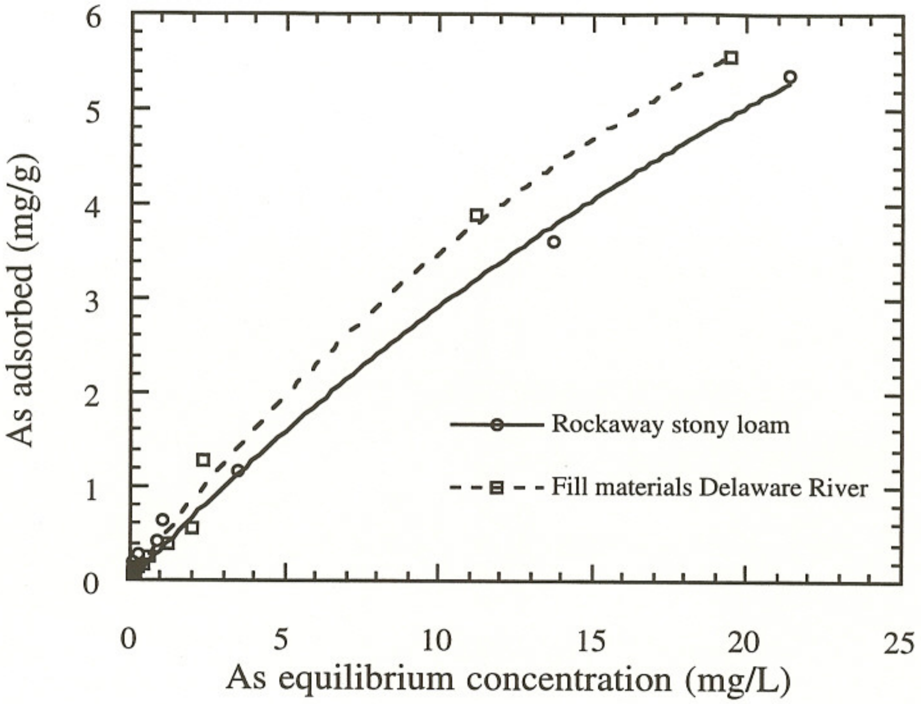

Figure 4.13 Langmuir isotherm of As(V) for Rockaway stony loam and Fill materials from Delaware River.

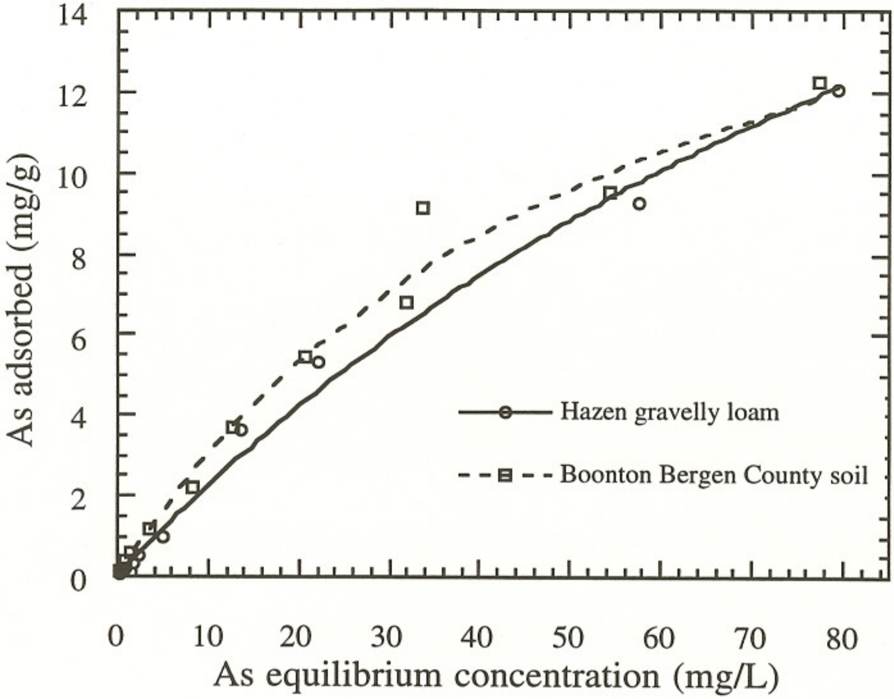

Figure 4.14 Langmuir isotherm of As(V) for Hazen gravelly loam and Boonton Bergen County soil.

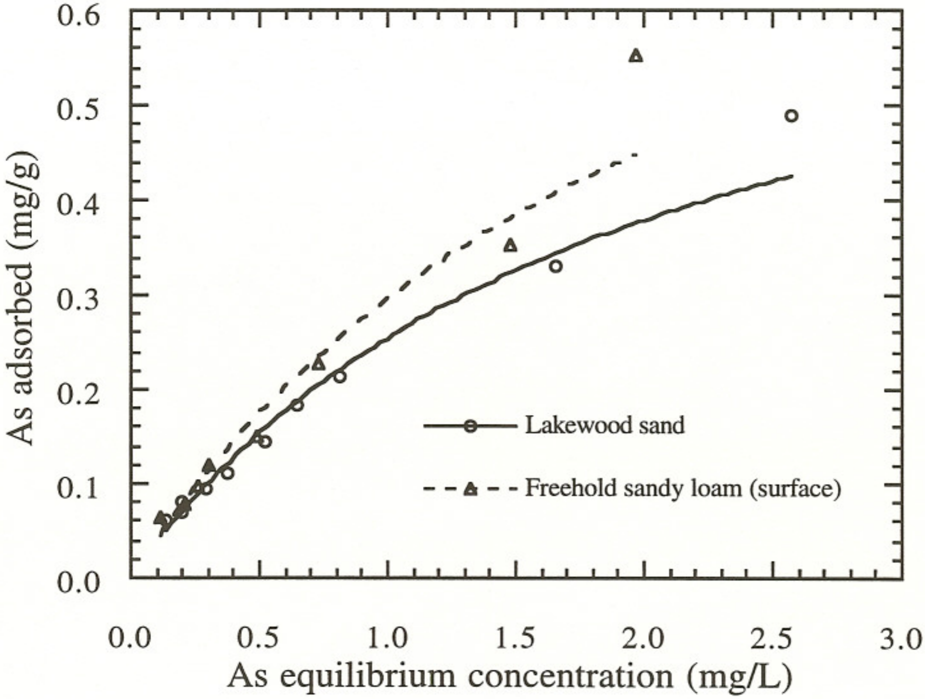

Figure 4.15 Langmuir isotherm of As(V) for Lakewood sand and Freehold sandy loam (surface).

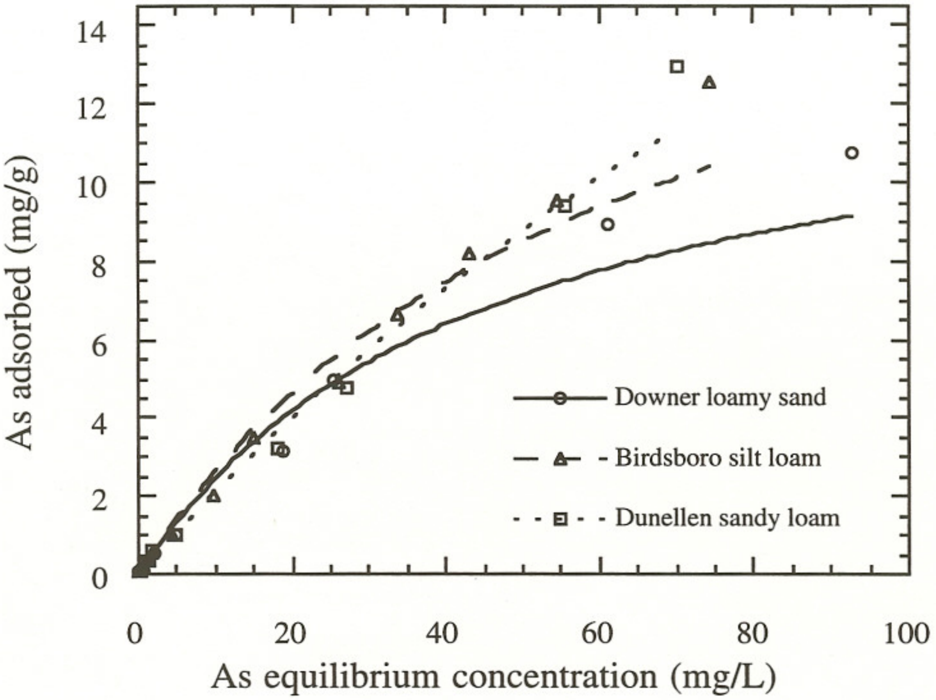

Figure 4.16 Langmuir isotherm of As(V) for Downer loamy sand, Birdsboro silt loam, and Dunellen sandy loam.

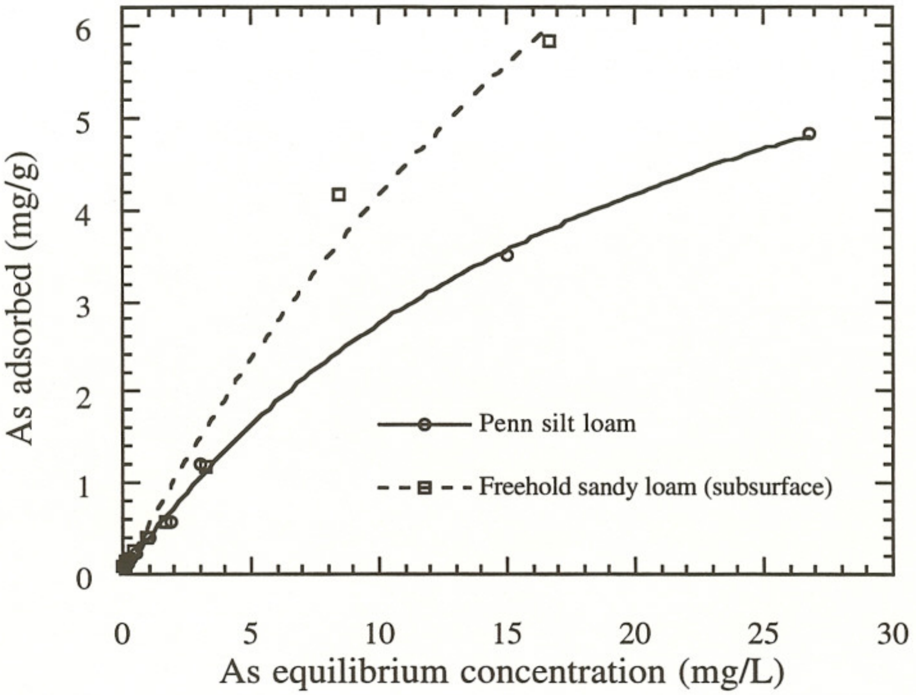

Figure 4.17 Langmuir isotherm of As(V) for Penn silt loam and Freehold sandy loam (subsurface).

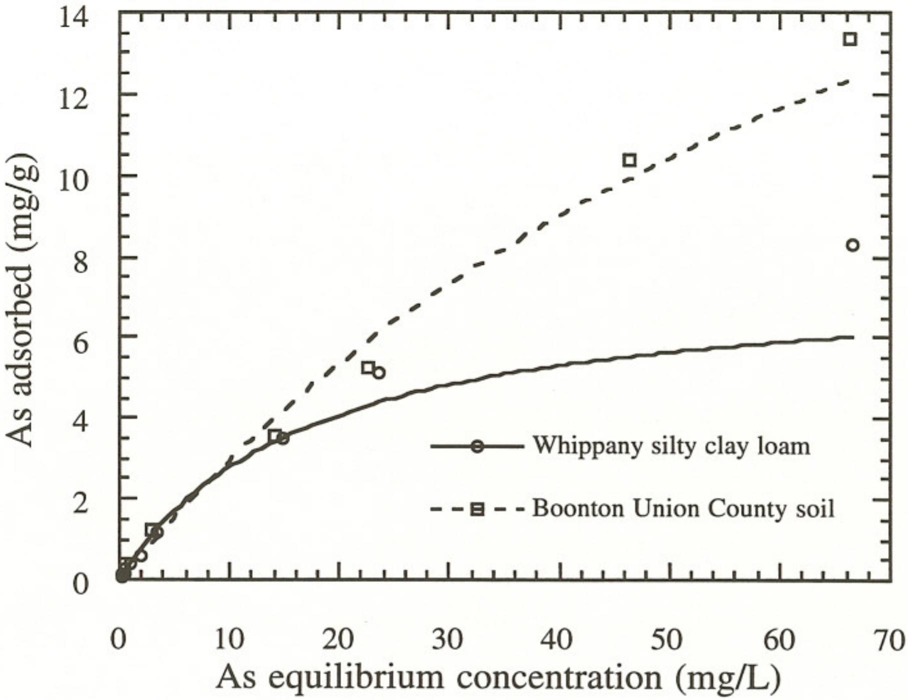

Figure 4.18 Langmuir isotherm of As(V) for Whippany silty clay loam and Boonton Union County soil.

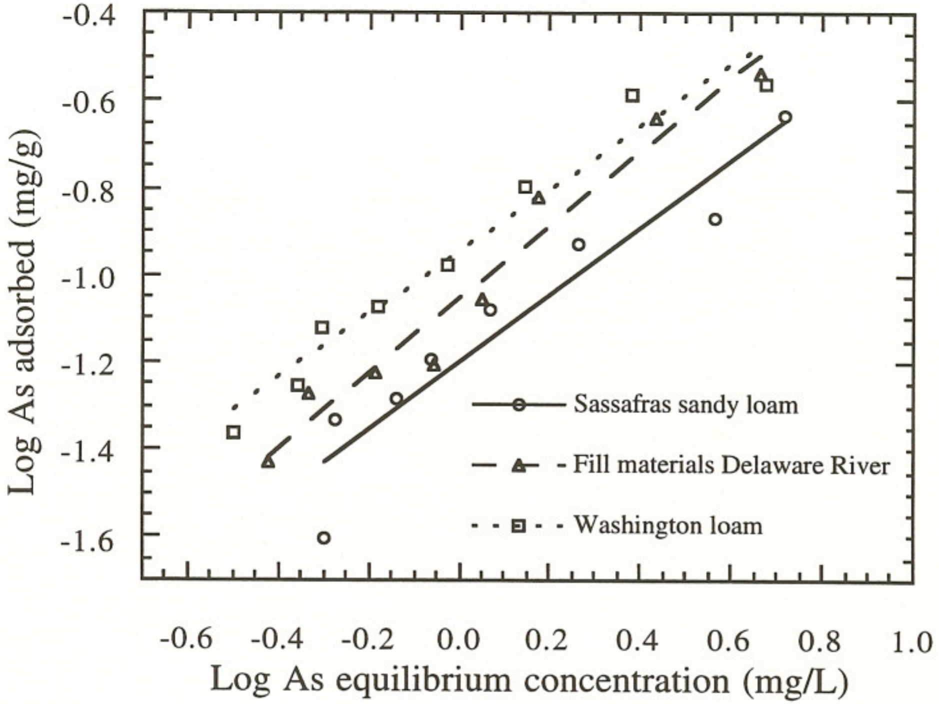

Figure 4.19 Freundlich isotherm of As(III) for Sassafras sandy loam, Fill materials from Delaware River, and Washington loam.

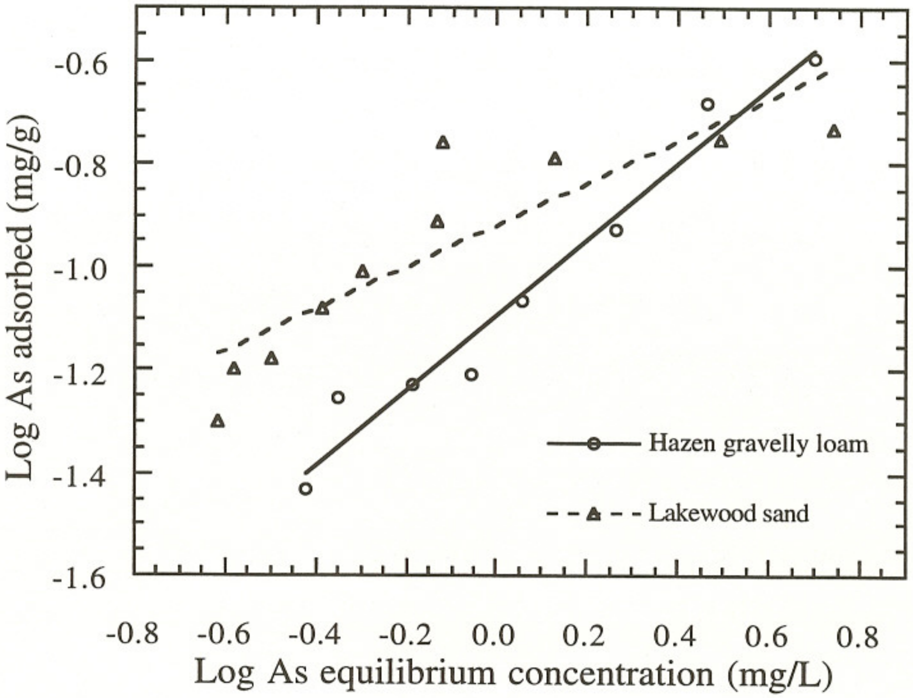

Figure 4.20 Freundlich isotherm of As(III) for Hazen gravelly loam and Lakewood sand.

