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**SORPTION/DESORPTION AND TRANSPORT
OF MERCURY AND ARSENIC IN NEW JERSEY SOILS**

Year 2

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by

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Chapter 1

INTRODUCTION

Decades of mining, manufacture and disposal of heavy metals and metal-containing materials have caused serious environmental pollution. Many areas near urban complexes, metalliferous mines and major road systems have been found to contain anomalously high concentrations of these metals (Adriano, 1992; Alloway, 1995). Elevated concentrations of heavy metals have also been identified in a large number of waters and biota (Lindqvist *et al.*, 1991; Kerndorff *et al.*, 1992). The pernicious effects of these metals become more evident with time as their accumulation in food chain continuously increases. Such delayed effects of chemicals released to the environment was subtly called 'chemical time bombs' (Alloway, 1995).

Mercury is one of the most useful and also most toxic heavy metals. People began to use Hg 3500 years ago (Nriagu, 1979). The early use of Hg was mainly limited to the manufacture of amalgams and medicines. Later on the Hg barometer and thermometer were invented in 1643 and 1720, respectively. By the turn of this century, Hg was mainly used to recover Au and Ag and to make fulminate and vermilion. Beginning from this century, a number of new applications of Hg have been found in industries and in agriculture. The consumption of Hg thus significantly increased. It is estimated that the annual anthropogenic release of Hg on a global basis was about 3×10^6 kg around the year 1900, and had increased to about three times that

amount during the 1970s (Andren and Nriagu, 1979). During last 20 years, Hg applications in agriculture, pharmaceuticals and general laboratory practice have declined. However, the uses in industries and dental fillings are still substantial (Steinnes, 1995). At present, the major Hg consumption areas include agriculture, chloralkali industry, dental preparations, electrical apparatus (batteries and others), general laboratory use, measuring and control apparatus, pharmaceuticals, paints (antifouling and mildew-proofing), and redistilled processes (U.S. Bureau of Mines, 1984).

Occupational Hg poisoning, e.g., in miners, has been documented for centuries (Steinnes, 1995). Mercury environmental pollution, however, was detected and caused increasing concern only during the recent decades. The first known case occurred in Minamata, Japan in the 1950s (Tsu Baki and Iru Kayama, 1977). About 150 people were poisoned by consumption of fish contaminated with high level of Hg released from a chloralkali plant. Later on, several cases of human and wildlife poisoning from methylmercury treated seeds were reported (Lindqvist et al., 1984). Extensive investigation conducted since then has shown that elevated Hg levels in fish were widespread globally (Lindqvist *et al.*, 1991).

Hg seems not a major problem with respect to phytotoxicity (Adriano, 1986). The levels at which toxicity symptoms are apparent are far above those encountered under normal conditions. However, high concentration of Hg in soil poses great potential for ground and surface water contamination. Recent studies concerning the cause of mercury contamination of fish have indicated that the soil system is a significant and sometimes even dominant source of mercury supply to lakes and

watercourses (Schlüter, 1993). Although the form of Hg in fish is primarily methylmercury (Stokes et al., 1987), inorganic Hg is generally considered to provide substrate for methylation (Robertson et al., 1987), especially in anoxic environments (Bennett et al., 1985; Gilmour and Henry, 1991).

Arsenic is another notorious element whose several compounds are very toxic. Humankind has been using arsenic for several thousand years. The major uses of arsenic today are as pesticides, wood preservatives, and as growth promoters for poultry and pigs (O'Neill, 1995). Arsenic differs from many of the common heavy metals in that the majority of the organo As compounds are less toxic than are inorganic As compounds. Among inorganic arsenic compounds, As(III) species are very toxic, while As(V) species are less toxic.

Whether the Hg and As applied to soils will be leached to surface and groundwater mainly depends on their retention and release behaviors in soils. The purpose of this study was to obtain quantitative information about the behavior of Hg and As in fifteen New Jersey soils with respect to sorption, desorption and the reaction kinetics. The preliminary results are presented in this report. Chapter 2 to chapter 5 presented the results regarding the sorption and desorption behavior of Hg on soils. Chapter 6 reported the development of a method for determination of As.