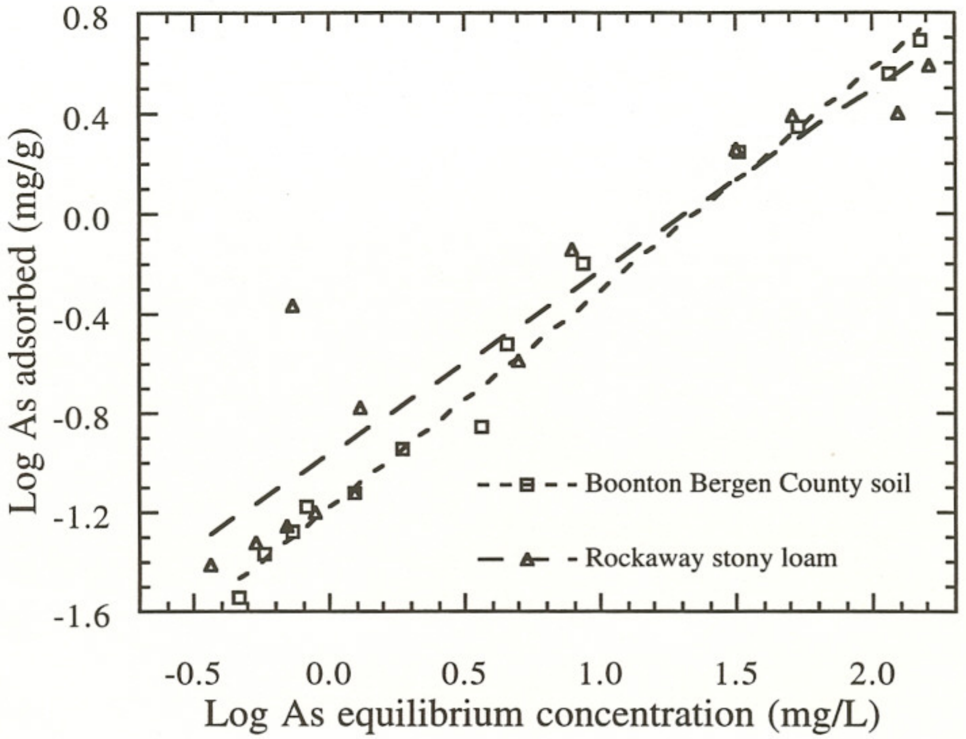

Figure 4.21 Freundlich isotherm of As(III) for Boonton Bergen County soil an Rockaway stony loam.

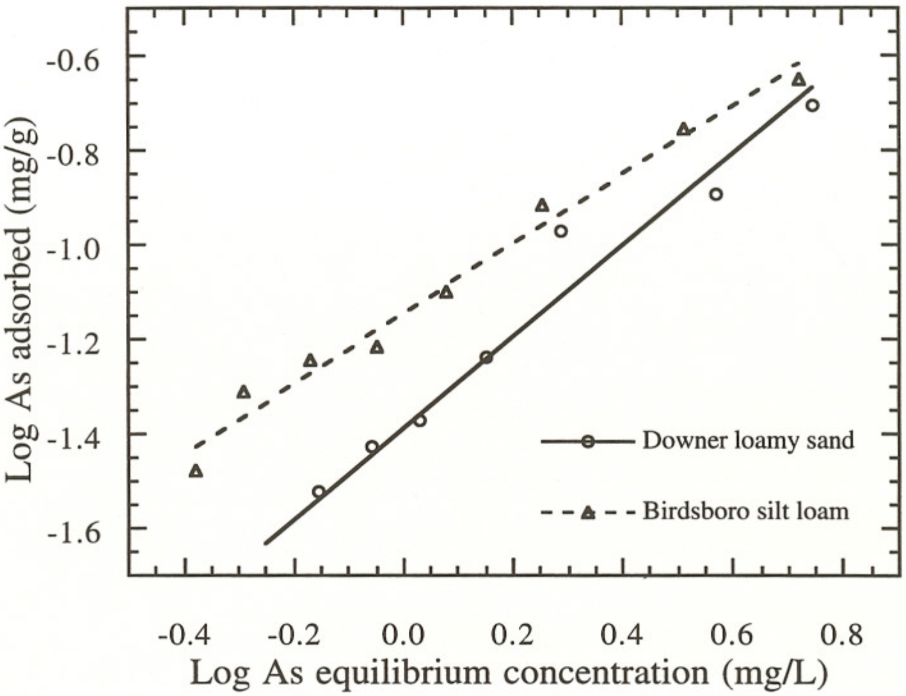

Figure 4.22 Freundlich isotherm of As(III) for Downer loamy sand and Birdsboro silt loam.

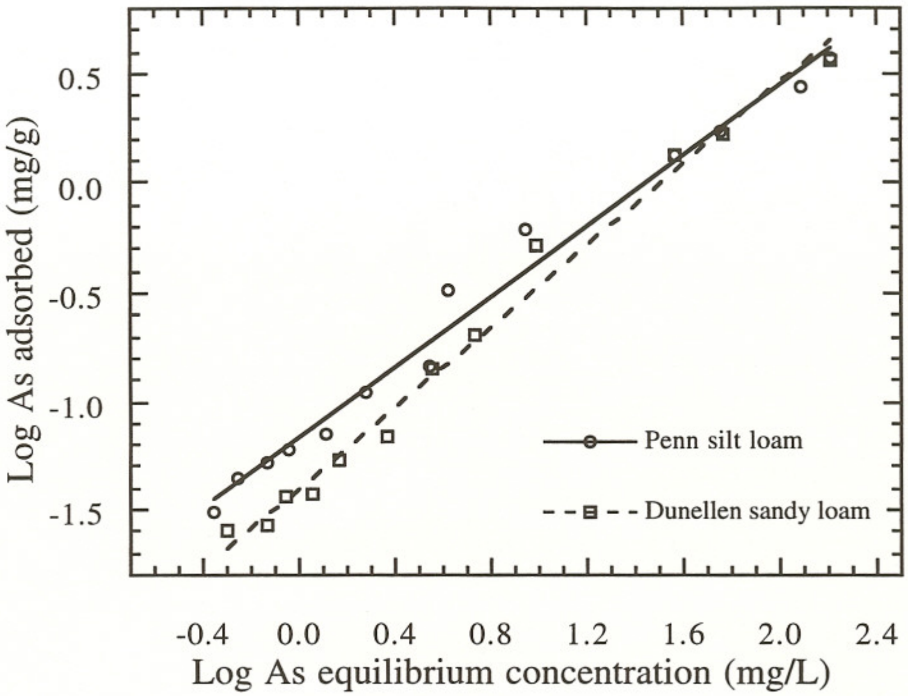

Figure 4.23 Freundlich isotherm of As(III) for Penn silt loam and Dunellen sandy loam.

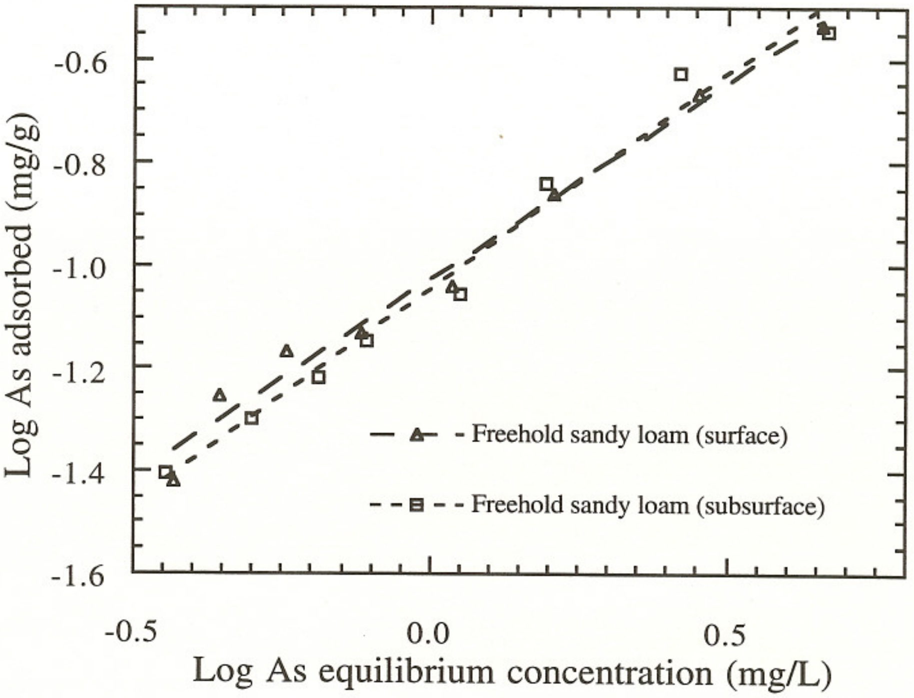

Figure 4.24 Freundlich isotherm of As(III) for Freehold sandy loam (surface) and Freehold sandy loam (subsurface).

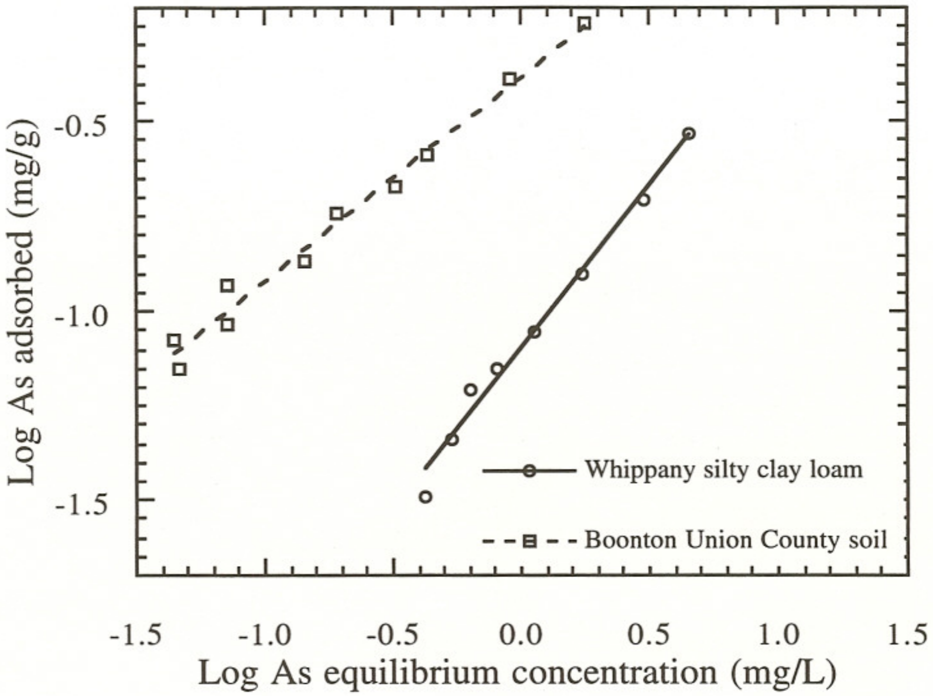

Figure 4.25 Freundlich isotherm of As(III) for Whippany silty clay loam and Boonton Union County soil.

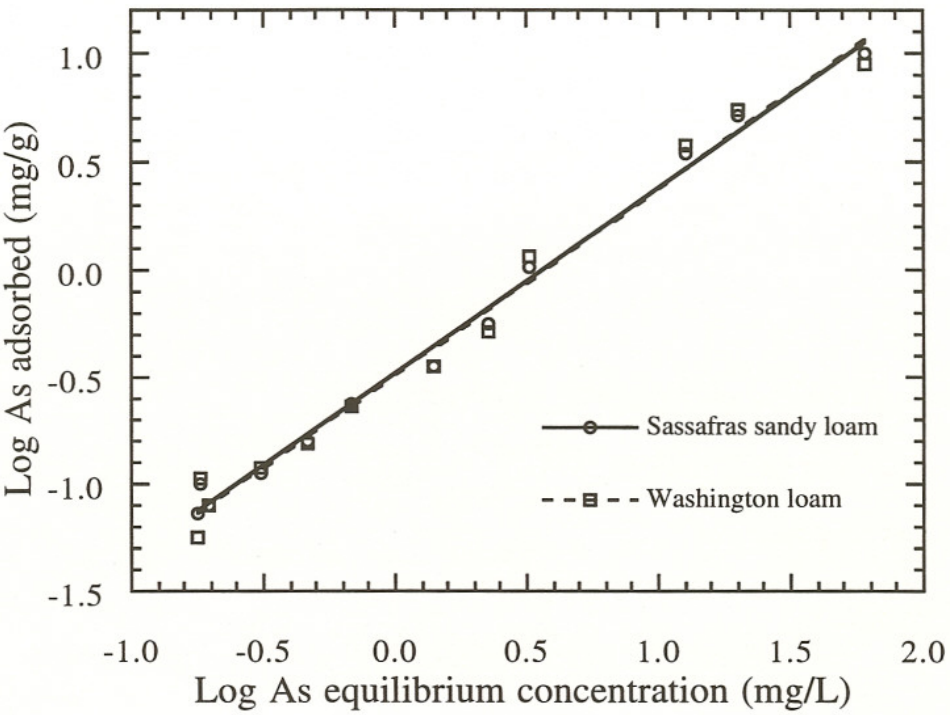

Figure 4.26 Freundlich isotherm of As(V) for Sassafras sandy loam and Washington loam.

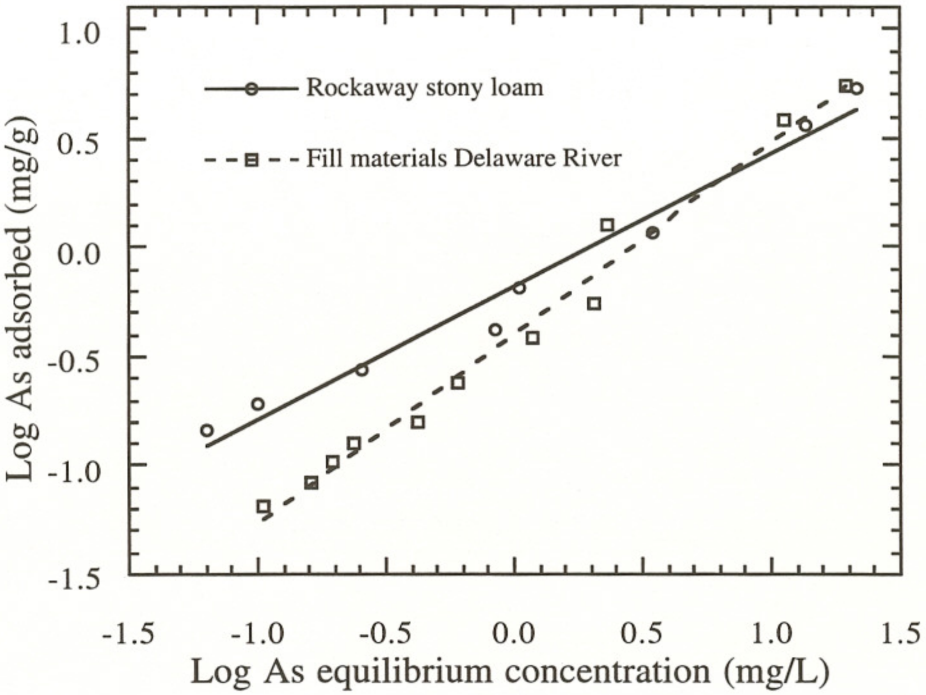

Figure 4.27 Freundlich isotherm of As(V) for Rockaway stony loam and Fill materials from Delaware River.

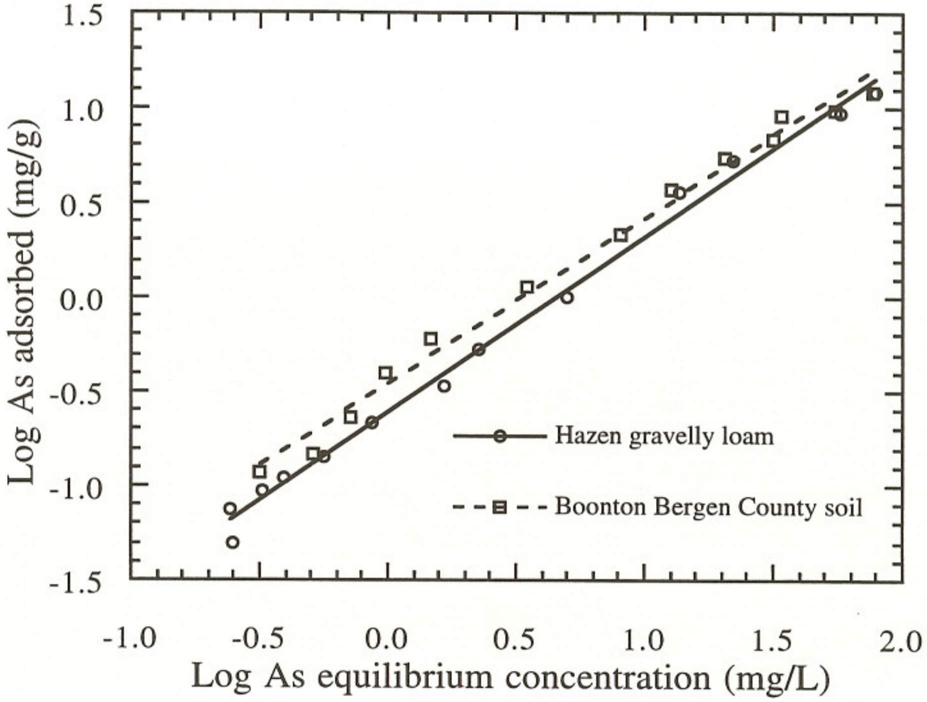

Figure 4.28 Freundlich isotherm of As(V) for Hazen gravelly loam and Boonton Bergen County soil.