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Chapter 2

LITERATURE REVIEW

2.1 Origin of Mercury in Soil

Natural source of Hg in soils is their parent rocks. The average crustal Hg concentration is about 20 ng g^{-1} (Steinnes, 1995). Igneous rocks generally contain very low level of Hg (about 10 ng g^{-1}). Some sedimentary rocks, such as sandstones and limestones, contain same level of Hg as igneous rocks, while the concentration of Hg in shales covers a wide range (Henriques, 1973; Connor and Shacklette 1975). It is believed that one of the important factors responsible for the concentration fluctuation of Hg in shales is the organic matter content (Cameron and Jonasson, 1972; McNeal and Rose, 1974). Rocks formed from volcanic debris or deposited near volcanic areas have more Hg. Rocks deposited in a reducing environment also contain high level of Hg due to the presence of S (Steinnes, 1995). The major Hg-bearing primary minerals are cinnabar (HgS) and livingstonite (HgSb_4S_7).

Some Hg that is present in soils came from atmospheric deposition. It is generally believed that more than 90% of the total atmospheric Hg are volatile species, in which Hg^0 is the predominant form (Johnson and Braman 1974; Slemr *et al.*, 1981; Iverfeldt and Lindqvist, 1986). Brosset (1981) suggested that Hg^0 is eventually oxidized into water-soluble forms in atmosphere, which are subsequently scavenged by wet or dry deposition. Typical concentrations of Hg in precipitation at remote areas

is estimated to be of the order of 2 to 10 ng L⁻¹, while levels in more polluted areas may be of the order of 5 times higher (Steinnes, 1995).

Besides the above two sources, considerable Hg is directly added to soils by human in forms of fertilizers, lime, manures, and sewage sludge (Andersson, 1979). Most commercial fertilizers have a Hg content of less than 50 ng g⁻¹, however, as high as more than 300 ng g⁻¹ Hg was found in P fertilizers (Frank et al., 1976; Andersson, 1977). Manure contains a higher level of Hg (30-360 ng g⁻¹ with a average of 90 ng g⁻¹). The concentration of Hg in lime for agriculture purposes ranges from less than 5 to 20 ng g⁻¹. Sewage slugs from wastewater treatment plants contain a wide range of Hg from 0.1 to 55 ng g⁻¹ (Allaway, 1995). It is estimated that the added amount of Hg to soil is typically of the order of 50 mg m² (Steinnes, 1995).

Depending on the soil origin and environmental and agricultural conditions, the Hg contents in soils spans several orders of magnitude. Steinnes (1995) searched literature on the Hg contents in soils of seven countries and reported a concentration range of 5 to 4600 ng g⁻¹ for various kinds of uncontaminated soils. The average concentration for different kinds of soils vary from 20 to 188 ng g⁻¹. Generally, organic soils have higher Hg contents than do mineral soils (John *et al.*, 1975; Frank *et al.*, 1976). In the vicinity of Hg mines and Hg-using industry sites, the soil contents of Hg can be much higher than those contained in uncontaminated soils. For example, 1 to 10 mg kg⁻¹ Hg were found in soils 0.5 km from a chloralkali plant (Bull *et al.*, 1977). The contents of Hg in soils around Hg mines can be as high as 100 mg kg⁻¹ (Lindberg et al., 1979; Morishita et al., 1982).

2.2 Aqueous Speciation of Mercury(II) and Methylmercury

Inorganic mercury may occur in three different valency states in the environment, namely Hg(0), Hg(I), and Hg(II). Under soil redox potential conditions which usually range from -0.4 to 0.8 v, Hg(I) does not occur as a stable species (Schlüter, 1993). Most of the Hg(0) goes to the atmosphere, and only little dissolves in aqueous solution according to Henry's law (Sanemasa, 1975). Hg(II) is therefore the dominant state in soil solution.

Due to the strong Lewis acid nature, Hg(II) rarely occurs as the free ionic form under natural conditions. As indicated in Figure 2.1 which is calculated based on the stability constants in Table 2.1 using the MINEQL⁺ computer program (Schecher and McAvoy; 1991), hydroxo Hg species begin to form at about pH 2 and become predominant at pH greater than 3. In the presence of Cl⁻ (which is a common ion in soil solution), Hg tends to form stable complexes with Cl⁻ at low pH, which eventually are replaced with hydroxo Hg species at higher pH. Increases in Cl⁻ concentration increase the pH value at which hydroxo Hg species become predominant over Hg-Cl complexes.

Under anaerobic conditions where S²⁻ is available, most soluble Hg precipitates together with S²⁻ due to the strong affinity of Hg for S (Fagerström and Jernelöv, 1972) and the extremely low solubility of HgS. In strongly alkaline soils the soluble HgS₂²⁻ ion will form. If the soil condition changes to aerobic, the HgS precipitate will be physicochemically oxidized to soluble Hg(II) species (Jensen and Jernelöv, 1972, Kromer et al., 1981).

Table 2.1 Aqueous equilibria of Hg(II)

| Equilibrium Reactions | Log K^a I = 0.1 M | Log K^a I = 0.01 M | Log K^b I = 0 |
|---|------------------------|-------------------------|--------------------|
| $\text{Hg}^{2+} + \text{H}_2\text{O} = \text{HgOH}^+ + \text{H}^+$ | -3.65 | -3.49 | |
| $\text{Hg}^{2+} + 2\text{H}_2\text{O} = \text{Hg}(\text{OH})_2 + 2\text{H}^+$ | -6.42 | -6.26 | |
| $\text{Hg}^{2+} + 3\text{H}_2\text{O} = \text{Hg}(\text{OH})_3^- + 3\text{H}^+$ | -21.10 | -21.10 | |
| $\text{Hg}^{2+} + \text{H}_2\text{O} = \text{HgO} + 2\text{H}^+$ | -2.81 | -2.65 | |
| $\text{Hg}^{2+} + \text{OH}^- + \text{Cl}^- = \text{HgOHCl}$ | 3.57 | -3.87 | |
| $\text{Hg}^{2+} + \text{Cl}^- = \text{HgCl}^+$ | 6.72 | 7.02 | |
| $\text{Hg}^{2+} + 2\text{Cl}^- = \text{HgCl}_2$ | 13.24 | 13.70 | |
| $\text{Hg}^{2+} + 3\text{Cl}^- = \text{HgCl}_3^-$ | 14.32 | 14.78 | |
| $\text{Hg}^{2+} + 4\text{Cl}^- = \text{HgCl}_4^{2-}$ | 14.93 | 15.23 | |
| $\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} = \text{CH}_3\text{HgOH} + \text{H}^+$ | | | -4.63 |
| $\text{CH}_3\text{Hg}^+ + \text{Cl}^- = \text{CH}_3\text{HgCl}$ | | | 5.25 |
| $\text{CH}_3\text{Hg}^+ + \text{S}^{2-} = \text{CH}_3\text{HgS}^-$ | | | 21.02 |

^aBaes and Mesmer (1976).

^bStumm and Morgan (1981).

Perhaps a large amount of soluble Hg(II) in soil is associated with the dissolved organic matter. Although no direct information on Hg speciation in soil pore water is available, the studies on Hg in river water have indicated that most of the soluble Hg may be present as organic complexes (Peng and Wang; 1982). Moreover, many studies on the origin of Hg in natural lakes have suggested that humic materials transferred Hg from soils to lakes (Surma-Aho et al., 1985).

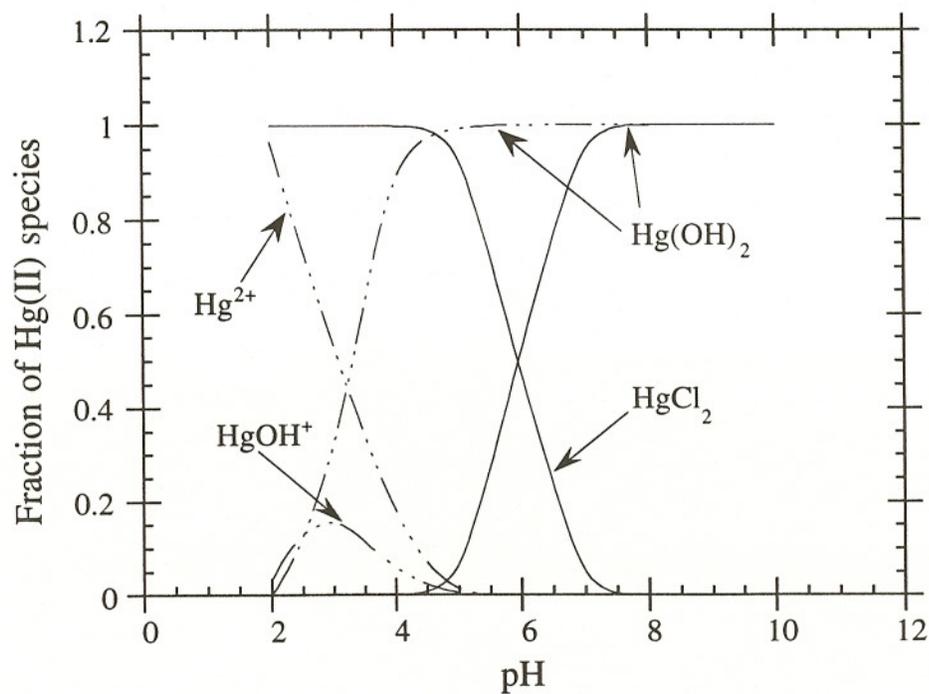


Figure 2.1 Hg(II) speciation as a function of pH and Cl^- concentration. Dashed lines refer to the absence of Cl^- ; solid lines denote a Cl^- concentration of 10^{-4} M.