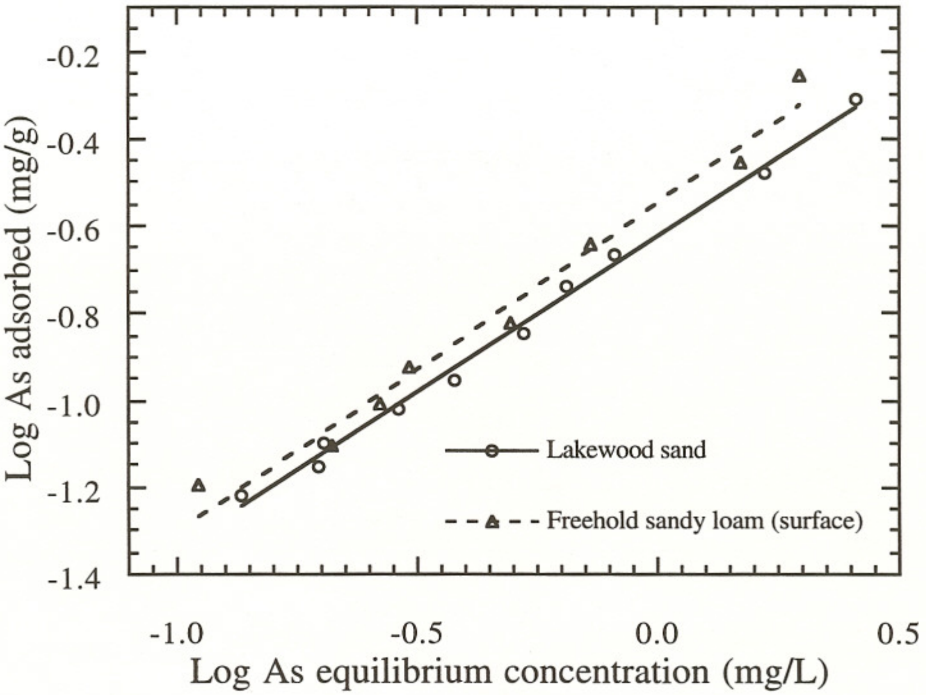

Figure 4.29 Freundlich isotherm of As(V) for Lakewood sand and Freehold sandy loam (surface).

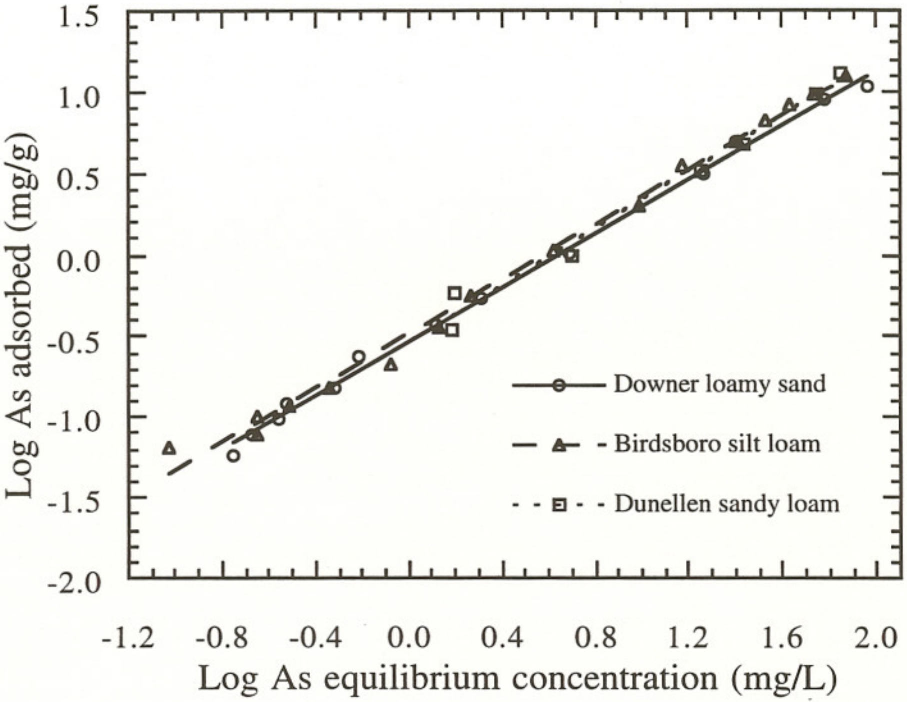

Figure 4.30 Freundlich isotherm of As(V) for Downer loamy sand, Birdsboro silt loam, and Dunellen sandy loam.

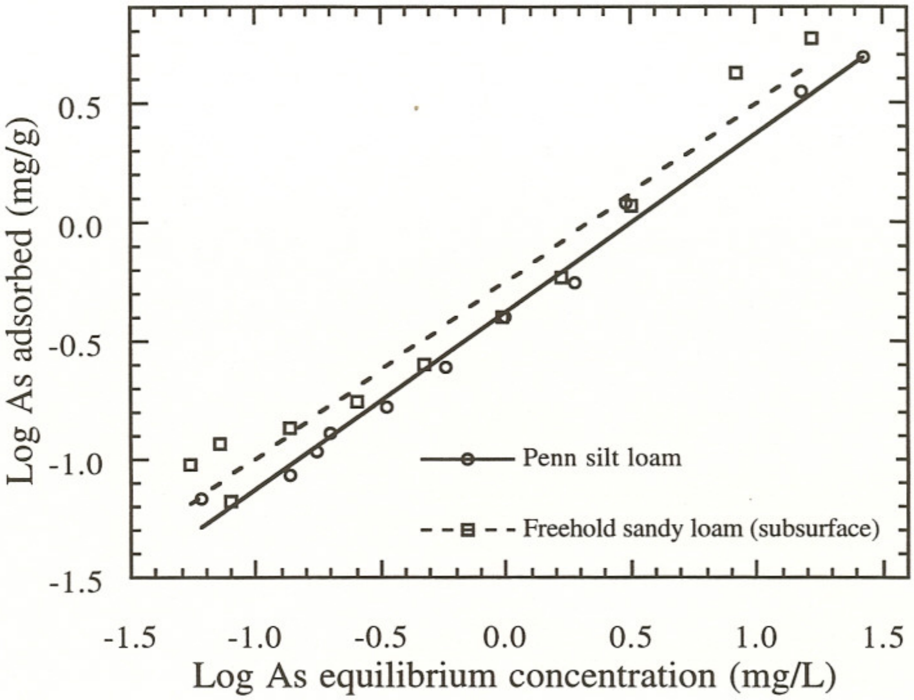

Figure 4.31 Freundlich isotherm of As(V) for Penn silt loam and Freehold sandy loar (subsurface).

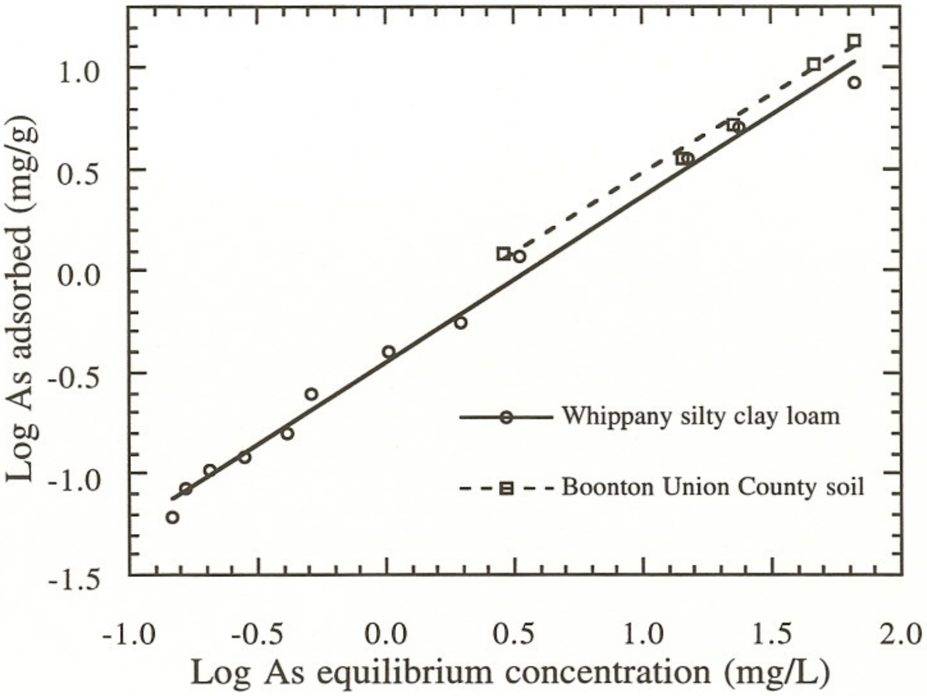

Figure 4.32 Freundlich isotherm of As(V) for Whippany silty clay loam and Boonton Union County soil.

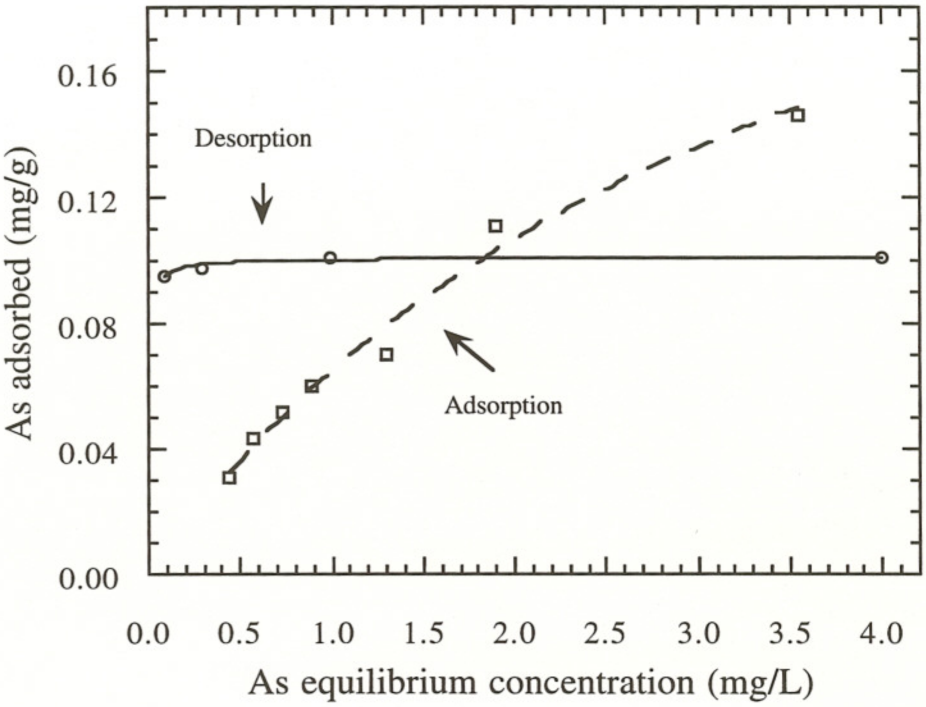

Figure 4.33 Adsorption and desorption isotherms for Penn silt loam. C_0 As(III): 6.70 x 10^{-5} M (5 mg/L).

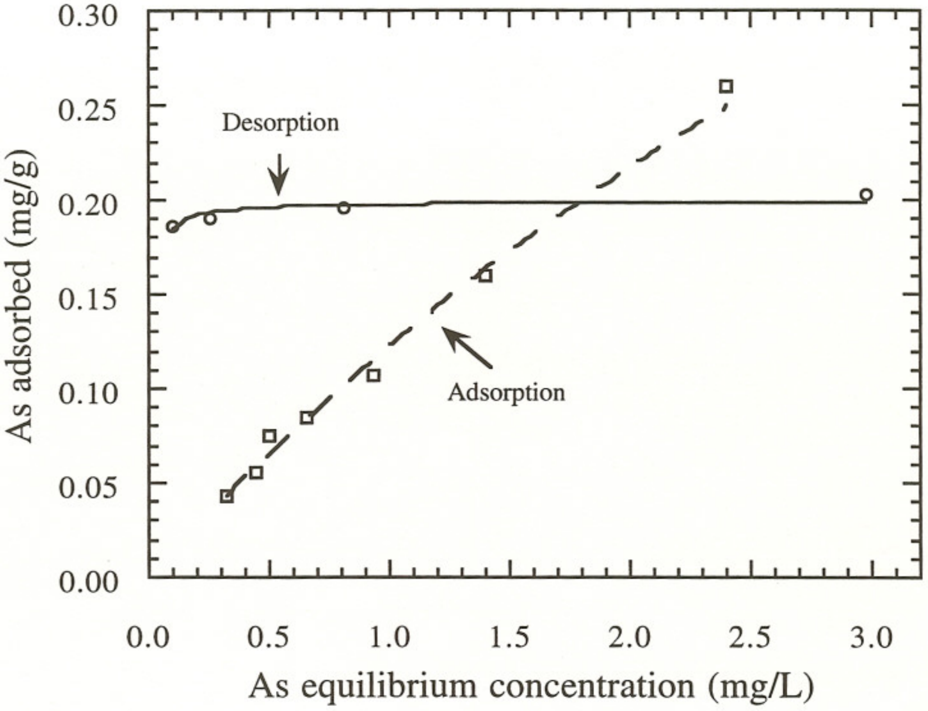

Figure 4.34 Adsorption and desorption isotherms for Washington loam. C_0 As(III): 6.70×10^{-5} M (5 mg/L).

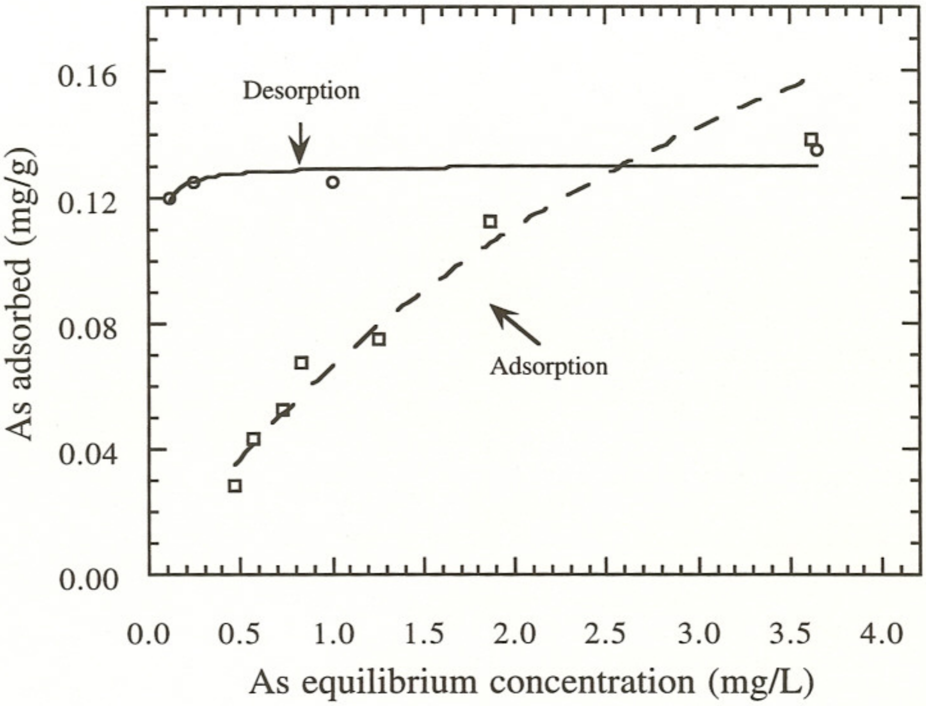

Figure 4.35 Adsorption and desorption isotherms for Boonton Bergen County soil. C_0 As(III): 6.70×10^{-5} M (5 mg/L).

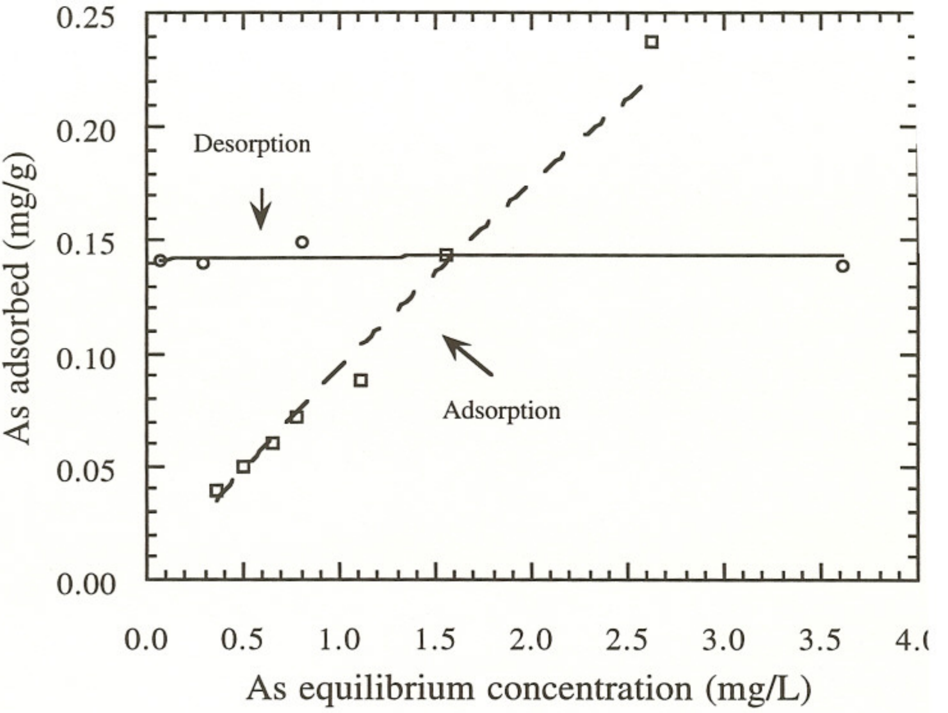

Figure 4.36 Adsorption and desorption isotherms for Freehold sandy loam (subsurface). C_0 As(III): 6.70 x 10^{-5} M (5 mg/L).

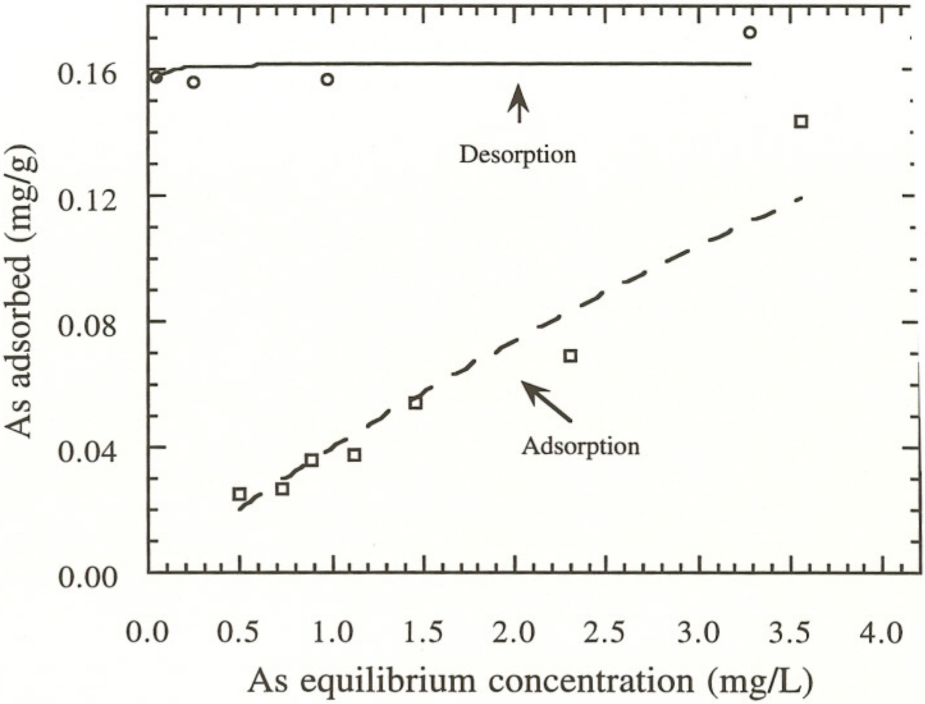

Figure 4.37 Adsorption and desorption isotherms for Dunellen sandy loam. C
As(III): 6.70×10^{-5} M (5 mg/L).

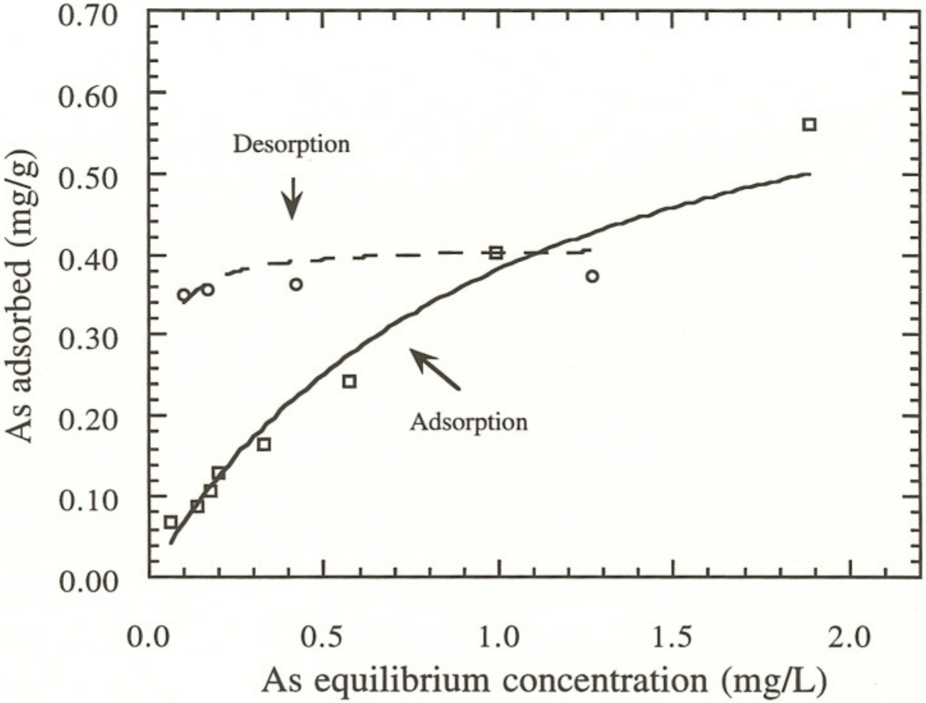

Figure 4.38 Adsorption and desorption isotherms for Penn silt loam. C_0 As(V): 6.70 10^{-5} M (5 mg/L).

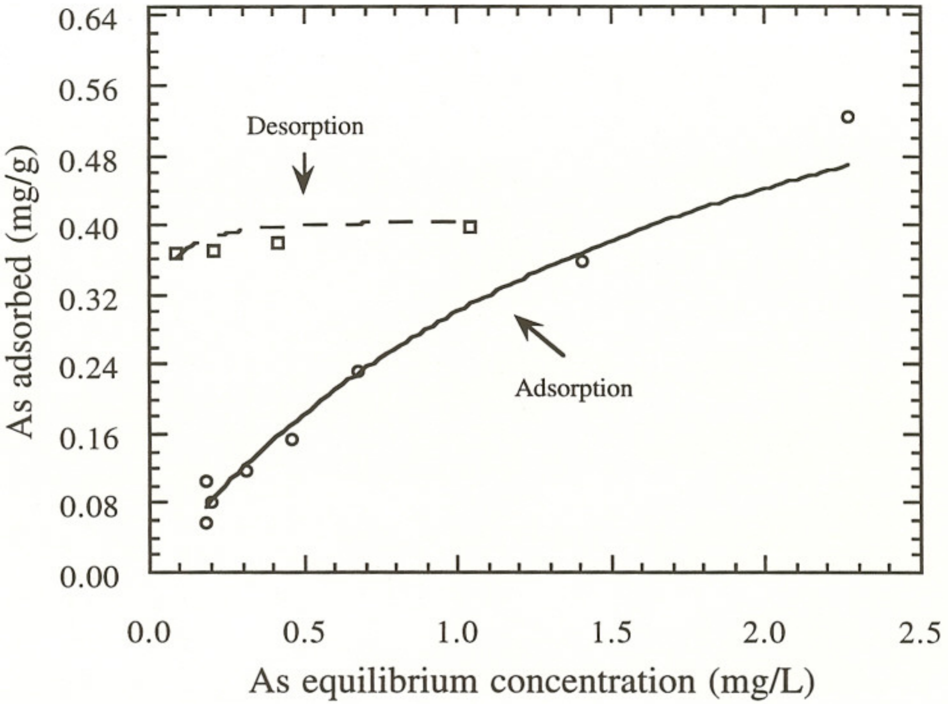

Figure 4.39 Adsorption and desorption isotherms for Washington loam. C_0 As(V
6.70×10^{-5} M (5 mg/L).

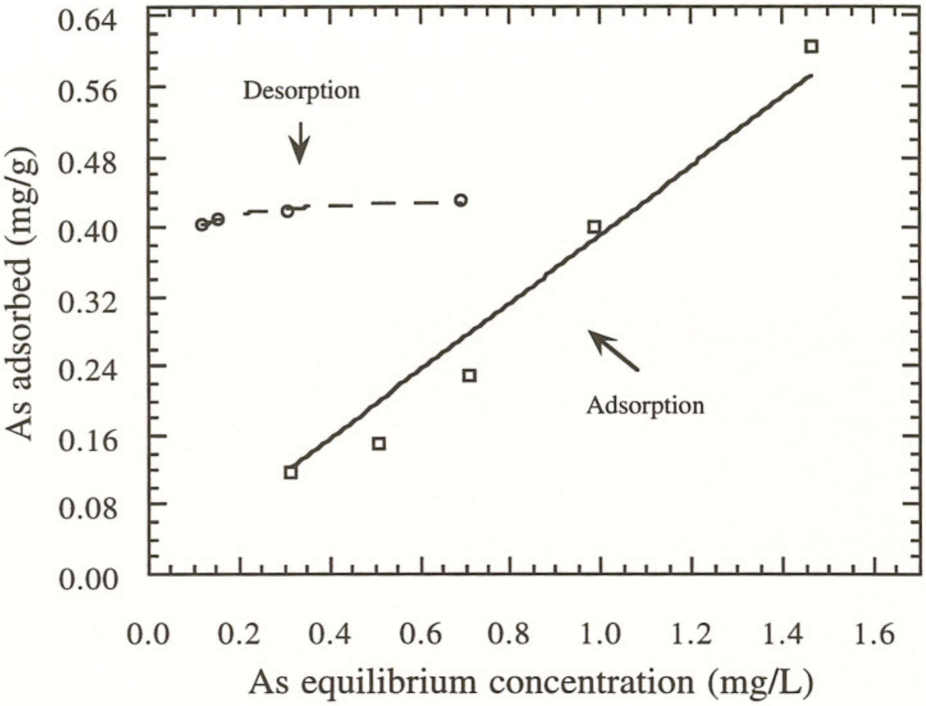

Figure 4.40 Adsorption and desorption isotherms for Boonton Bergen County soil. C_0 As(V): 6.70 x 10^{-5} M (5 mg/L).

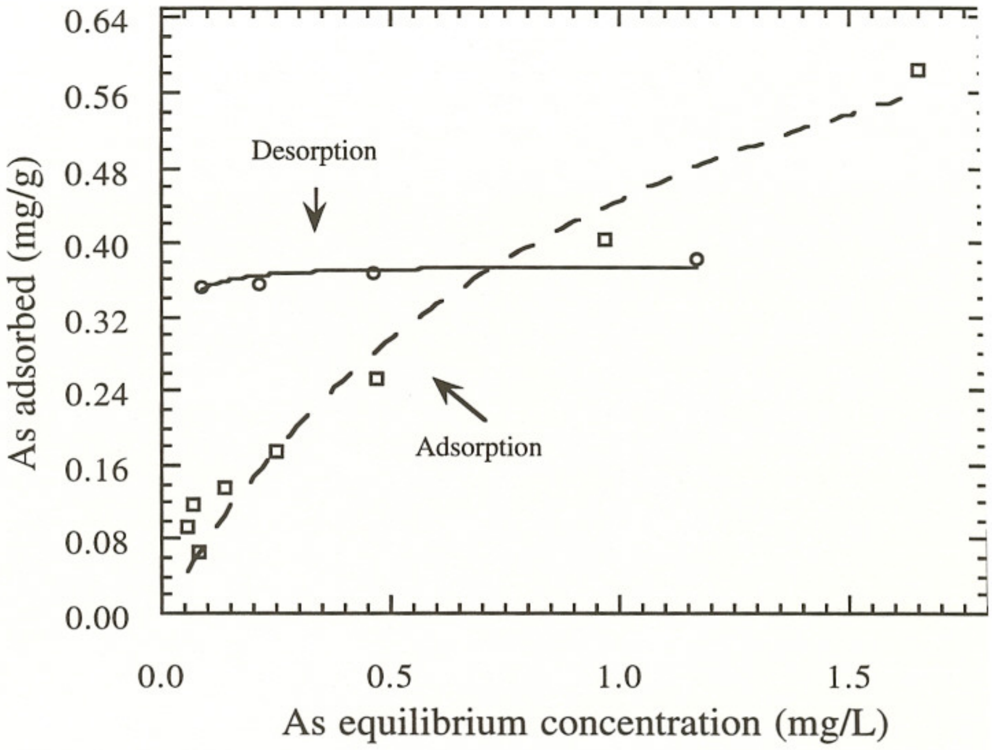

Figure 4.41 Adsorption and desorption isotherms for Freehold sandy loam (subsurface). C_0 As(V): 6.70 x 10^{-5} M (5 mg/L).

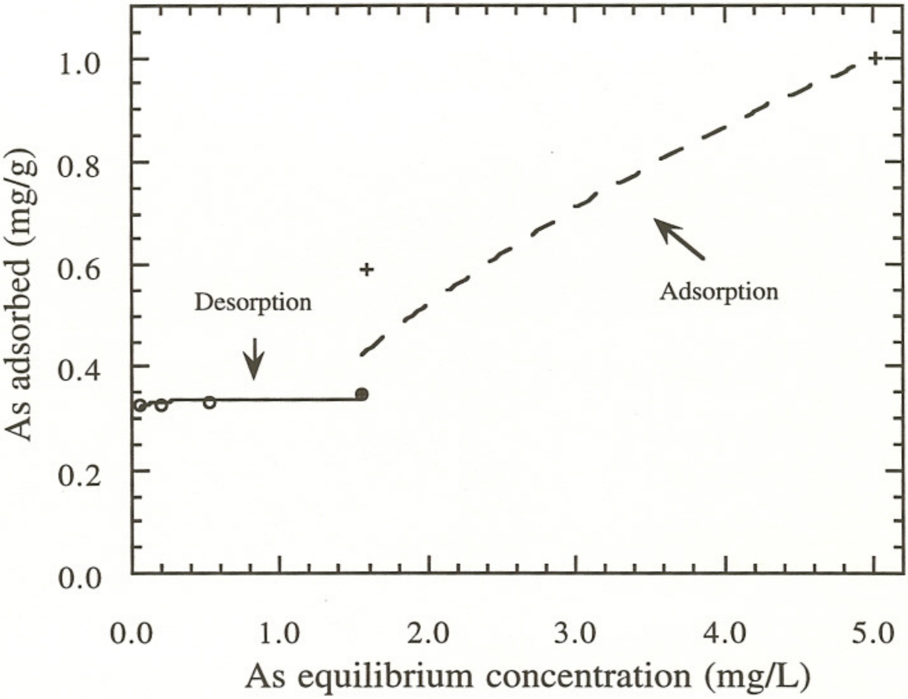

Figure 4.42 Adsorption and desorption isotherms for Dunellen sandy loam. C_0 As(V 6.70 x 10^{-5} M (5 mg/L).

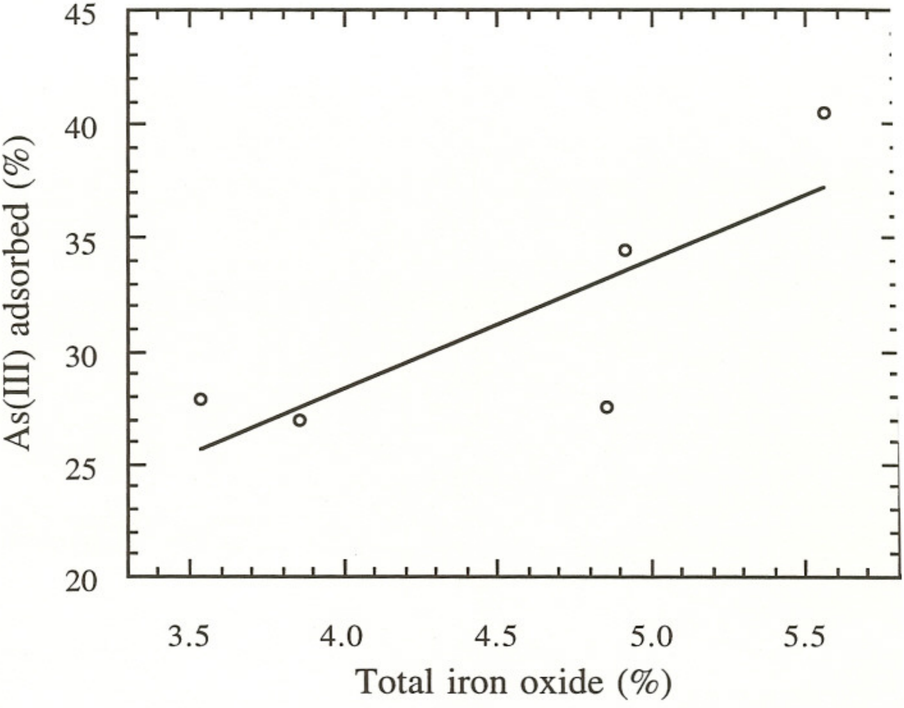

Figure 4.43 Iron oxide influence in the amount of As(III) adsorbed.

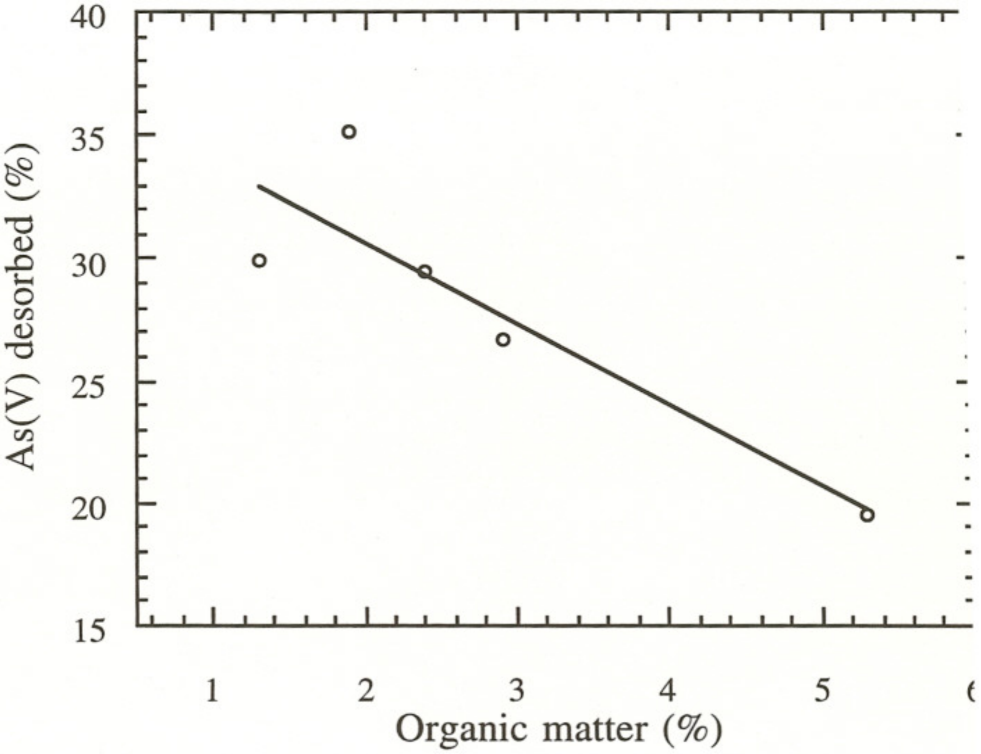

Figure 4.44 Organic matter influence in the amount of As(V) adsorbed.

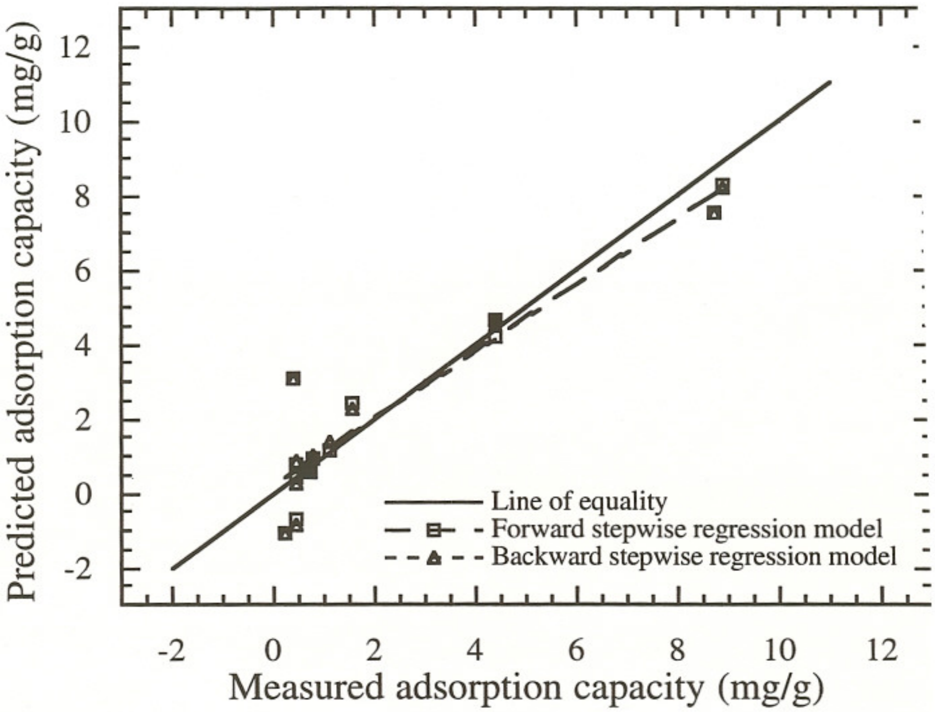

Figure 4.45 Comparison of the observed and predicted soil As(III) adsorptio capacity.

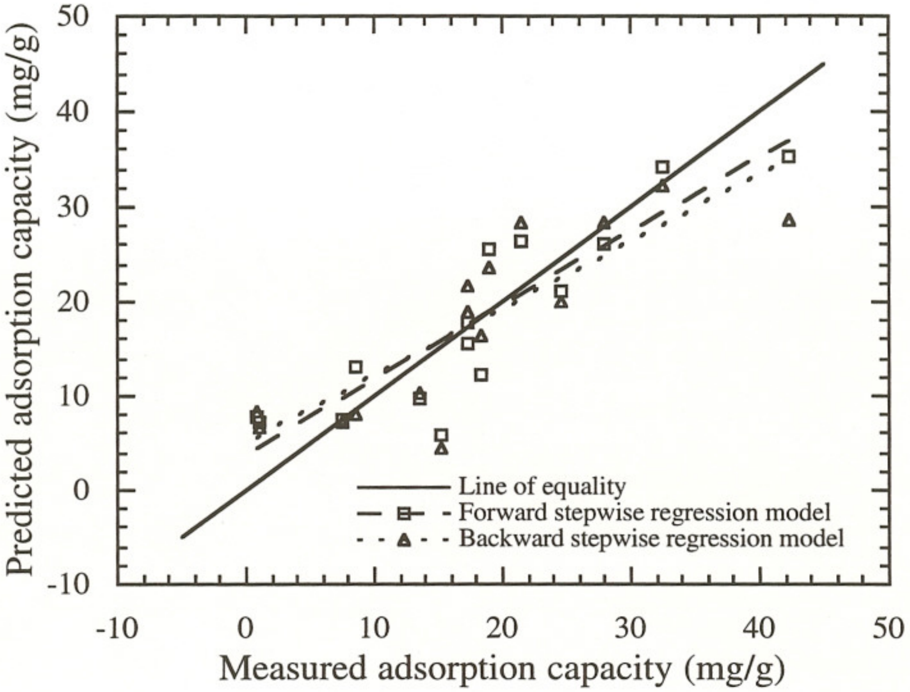

Figure 4.46 Comparison of the observed and predicted soil As(V) adsorption capacity.

Chapter 5

KINETICS OF ARSENIC SORPTION IN SOILS

5.1 Introduction

Different sorption equilibration times have being used for batch experiments ranging from a couple of hours to several weeks or even months. Generally, a plateau on the adsorption or desorption data plotted against time can indicate the appropriate equilibration time for a experiment. For example, the rate of arsenic sorption is reported to decrease with increasing of equilibration time, thus reaching a plateau.

McGeehan et al. (1992), employed linear-plateau regression analysis to model adsorption data of arsenic and verified the suitability of this method to identify the maximum adsorption and facilitate statistical comparison of As sorption rates and maxima. They concluded in their experiment using three Idaho soils, that 2 from 8 hours were required to reach the adsorption equilibrium depending on soil characteristics and arsenic species involved. The method that they used was also employed in evaluating fertilizer response (Anderson and Nelson, 1975).

The process of identification of the plateau using the linear-plateau regression analysis divides the sorption data in two portions (McGeehan et al., 1992). The first one is characterized by rapid sorption and during the second one the sorption is decreased. These authors observed that adsorption of As(III) and As(V) in soils was rapid at the beginning and slower with increasing equilibration time. They also reported no evidence of oxidation or reduction of the arsenic species studied within 48 hours of equilibration time.

Even though linear-plateau regression analysis is generally not used for the quantitative study of the sorption of arsenic, all adsorption processes occur in two steps, the first one characterized by rapid sorption and the second one by decreasing sorption. But at least qualitatively the adsorption maximum can be determined.

Ghosh and Yuan (1987) studied the kinetics of arsenic removal by alumina, establishing adsorption capacities for this adsorbent. They observed that the removal of arsenate was rapid in the first 24 hours of the experiment, slowing as the reaction reached equilibrium. According to these authors, 95% of the arsenic present in solution was adsorbed in less than 24 hours. Also, temperatures of 20 °C or higher didn’t affect adsorption. Arsenite adsorption was found to be different, the rate of approach to equilibrium was much slower, even though a two-step removal was involved, similar to that for arsenate. The removal of arsenate was greater than was that of arsenite.

Maeda et al. (1992) used iron(III) hydroxide-loaded coral limestone to adsorb arsenic species. They concluded that 8 hours was enough equilibration time for As(V) adsorption. However, they found that for As(III) the equilibrium was approached just after the first 24 hours. It was presumed during their experiment that the oxidation of As(III) didn't occur while the equilibration was taking place.

Bowell (1994) conducted sorption experiments of arsenic by oxides and oxyhydroxides in soils; sorption equilibrium was reached after 12 hours for As(III) and 48 hours for As(V) and 72 hours for monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA).

Sakata (1987) studied the relationship between adsorption of arsenic(III) and boron by soil and soil properties. He stated that preliminary experiments indicated that the adsorption equilibrium was established in less than 24 hours for As(III) and 10 hours for boron after As(III) or boron was added to the soil suspension, fifteen subsurface soils collected from different sites in Japan.

Adsorption solely due to electrostatic processes is usually very rapid, on the order of seconds. The adsorption of arsenic is on the order of hours, which indicates a specific adsorption or formation of a chemical bond between the arsenic species and the adsorbent (Pierce and Moore, 1982).

Also, adsorption mechanisms can be inferred from kinetics experiments. Bruemmer et al. (1988), suggested that the adsorption of metals such as nickel, zinc and cadmium on pure goethite occurred on internal and external surface sites. They observed that adsorption was increased with time, meaning that the adsorption continued on the internal sites of goethite, which could be characterized as a diffusion-controlled process.

Since adsorption kinetics is a particular factor depending basically on the adsorbent nature, batch experiments were conducted during this research in order to evaluate the adsorption behavior of two arsenic species, As(III) and As(V), in five soils with different characteristics.

5.2 Sorption methods

Sorption experiments were performed using a batch technique for kinetics experiments. A series of standards, depending on the analytical method used, were prepared by dilution from more concentrated As(III) and As(V) standard solutions.

1 ml of 1 M $NaNO_3$, to adjust the ionic strength, was added to 11 plastic flasks of 125 ml containing a soil solution ratio of 1.0 g ± 0.01 g per 100 ml DI water. Then 0.75 ml of 100 mg/L As(III) standard solution and 0.5 ml of 1000 mg/L As(V)

standard solution were added to 100 ml of soil suspension in order to obtain 0.75 and 5 mg/L of arsenic of As(III) and As(V), respectively.

The pH was adjusted using NaOH in order to obtain samples at natural pH, i.e. 0.3 M NaOH was added to neutralize the hydrochloric acid contained in the arsenic standard solutions. The suspensions were shaken for 4, 8, 12, 18, 24, 30, 40, 48, 72, 168 and 336 hours at a room temperature of about 25°C (± 3°C) at a rate of 100 rpm on a rotatory shaker. After equilibration, the suspensions were filtered using a plastic syringe and a 0.45 μm membrane filter placed on a filter holder.

An aliquot of each filtrate was used to determine the amount of total arsenic in solution. The amount adsorbed was then obtained by difference between the initial amount of arsenic added and the amount of arsenic in solution after the equilibration. Two soils were used to study the kinetics of As(V) sorption, Lakewood sand and Boonton Union soil. For the study of As(III) sorption another soil was included, Hazen gravelly loam.

Hydride generation atomic absorption and colorimetric methods were used, respectively, to analyze As(III) and As(V) remaining in solution.

5.3 Results and discussion

In both studies, it was verified that 48 hours is enough time to reach the adsorption equilibrium. Most authors report that 24 hours is suitable for adsorption. However, since soils are the matrix being used, and soils are a very heterogeneous system, it was necessary to study the kinetics of arsenic sorption using soils as adsorbents.

Based on the adsorption kinetics of arsenic(III) on three soils and As(V) on two soils, respectively shown in Figures 5.1 and 5.3, an equilibration time of 48 hours was chosen for the sorption experiments of arsenic. Oxidation-reduction reactions of arsenic species occurred at times up to 40 hours. However, just total arsenic in solution was considered when deciding a suitable time for the sorption equilibrium.

It was also seen during the experiment using As(V) as source of arsenic that the reduction of As(V) was almost insignificant, agreeing with literature findings. Results show that after 168 hours of equilibrium 2.2% of the total arsenic in solution was As(III) for Lakewood sand and 1.0% of the total arsenic in solution was As(III) for Boonton Union soil.

Equilibrium pH was reached around eight hours of equilibration for all spiked samples. Figures 5.2 and 5.6 show that the solution pH decreased slightly by 0.1 to 0.3 pH units after the first 40 hours reaching a plateau after that. This behavior was also observed by McGeehan et al. (1992). In their experiment using three soils from Idaho, the pH of the soil suspensions decreased slightly during equilibration.

The arsenic species behavior during the kinetics experiment is depicted in Figures 5.4, and 5.5.

Figures 5.7 and 5.8 were obtained based on desorption data. It is observed that the desorption equilibrium is well established after the first 24 hours of the desorption process when As(III) or As(V) are used as initial source of arsenic.

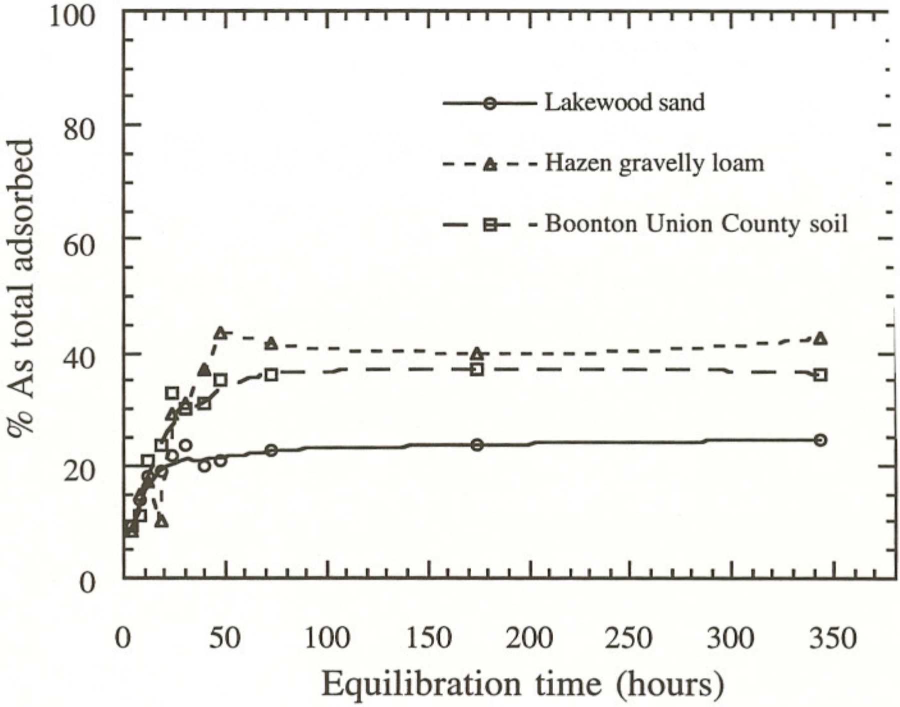

Figure 5.1 Kinetics of As(III) adsorption. C_0 As(III): 0.75 mg/L.

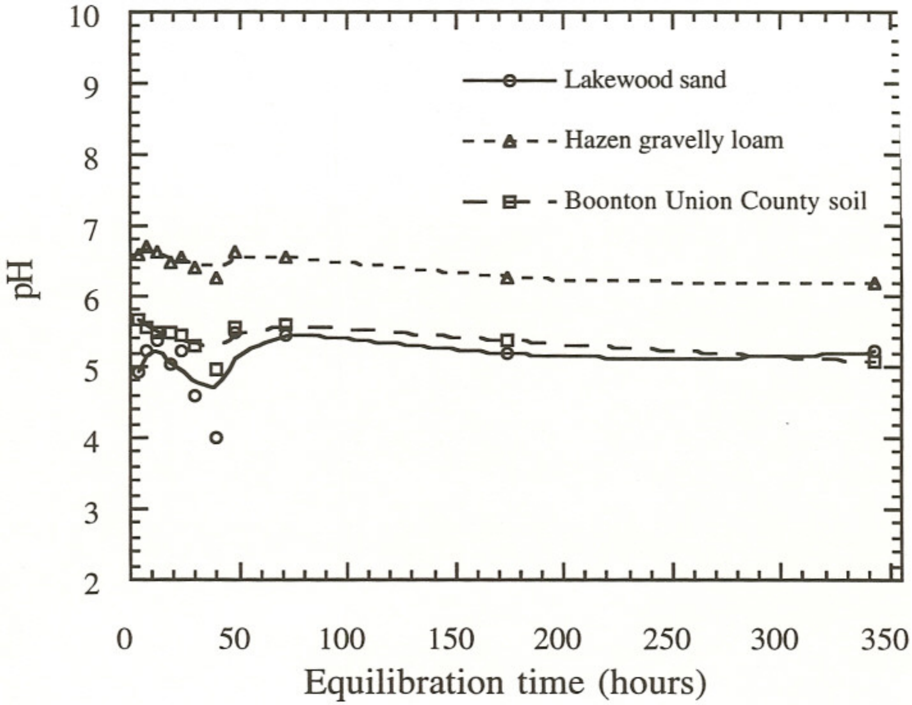

Figure 5.2 pH during kinetics experiment. C_0 As(III): 0.75 mg/L.

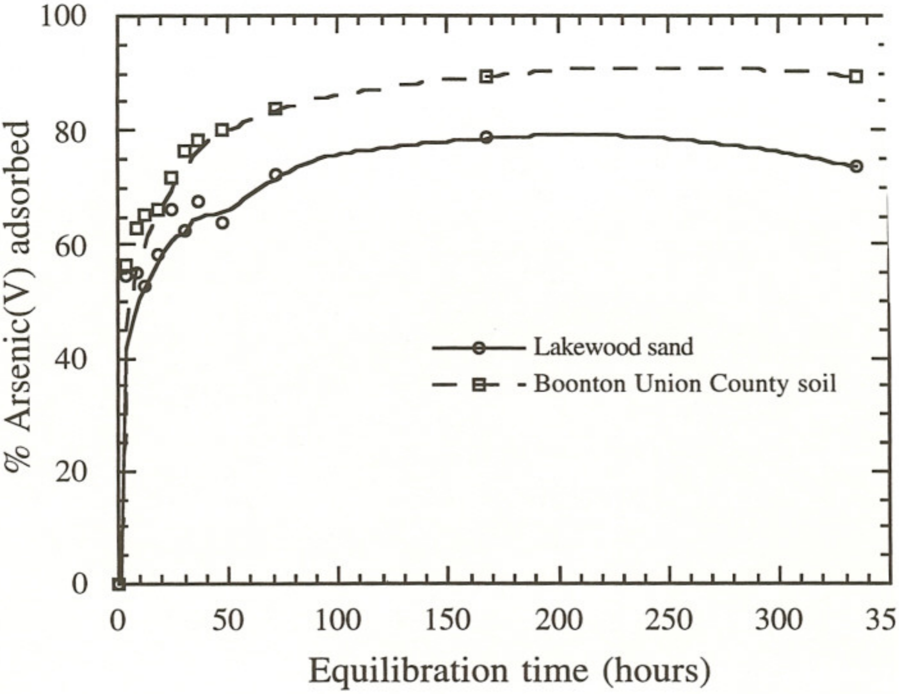

Figure 5.3 Kinetics of As(V) adsorption. C_0 As(V): 5.0 mg/L.

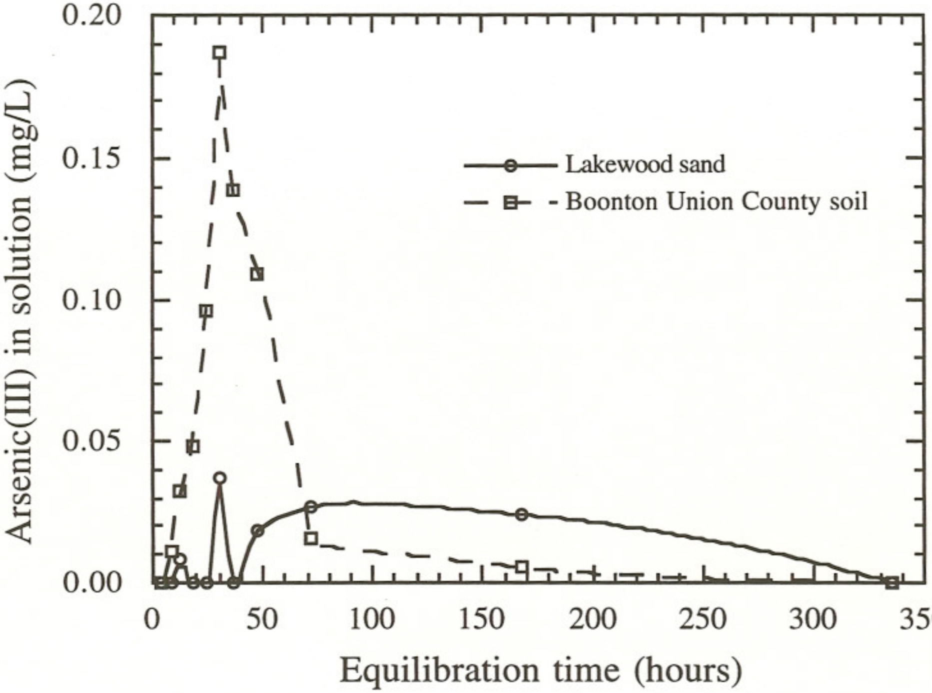

Figure 5.4 As(III) behavior during kinetics experiment. C_0 As(V): 5.0 mg/L.

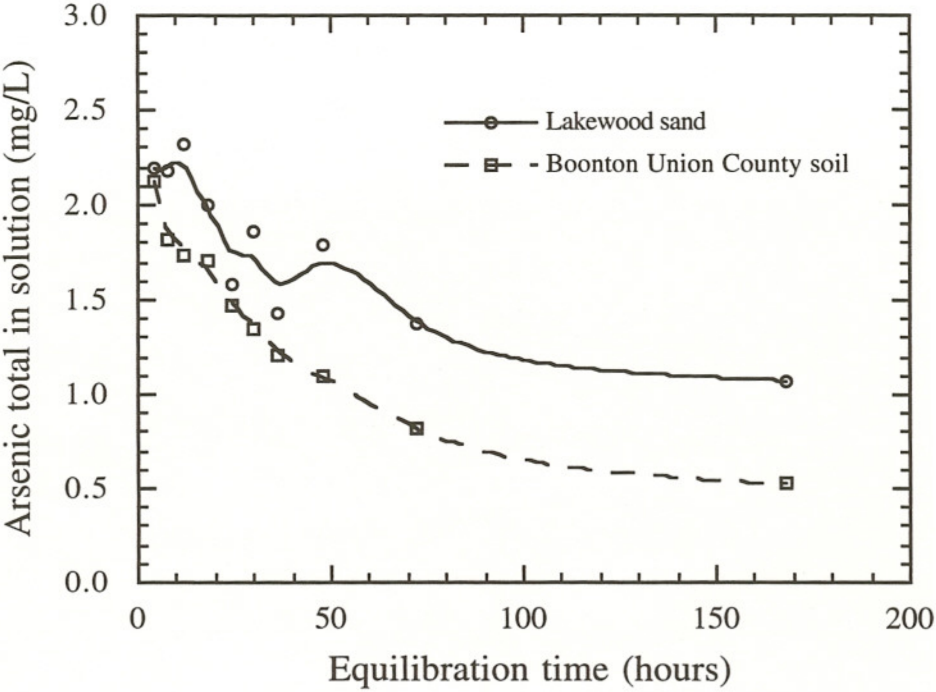

Figure 5.5 Total As behavior during kinetics experiment. C_0 As(V): 5.0 mg/L

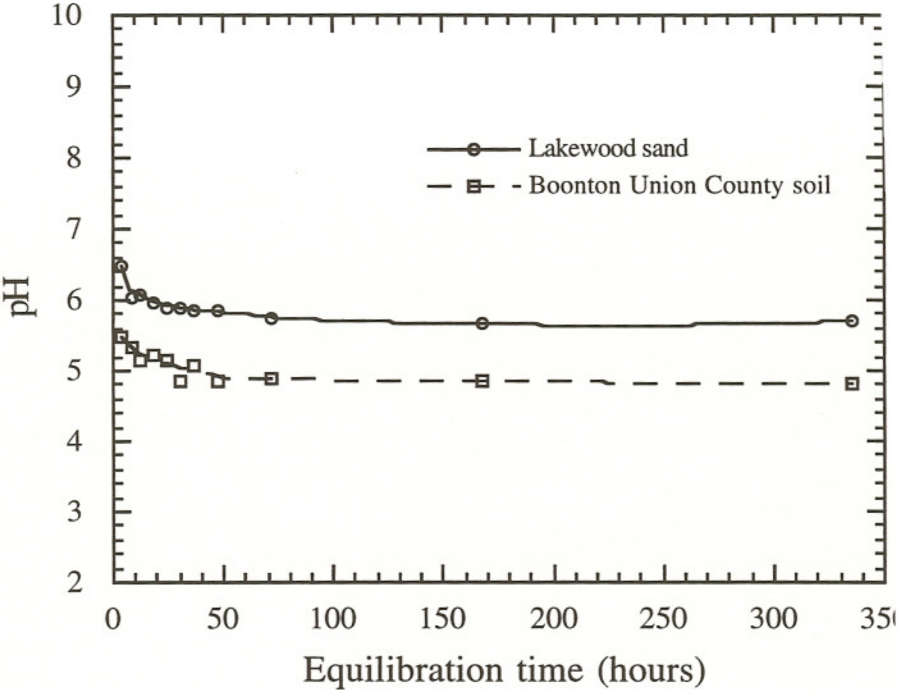

Figure 5.6 pH during kinetics experiment. C_0 As(V): 5.0 mg/L.

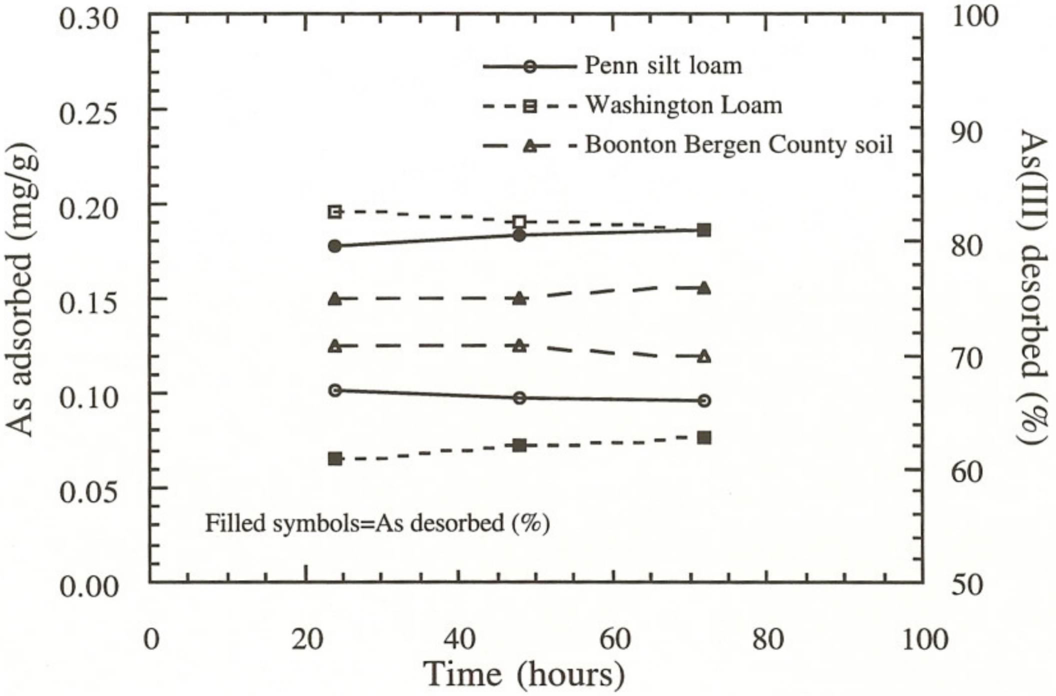

Figure 5.7 Kinetics of soil desorption of As(III) for Penn silt loam, Washington loam, and Boonton Bergen County soil. C_0 As(III): 5.0 mg/L.

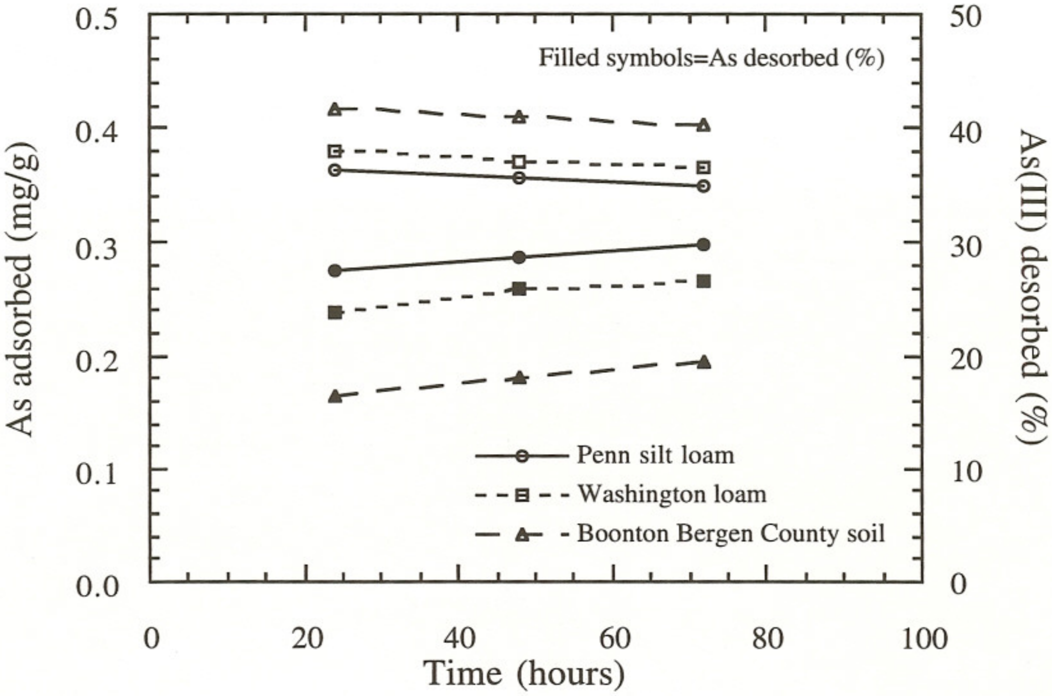

Figure 5.8 Kinetics of soil desorption of As(V) for Penn silt loam, Washington loam, and Boonton Bergen County soil. C_0 As(V): 5.0 mg/L.

Chapter 6

CONCLUSION

This research was addressed to study the adsorption and desorption behavior of two arsenic species in fifteen New Jersey soils.

The adsorption of arsenic(III) as a function of pH was characterized by a pH range of maximum adsorption around pH 6 to 9, while the maximum As(V) adsorption occurred in the 4 to 5 pH range. Similar behavior was described by several other researchers, even though some used different adsorbents (Manning and Goldberg, 1996; Bowell, 1994; Pierce and Moore, 1980; Frost and Griffin, 1977).

No relationship was found between the adsorption pH and a partition coefficient of arsenic species. However, the adsorption envelopes obtained are important in determining at which environmental pH adsorption is favored.

Adsorption isotherms were used in order to develop models to predict the arsenic behavior in soils. Therefore, this research will make possible the prediction of arsenic adsorption based on soil characteristics including organic matter content, iron oxide, aluminum oxide, manganese oxide, BET surface area, cation exchange capacity (CEC), and clay, silt, and sand content.

The adsorption model was generated using two statistical tools, the forward stepwise linear regression and the backward linear regression. The results indicate that the predicted values obtained using the models are in agreement with measured adsorption capacities.

Desorption of arsenic species was accomplished after their adsorption. As(III) is weakly retained in the soil matrix than is As(V). This might be due to different processes involving the adsorption. As(V) is adsorbed through electrostatic interactions while As(III) adsorption is believed to occur through hydrogen bonding.

In addition, desorption of arsenic species from five selected soils revealed that As(III) is desorbed as As(V). Its oxidation occurring during the desorption process. As(V), however, is desorbed as As(V). This result is very important when considering the lesser toxicity of arsenic(III) species.

Kinetics of arsenic(III) and arsenic(V) adsorption in New Jersey soils show that the equilibration time is reached around 48 hours. This is an important result since most of the research in arsenic adsorption is done using 24 hours as a standard equilibration time. Soils are a very heterogeneous system and its adsorption capacity must be determined accurately after a proper equilibration time between the adsorbate and adsorbent.

Appendix A

STANDARD OPERATING PROCEDURE FOR THE USE OF THE PERKIN ELMER 5000 ATOMIC ABSORPTION SPECTROPHOTOMETER

1. Prepare samples and standards. Warm up AA at least 15 min before running it. Turn "ON" the power switch and the next switch to the "RUN" position.

2. Install the lamp (hollow cathode lamp). Plug in the lamp connector.

3. Set: wavelength (193.7 nm): push # and [λ peak].

4. Set: slit band (0.7 nm): push # and [slit high].

5. Position the lamp at the window: push # and [lamp position number]. This entry should match the position where the lamp is installed. Set the lamp current: push # and [lamp current]. The current should be below the maximum one printed at the box or on the lamp. Lamp energy should always be kept above 40 or 50.

6. Align the lamp: push [SETUP] and gently turn the two knobs holding the lamp until the best energy reading is obtained. If the keyboard shows a maximum reading, push [GAIN] and continue to adjust the knobs. Once the best reading is obtained, push [SETUP] again to continue. Close the lamp compartment door.

7. Sampling time: push # (0.5), [t], [HOLD]. This tells the AA to read samples every 0.5 seconds.

8. Set the instrument to work in the continuous mode. The MHS-10 system generates time dependent, peak-shaped signals. Set AA/BG switch to AA.

9. Switch "ON" the variac to the 85 position.

10. Wait about 30 minutes until the desired temperature is reached.

11. Zero the display on the spectrophotometer.

12. Open the nitrogen gas valve. Since arsenic is determined at a wavelength where air already absorbs light, when nitrogen is introduced into the system, the absorbance signal falls. Wait until the absorbance is stabilized and zero the display on the spectrophotometer again.

13. Dispense reducing reagent into the reaction flask by pushing down and holding the plunger located on the MHS-10 system until the peak maximum is achieved. Release the plunger to stop the addition of the reductant.

14. Remove the reaction flask and wash it as suggested by the manufacturer's standard procedures.

15. Analyze all samples as described above.

16. To finalize operation: remove the lamp: push 1 and [LAMP #]. Carefully remove and store the lamp.

17. Unplug the variac transformer.

18. Turn everything else “OFF”.

Some precautions were taken when working with the hydride generation system. These are:

1. The variac transformer dial must not be turned beyond 90 to avoid problems with the heated wires wrapped around the quartz cell.

2. When cooling the quartz cell, wait until the temperature reaches 50°C to turn the variac off. After that remove cell carefully and store it in a safe place.

3. Make sure that the transfer hose is not restricted in any way

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Adsorption/Desorption and Transport of Mercury and Arsenic in New Jersey Soils

Supplementary Report

Final Report
Part III

November, 1998

Yujun Yin, Fabiana Dias, Herbert E. Allen, and C. P. Huang
Department of Civil and Environmental Engineering
University of Delaware
Newark, DE 19716

Project Manager
Paul F. Sanders, Ph.D.
Division of Science and Research
New Jersey Department of Environmental Protection
Trenton, NJ 08625

This report is a supplement to the previously submitted final report titled "Adsorption/Desorption and Transport of Mercury and Arsenic in New Jersey Soils" Part I by Yujun Yin, Herbert E. Allen and C. P. Huang and Part II by Fabiana Dias, Yujun Yin, Herbert E. Allen and C. P. Huang. In this report, models for prediction of the soil-specific adsorption of mercury(II) at the natural soil pH and a model for prediction of the partitioning of mercury(II) as a function of pH at low mercury loading levels are recommended. The raw data for adsorption of As(III) and As(V) as a function of pH as well as adsorption isotherms for both species are also included.

1. Recommendations on Use of a Model for Prediction of Adsorption Isotherms of Mercury(II) on New Jersey Soils at Natural Soil pH

Adsorption isotherms of Hg(II) on soils followed either L-shape or S-shape (See Chapter 4 of the final report Part I for details). In this study, we used three empirical models, Langmuir, Freundlich and Gunary equations, and one model developed in this study to describe adsorption isotherms. The goodness of fit is judged based on the value of residual sum of squares (RSS), which is calculated according to the following equation.

$$RSS = \sum_{i=1}^{n} \frac{\left(Y_p - Y_e\right)^2}{Y_e}$$

where n is the number of data points used in modeling, Y_e and Y_p are the concentrations of metals experimentally determined and model predicted, respectively.

As indicated in Chapter 4 of the final report, the Langmuir equation (eq. 4.7) could only describe all L-type isotherms with RSS < 0.94 (Table 4.2), whereas the Freundlich equation (eq. 4.8) could only describe the L-type isotherm for one soil with a RSS of 0.43 (Table 4.2). Both Langmuir and Freundlich equations poorly described S-type isotherms with RSS > 1.93 for the Langmuir equation and > 2.39 for the Freundlich equation. Both Gunary equation (eq. 4.9) and the model developed in this study (eqs. 4.21 and 4.22) were able to describe adsorption isotherms of Hg(II) on all soils. The RSS values obtained by the model developed in this study, however, are generally smaller than those obtained by the Gunary equation. The RSS values for the model developed in this study is less than 0.94 for all soils except Boonton Bergen loam (no. 15). Based on the goodness of model fit, we recommend that the model (eqs. 4.21 and 4.22) developed in this study be used for prediction of mercury(II) adsorption on all soils. Equation 4.21 can be used for the prediction of the S-shaped adsorption isotherms of mercury(II) on soils no. 4, 5, 7, 8, 11, 12, 13, 14 and 15, and equation 4.22 for L-shaped isotherms for soils no. 1, 2, 3, 6, 9, and 10. The parameters needed for calculation of adsorption on each soil are listed in Table 4.4.

2. Recommendations on Use of Models for Prediction of Adsorption of Mercury(II) on New Jersey Soils as a Function of pH

In this study, generalized equations were developed to describe adsorption of Hg(II) (eq. 8.20) as a function of pH.

$$C_w = \frac{1 + K_{HL}[H^+] + K_{HgL}DOC}{1 + K_{HL}[H^+] + K_{HgL}DOC + A\dfrac{1 + K_{HL}[H^+]}{1 + K_{\equiv SOH}[H^+]}} T_{Hg}$$

As discussed in Chapter 8 of the final report, the variables in the generalized equation include pH, the concentration of dissolved organic C (DOC) (L μmol^{-1}), and the concentration of soil organic C (SOC) (g kg^{-1}). All these variables can be directly determined for either soil solution phase or solid phase. The parameters needed for use of the equation include the stability constant (K_{HgL}) for Hg binding with dissolved organic matter measured as DOC, the stability constant for proton binding with soil solid surface ($K_{\equiv SOH}$), the stability constant for proton binding with dissolved organic matter K_{HL}, and parameter A which depends on soil binding capacity and strength for Hg. All these parameters were obtained by model fitting to the experimental data. The values of K_{HL}, $K_{\equiv SOH}$, and A are not varying with total Hg loading (initially added total Hg concentration). The value of K_{HgL}, however, depended on initial total Hg concentration because of the complex nature of Hg-organic ligand binding as discussed in Chapter 8 of the final report.

Because Hg(II) has very strong binding affinity for soil solids, the competition of protons for the surface sites is negligible. Thus, $K_{\equiv SOH}$ can be eliminated from the generalized equation (8.20) for Hg(II) adsorption. The values of K_{HL} and A are 0.32 L μmol^{-1} and 0.81. The values of K_{HgL} is 0.01096 L μmol^{-1} for an initial total Hg(II) concentration of 1×10^{-7} M and 0.00478 L μmol^{-1} for an initial total Hg(II) concentration of 1×10^{-6} M. After substitution of the model fitting parameters, the generalized equation for Hg(II) adsorption at an initial total concentration of 1×10^{-7} M is:

$$C_w = \frac{1 + 0.32[H^+] + 1.096 \times 10^{-2} DOC}{1 + 0.32[H^+] + 1.096 \times 10^{-2} DOC + 0.81 SOC(1 + 0.32[H^+])} T_{Hg}$$

The generalized equation for Hg(II) adsorption at an initial total concentration of 1×10^{-6} M is:

$$C_w = \frac{1 + 0.32[H^+] + 4.78 \times 10^{-3} DOC}{1 + 0.32[H^+] + 4.78 \times 10^{-3} DOC + 0.81 SOC(1 + 0.32[H^+])} T_{Hg}$$

As shown in Chapter 8 of the final report, the predicted aqueous Hg(II) concentration using the above equations agreed well with the measured at each initial total

Hg(II) concentration. Based on this study, it is possible to obtain the K_{HgL} values by linear interpolation based on the K_{HgL} values obtained in this study for an initial total Hg(II) concentration range of 1 x 10^{-6} M to 1 x 10^{-7} M. Based on the interpolated K_{HgL} value, together with the predetermined K_{HL} and A values, adsorption of Hg(II) can be predicted.

3 Raw Data for Adsorption of As(III) and As(V) as a Function of pH

3.1 Adsorption of As(III) as a function of pH

Adsorption of As(III) and As(V) as a function of pH has been discussed in Chapter 3 of the final report Part (II). The following is a list of the raw experimental data for adsorption of both species as a function of pH on fifteen New Jersey soils at two initial concentrations, 0.1 and 0.75 ppm.

Table 3.1.1 Adsorption edge data for As(III) on fifteen New Jersey Soils. Initial As(III) concentration = 0.1 ppm; soil:water = 1 g 100 mL^{-1}; I = 0.01 M $NaNO_3$; T = 25 ± 2°C.

Sassafras sandy loam		Lakewood sand		Penn silt loam	
pH	% ads	pH	% ads	pH	% ads
2.62	52.62	8.57	14.30	2.70	0.00
3.16	8.67	2.58	0.00	3.27	0.00
6.43	32.34	2.76	0.00	5.98	6.98
6.94	88.12	2.89	0.00	7.05	19.05
7.31	97.42	3.12	9.53	7.41	45.75
3.46	8.67	3.80	16.69	3.56	0.00
4.58	5.29	7.21	52.47	4.55	0.00
7.77	29.80	10.10	23.84	7.20	42.31
8.38	0.00	10.72	23.84	8.32	0.00
9.25	0.00	11.56	0.00	9.35	0.00

Whippany silt clay loam		Washington loam		Freehold sandyloam (A horizon)	
pH	% ads	pH	% ads	pH	% ads
3.12	18.62	2.66	73.73	2.70	0.00
3.27	22.97	3.67	58.69	3.09	0.00
5.83	26.46	6.32	48.66	6.79	41.45
6.47	50.85	6.79	72.90	7.52	23.35
7.51	41.27	7.44	67.88	7.83	24.21
6.19	33.43	4.32	57.02	3.30	0.00
7.08	55.20	5.87	50.33	4.36	38.86
7.99	37.78	7.91	62.03	7.87	24.21
8.98	18.62	10.18	41.97	8.55	0.00
9.27	0.00	11.16	0.00	9.65	0.00

Freehold sandyloam (B horizon)		Rockaway stony loam		Fill matierals from Delaware River	
pH	% ads	pH	% ads	pH	% ads
2.76	25.94	3.27	8.16	2.53	31.30
3.40	0.00	3.40	12.52	2.48	16.95
6.44	41.45	5.94	20.36	6.10	40.07
7.28	43.17	6.24	22.10	6.97	58.41
7.60	62.98	7.80	45.62	7.87	60.01
3.64	21.63	6.70	27.33	3.87	40.87
4.81	13.01	7.50	63.04	4.07	19.34
7.41	49.20	9.72	17.75	8.73	48.85
8.33	32.83	10.23	4.68	9.96	0.00
9.47	1.81	11.01	0.00	10.88	5.79

Downer loamy sand		Boonton Union loam		Dunellen sandy loam	
pH	% ads	pH	% ads	pH	% ads
8.93	40.51	6.82	42.93	2.62	16.15
2.59	12.79	2.79	35.77	2.56	19.34
2.76	0.00	3.21	40.54	6.28	21.73
3.17	1.12	3.43	40.54	6.96	12.17
9.59	34.67	3.83	50.09	7.32	25.72
10.53	0.00	4.52	57.24	3.60	3.39
11.21	1.12	6.64	42.93	4.77	12.96
3.05	0.00	7.86	31.00	7.67	52.83
5.70	20.08	9.39	73.94	9.27	22.53
2.73	0.00	10.02	50.09	10.69	0.00

Birdsboro silt loam		Hazen gravelly loam		Boonton Bergen County loam	
pH	% ads	pH	% ads	pH	% ads
7.20	50.72	7.42	82.82	28.91	2.75
2.65	15.71	2.83	56.56	35.29	2.62
2.99	36.13	3.49	55.10	39.28	5.80
3.79	28.84	4.64	52.18	41.67	6.62
7.96	12.79	8.66	0.00	52.83	7.10
9.81	31.75	10.17	12.79	12.96	3.60
11.02	0.00	11.14	23.00	49.64	4.60
3.51	27.38	4.02	53.64	71.97	6.90
6.08	100.00	6.33	43.43	69.58	8.34
3.06	34.67	3.42	53.64	7.38	10.24

Table 3.1.2 Adsorption edge data for As(III) on fifteen New Jersey Soils. Initial As(III) concentration = 0.75 ppm; soil:water = 1 g 100 mL^{-1}; I = 0.01 M $NaNO_3$; T = 25 ± 2°C.

Sassafras sandy loam		Lakewood sand		Penn silt loam	
pH	% ads	pH	% ads	pH	% ads
7.35	64.65	2.73	37.68	7.18	47.80
2.74	47.69	2.7	27.36	2.87	34.46
2.70	45.73	3.01	33.06	3.25	31.13
3.13	47.03	3.35	35.09	3.43	23.35
3.71	33.98	3.28	30.98	4.20	22.24
5.78	47.03	7.07	47.08	6.73	30.02
6.25	48.34	7.73	56.42	7.53	46.13
7.61	72.48	8.11	39.57	9.71	40.58
8.90	0.00	8.79	40.79	10.53	22.79
8.40	0.00	9.31	30.27	11.30	16.68
8.00	33.98	4.15	35.75		
		5.54	38.32		

Whippany silt clay loam		Washington loam		Freehold sandyloam (A horizon)	
pH	% ads	pH	% ads	pH	% ads
7.18	18.97	7.50	70.53	7.71	30.02
2.91	24.19	3.04	58.13	2.66	0.00
2.85	19.63	2.94	47.03	2.62	7.23
3.46	17.02	3.89	54.21	3.05	0.00
4.27	12.45	5.20	32.68	3.72	0.00
6.20	16.36	6.57	37.25	8.64	4.45
7.03	28.11	7.27	68.57	9.45	20.01
7.39	15.06	7.59	69.22	10.58	25.57
8.23	0.00	8.30	0.00	10.92	24.46
8.82	0.00	8.42	0.00	11.06	9.45
				5.25	0.00
				6.10	23.35

Freehold sandyloam (B horizon)		Rockaway stony loam		Fill matierals from Delaware River	
pH	% ads	pH	% ads	pH	% ads
7.03	50.02	7.16	37.24	7.16	69.50
2.77	0.00	3.07	29.46	2.74	34.14
2.71	17.79	3.09	39.46	2.70	5.12
3.44	0.00	3.69	28.90	3.13	22.35
4.20	0.00	4.20	25.01	3.63	16.91
6.91	63.36	6.31	33.91	6.72	55.90
8.62	46.69	7.39	35.57	7.67	54.09
9.89	0.00	8.59	26.13	8.60	6.03
10.63	14.45	9.52	24.46	9.68	7.84
10.86	0.00	11.11	10.56	9.70	14.19
5.37	25.01				
6.04	41.69				

Downer loamy sand		Boonton Union loam		Dunellen sandy loam	
pH	% ads	pH	% ads	pH	% ads
6.62	50.56	3.06	61.05	7.41	50.46
2.75	38.13	3.66	51.73	2.88	29.61
2.70	35.14	4.16	47.62	2.72	39.58
3.15	32.00	6.24	51.24	3.50	32.33
3.82	34.37	7.16	50.23	4.23	36.86
6.45	55.54	7.47	53.67	6.84	41.39
9.09	49.97	7.67	52.71	7.43	52.28
10.57	43.03	3.14	61.45	8.42	16.91
11.02	40.28	3.12	55.52	8.83	40.49
11.15	5.38	3.09	60.25	9.40	43.21
		8.7	65.19		
		9.05	65.90		

Birdsboro silt loam		Hazen gravelly loam		Boonton Bergen County loam	
pH	% ads	pH	% ads	pH	% ads
6.84	26.13	7.18	67.29	7.28	100.00
2.85	53.47	3.07	66.11	3.04	100.00
2.83	53.47	4.02	63.19	2.96	32.52
3.57	50.58	5.37	53.39	3.54	100.00
4.53	53.00	8.71	56.58	4.20	13.25
7.04	31.15	9.87	46.30	6.66	100.00
7.43	43.68	10.68	52.84	7.30	49.07
8.33	38.97	10.91	46.93	7.84	42.54
8.74	100.00	3.02	62.31	8.36	37.10
9.20	100.00	6.45	58.09	10.32	25.39

3.2 Adsorption of As(V) as a function of pH

Table 3.2.1 Adsorption edge data for As(V) on fifteen New Jersey Soils. Initial As(V) concentration = 0.1 ppm; soil:water = 1 g 100 mL^{-1}; I = 0.01 M $NaNO_3$; T = 25 ± 2°C.

Sassafras sandy loam		Lakewood sand		Penn silt loam	
pH	% ads	pH	% ads	pH	% ads
2.65	91.26	2.43	70.36	2.64	90.94
3.11	88.95	2.66	87.12	3.57	94.21
4.09	93.65	2.87	98.29	5.90	81.96
6.47	85.09	5.03	98.29	6.51	76.24
7.09	63.51	9.00	35.91	7.54	52.54
3.53	96.65	2.67	81.53	3.61	88.49
4.65	95.88	3.00	97.36	4.50	92.58
7.98	84.32	9.40	36.84	7.53	53.36
8.26	41.93	10.54	0.00	8.15	50.91
8.90	0.00	11.07	0.00	9.41	0.00

Whippany silt clay loam		Washington loam		Freehold sandyloam (A horizon)	
pH	% ads	pH	% ads	pH	% ads
3.52	96.66	2.83	98.97	2.68	99.93
3.77	90.94	3.66	97.42	3.13	97.48
5.80	87.67	5.81	89.72	6.83	82.77
6.42	79.50	6.58	70.45	7.48	72.97
7.48	65.62	7.13	74.30	7.85	62.35
6.22	84.41	4.35	95.11	3.34	93.39
7.19	70.52	6.34	86.63	4.31	87.67
8.06	21.50	7.45	51.18	7.80	66.43
8.99	17.41	8.12	32.68	8.62	0.00
9.34	0.00	8.96	2.62	9.69	0.00

Freehold sandyloam (B horizon)		Rockaway stony loam		Fill matierals from Delaware River	
pH	% ads	pH	% ads	pH	% ads
2.74	94.21	3.20	98.01	3.50	81.46
3.51	90.13	3.54	99.59	2.40	84.62
6.40	78.69	6.07	99.59	6.25	74.37
7.32	64.80	6.32	72.80	7.13	68.07
7.89	58.26	6.55	68.07	7.90	62.55
3.61	87.67	6.63	54.67	3.81	87.77
4.85	81.14	7.61	49.15	3.34	89.35
7.49	63.16	9.67	28.66	8.74	26.30
8.13	28.03	10.30	6.60	9.92	12.11
9.59	0.00	11.03	0.00	10.76	0.00

Downer loamy sand		Boonton Union loam		Dunellen sandy loam	
pH	% ads	pH	% ads	pH	% ads
2.59	23.45	2.79	97.36	2.80	84.62
3.05	86.67	3.12	96.43	2.62	83.04
5.96	83.88	3.54	92.70	6.33	68.85
7.33	0.00	5.32	93.63	7.50	42.85
7.83	0.00	6.32	84.32	7.83	39.70
3.29	83.88	3.19	97.36	3.81	85.40
3.87	81.10	3.78	96.43	4.70	81.46
7.87	0.00	6.37	84.32	7.86	34.97
8.93	1.13	8.34	0.00	9.25	13.69
10.15	0.00	10.45	0.00	10.84	0.00

Birdsboro silt loam		Hazen gravelly loam		Boonton Bergen County loam	
pH	% ads	pH	% ads	pH	% ads
2.82	50.41	2.97	34.61	2.67	71.22
3.58	81.10	4.24	41.11	3.04	71.99
6.73	75.52	6.91	56.92	3.93	66.59
7.29	0.00	7.33	36.46	5.92	65.05
7.49	3.92	7.65	16.01	7.15	19.58
3.99	81.10	5.19	64.36	3.32	78.93
5.45	86.67	6.34	63.43	4.05	78.93
7.36	0.00	7.80	0.00	7.49	11.10
8.53	1.13	8.29	0.00	8.25	11.87
9.67	0.00	9.67	0.00	9.11	0.00

Table 3.2.2 Adsorption edge data for As(V) on fifteen New Jersey Soils. Initial As(V) concentration = 0.75 ppm; soil:water = 1 g 100 mL^{-1}; I = 0.01 M $NaNO_3$; T = 25 ± 2°C.

Sassafras sandy loam		Lakewood sand		Penn silt loam	
pH	% ads	pH	% ads	pH	% ads
7.50	10.80	7.56	0.00	7.15	28.06
2.70	41.26	2.75	15.93	2.84	41.77
3.29	38.87	6.05	40.18	3.42	42.36
4.01	37.68	3.34	26.84	3.59	42.36
5.89	34.69	4.85	48.07	4.29	38.79
6.32	28.12	7.77	0.00	6.53	34.61
7.80	0.00	9.79	0.00	7.59	20.31
8.94	0.00	10.28	0.00	9.78	4.81
9.97	0.00	11.00	0.00	10.49	0.00
4.71	35.89	3.43	37.15	5.05	37.00

Whippany silt clay loam		Washington loam		Freehold sandyloam (A horizon)	
pH	% ads	pH	% ads	pH	% ads
6.36	31.09	7.26	0.00	7.72	25.67
3.06	39.58	3.10	31.70	2.73	41.17
3.64	43.22	3.54	34.09	3.05	42.36
2.94	26.84	4.17	37.08	3.83	43.55
6.38	41.40	5.35	23.94	6.65	37.00
6.97	20.78	6.69	19.16	7.63	30.44
8.92	0.00	7.31	0.00	9.09	16.13
10.09	0.00	8.01	0.00	10.2	2.42
11.02	0.00	10.14	0.00	11.02	0.00
4.31	53.52	4.87	29.32	5.14	48.92

Freehold sandyloam (B horizon)		Rockaway stony loam		Fill matierals from Delaware River	
pH	% ads	pH	% ads	pH	% ads
7.14	28.06	7.50	22.83	7.26	15.75
2.75	41.77	2.70	32.27	3.10	32.27
3.17	45.34	3.29	32.86	3.54	36.99
4.04	48.92	4.01	34.63	4.17	36.99
6.91	34.02	5.89	30.50	5.35	38.76
7.52	17.33	6.32	27.55	6.69	22.24
8.59	0.00	7.80	9.85	7.31	5.13
9.47	0.00	8.94	0.00	8.01	0.00
10.89	0.00	9.97	0.00	10.14	0.00
5.25	52.50	4.71	29.32	4.87	29.91

Downer loamy sand		Boonton Union loam		Dunellen sandy loam	
pH	% ads	pH	% ads	pH	% ads
5.06	18.40	5.76	38.97	7.25	20.47
2.75	0.00	3.22	65.65	2.89	35.22
3.01	10.82	3.70	77.17	3.59	39.94
3.29	15.49	4.11	69.90	3.72	42.30
6.14	0.00	4.75	63.23	6.52	38.76
7.94	0.00	5.97	43.22	7.60	28.14
10.28	0.00	7.86	20.17	8.24	18.11
10.86	0.00	8.86	0.00	9.85	0.00
11.34	0.00	10.24	0.00	10.05	0.00
3.96	35.31	4.34	69.90	5.14	32.86

Birdsboro silt loam		Hazen gravelly loam		Boonton Bergen County loam	
pH	% ads	pH	% ads	pH	% ads
6.63	25.40	6.72	12.57	7.25	0.00
5.03	40.56	3.14	31.81	2.89	38.27
3.45	34.15	4.03	32.40	3.59	37.08
4.11	28.90	5.17	31.23	3.72	40.66
5.85	29.48	6.44	28.32	6.52	27.52
7.78	0.00	7.26	0.00	7.60	4.23
9.14	0.00	9.61	0.00	8.24	0.00
10.46	0.00	10.58	0.00	9.85	0.00
11.28	0.00	11.32	0.00	10.05	0.00
		8.04	0.00	5.14	41.86

4.1 Raw Data for Adsorption isotherm of As(III) and As(V)

4.1 Adsorption isotherm for As(III)

Adsorption of As(III) and As(V) has been elucidated in Chapter 4 of the final report Part II. The following is a list of the raw experimental data for adsorption isotherm of both As(III) and As(V) on fifteen New Jersey soils at the natural soil pH.

Table 4.1.1 Adsorption isotherm data for As(III) on fifteen New Jersey Soils. Soil:water = 0.4 g 40 mL^{-1}; I = 0.01 M $NaNO_3$; T = 25 ± 2°C.

Sassafras sandy loam pH = 5.78		Lakewood sand pH = 4.18		Penn silt loam pH =4 .76	
C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)
0.5010	0.0249	0.2419	0.0503	0.4449	0.0305
0.5331	0.0467	0.2633	0.0631	0.5625	0.0438
0.7281	0.0522	0.3167	0.0664	0.7308	0.0519
0.8643	0.0636	0.4075	0.0834	0.8964	0.0604
1.1715	0.0828	0.5010	0.0979	1.2998	0.0700
1.8287	0.1171	0.7415	0.1231	1.8901	0.1110
3.6399	0.1360	0.7575	0.1727	3.5384	0.1462
5.1786	0.2321	1.3398	0.1617	4.2089	0.3291
		3.1323	0.1770	8.7903	0.6210
		5.5419	0.1847	36.5592	1.3441
				57.6363	1.7364
				122.4169	2.7583
				162.5142	3.7486

Whippany silt clay loam pH = 6.16		Washington loam pH = 6.03		Freehold sandyloam (A horizon) pH = 5.22	
C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)
0.4262	0.0324	0.3194	0.0431	0.3701	0.0380
0.5384	0.0462	0.4396	0.0560	0.4396	0.0560
0.6293	0.0621	0.4984	0.0752	0.5732	0.0677
0.7976	0.0702	0.6560	0.0844	0.7628	0.0737
1.1235	0.0877	0.9365	0.1064	1.0914	0.0909
1.7432	0.1257	1.4013	0.1599	1.6177	0.1382
3.0255	0.1975	2.4057	0.2594	2.8385	0.2162
4.5856	0.2914	4.7672	0.2733	4.5936	0.2906

Freehold sandyloam (B horizon) pH = 6.44		Rockaway stony loam pH = 4.69		Fill matierals from Delaware River pH = 4.77	
C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)
0.3594	0.0391	0.3621	0.0388	0.3781	0.0372
0.4984	0.0502	0.5277	0.0472	0.4663	0.0534
0.6480	0.0602	0.6907	0.0559	0.6506	0.0599
0.7842	0.0716	0.8750	0.0625	0.8777	0.0622
1.1181	0.0882	1.2383	0.0762	1.1181	0.0882
1.5616	0.1438	1.3105	0.1690	1.5028	0.1497
2.6301	0.2370	0.7361	0.4264	2.6996	0.2300
4.6630	0.2837	4.9115	0.2589	4.6123	0.2888
		7.8687	0.7131		
		31.7507	1.8249		
		50.7842	2.4216		
		124.7384	2.5262		
		161.0369	3.8963		

Downer loamy sand pH = 4.74		Boonton Union loam pH = 5.14		Dunellen sandy loam pH = 5.57	
C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)
0.5625	0.0188	0.0469	0.0702	0.4957	0.0254
0.7014	0.0299	0.0442	0.0838	0.7334	0.0267
0.8750	0.0375	0.0709	0.0928	0.8884	0.0362
1.0727	0.0427	0.0709	0.1178	1.1288	0.0371
1.4200	0.0580	0.1431	0.1354	1.4574	0.0543
1.9275	0.1072	0.1912	0.1805	2.3042	0.0696
3.7227	0.1277	0.3274	0.2145	3.5651	0.1435
5.5446	0.1955	0.4342	0.2557	5.4618	0.2038
		0.8991	0.4083	9.7520	0.5248
		1.7673	0.5697	36.7194	1.3281
				58.1972	1.6803
				164.2025	3.5798

Birdsboro silt loam pH = 5.69		Hazen gravelly loam pH = 6.06		Boonton Bergen County loam pH = 5.12	
C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)
0.4182	0.0332	0.3781	0.0372	0.4663	0.0284
0.5144	0.0486	0.4449	0.0555	0.5678	0.0432
0.6800	0.0570	0.6560	0.0594	0.7228	0.0527
0.8911	0.0609	0.8777	0.0622	0.8269	0.0673
1.2036	0.0796	1.1368	0.0863	1.2517	0.0748
1.7940	0.1206	1.8234	0.1177	1.8741	0.1126
3.2365	0.1763	2.9213	0.2079	3.6185	0.1381
5.2507	0.2249	4.9836	0.2516	4.4707	0.3029
				8.7101	0.6290
				32.5120	1.7488
				52.7877	2.2212
				113.5533	3.6447
				151.3292	4.8671

4.2 Adsorption isotherm for As(V)

Table 4.2.1 Adsorption isotherm data for As(V) on fifteen New Jersey Soils. Soil:water = 0.4 g 40 mL^{-1}; I = 0.01 M $NaNO_3$; T = 25 ± 2°C.

Sassafras sandy loam pH = 5.78		Lakewood sand pH = 4.18		Penn silt loam pH = 4.76	
C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)
0.0148	0.0735	0.1357	0.0606	0.0603	0.0690
0.2125	0.0787	0.1963	0.0700	0.1377	0.0862
0.2633	0.0987	0.2016	0.0794	0.1751	0.1075
0.3808	0.1119	0.2913	0.0953	0.1992	0.1301
0.4262	0.1574	0.3783	0.1114	0.3301	0.1670
0.6132	0.2387	0.5259	0.1435	0.5705	0.2430
1.4868	0.3513	0.6446	0.1843	0.9952	0.4005
1.9275	0.5572	0.8133	0.2149	1.8875	0.5613
4.6630	1.0337	1.6570	0.3310	3.0201	1.1980
15.2016	3.4798	2.5692	0.4879	14.9611	3.5039
23.6164	5.1384	0.6867	1.4600	26.7419	4.8258
51.2971	9.8703	8.4381	4.2393	43.9108	10.6089
73.2451	12.6755	18.2854	5.7849	70.5016	12.9498
		35.8393	11.6444		
		33.3399	16.9993		

Whippany silt clay loam pH = 6.16		Washington loam pH = 6.03		Freehold sandyloam (A horizon) pH = 5.22	
C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)
0.1457	0.0604	0.1805	0.0570	0.1110	0.0639
0.1644	0.0836	0.1965	0.0804	0.2099	0.0790
0.2072	0.1043	0.1831	0.1067	0.2660	0.0984
0.2820	0.1218	0.3114	0.1189	0.3060	0.1194
0.4075	0.1592	0.4610	0.1539	0.4930	0.1507
0.5064	0.2494	0.6773	0.2323	0.7308	0.2269
1.0326	0.3967	1.4093	0.3591	1.4814	0.3519
1.9596	0.5540	2.2668	0.5233	1.9649	0.5535
3.3407	1.1659	3.2606	1.1739	3.1403	1.1860
14.8810	3.5119	12.7973	3.7203	8.7502	4.1250
23.6565	5.1344	20.2104	5.4790	17.8462	5.7154
66.7029	8.3297	61.2159	8.8784	19.8524	13.0148
		60.5828	13.9417	41.3783	15.8622

Freehold sandyloam (B horizon) pH = 6.44		Rockaway stony loam pH = 4.69		Fill matierals from Delaware River pH = 4.77	
C_W (mg/L)	C_S (mg/g)	C_W (mg/L)	C_S (mg/g)	C_W (mg/L)	C_S (mg/g)
0.0790	0.0671	0.0790	0.0671	0.1057	0.0644
0.0549	0.0945	0.0496	0.0950	0.1618	0.0838
0.0709	0.1179	0.0522	0.1198	0.1965	0.1054
0.1377	0.1362	0.0629	0.1437	0.2392	0.1261
0.2526	0.1747	0.1003	0.1900	0.4182	0.1582
0.4690	0.2531	0.2526	0.2747	0.6025	0.2397
0.9685	0.4031	0.8483	0.4152	1.1849	0.3815
1.6497	0.5850	1.0460	0.6454	2.0397	0.5460
3.2205	1.1780	3.4609	1.1539	2.3389	1.2661
8.4297	4.1570	13.7590	3.6241	11.2346	3.8765
16.6842	5.8316	21.3724	5.3628	19.4891	5.5511
24.0732	12.5927	43.4887	10.6511	19.8524	13.0148
32.3037	16.7696	64.3815	13.5619	35.4692	16.4531

Downer loamy sand pH = 4.74		Boonton Union loam pH = 5.14		Dunellen sandy loam pH = 5.57	
C_W (mg/L)	C_S (mg/g)	C_W (mg/L)	C_S (mg/g)	C_W (mg/L)	C_S (mg/g)
0.1778	0.0572	0.0355	0.0714	0.1564	0.0594
0.2152	0.0785	0.0593	0.0831	0.2099	0.0790
0.2766	0.0973	0.0724	0.0926	0.3568	0.0893
0.2980	0.1202	0.0830	0.1165		
0.4823	0.1518	0.1173	0.1380	0.4930	0.1507
0.6079	0.2392	0.2227	0.1773	0.8403	0.2160
1.3292	0.3671	0.2886	0.2206	1.5482	0.3452
2.0584	0.5442	0.3387	0.2655	1.5883	0.5912
4.9435	1.0056	0.7421	0.4243	5.0237	0.9976
18.6476	3.1352	1.4355	0.6036	18.0466	3.1953
25.4997	4.9500	2.9014	1.2099	27.0224	4.7978
61.0049	8.8995	14.1725	3.5828	55.7289	9.4271
92.6606	10.7339	22.7147	5.2285	70.0795	12.9921
		46.4617	10.3538		
		66.2487	13.3751		

Birdsboro silt loam pH = 5.69		Hazen gravelly loam pH = 6.06		Boonton Bergen County loam pH = 5.12	
C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)	C_w (mg/L)	C_s (mg/g)
0.0950	0.0655	0.2473	0.0503	0.2686	0.0481
0.2232	0.0777	0.2419	0.0758	0.2579	0.0742
0.2232	0.1027	0.3221	0.0928	0.3060	0.0944
0.3087	0.1191	0.3915	0.1108	0.3140	0.1186
0.4556	0.1544	0.5678	0.1432	0.5064	0.1494
0.8296	0.2170	0.8643	0.2136	0.7067	0.2293
1.3532	0.3647	1.6364	0.3364	0.9872	0.4013
1.8714	0.5629	2.2641	0.5236	1.4627	0.6037
4.2222	1.0778	5.0237	0.9976	3.4609	1.1539
9.6318	2.0368	13.5988	3.6401	8.1492	2.1851
14.8810	3.5119	21.9735	5.3027	12.8374	3.7163
26.0206	4.8979	57.4172	9.2583	20.8114	5.4189
33.6340	6.6366	79.3652	12.0635	31.9110	6.8089
43.0666	8.1933			33.7809	9.1219
54.4627	9.5537			54.4627	9.5537
74.3003	12.5700			77.4658	12.2534