Methylmercury in aqueous solution acts as a soft acid and has a strong tendency to bind with S^{2-} , OH^- , Cl^- . In the presence of Cl^- , CH_3HgCl is predominant at low pH (Figure 2.2). Increases in pH result in an increase of the fraction of CH_3HgOH , which eventually becomes the predominant species. In the presence of S^{2-} or organic matter, CH_3Hg^+ will prevail as CH_3HgS complex or bound to the S group of organic matter (Baughman et al., 1973).

2.3 Sorption, Desorption, and Transformation Reactions of Hg(II) and Methylmercury in Soils

2.3.1 General Theory of Metal Sorption and Desorption on Soils

Extensive research has been done to investigate the factors controlling metal retention on and release from soils. Among these factors, pH is one of the most important. For example, Christensen (1989) determined the distribution coefficients for 63 Danish agricultural soils and found that the distribution coefficients correlated very well with soil pH ($r = 0.72$). pH affects the sorption of metals from pore water by affecting both soil solid surface charge and soluble metal speciation. Increases in pH weaken proton competitive binding and increase surface potential, which consequently increase both electrostatic and specific binding of metals to solid surface. In addition, increases in pH may result in the formation of hydroxo metal species. The sorption of metals on solid surface have frequently been reported to significantly increases as hydroxo species became predominant (James and Healy, 1972; Tewari and Lee, 1975; Elliott *et al.*, 1986, Huang *et al.*, 1986). James and Healy (1972) suggested that this resulted from the smaller solvation energy of hydroxo metal species than that of aquo

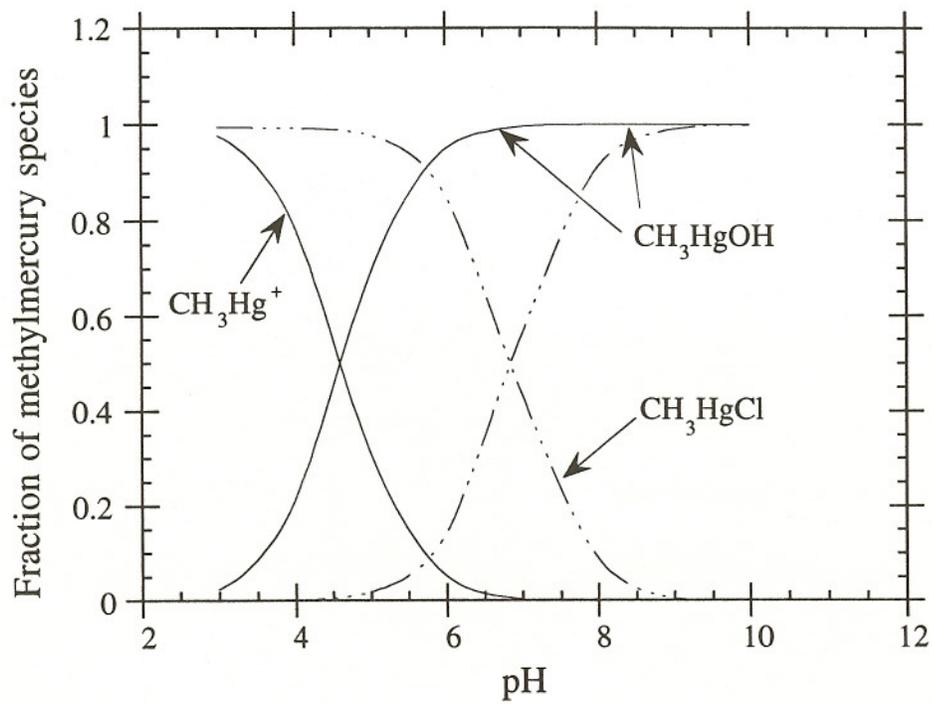


Figure 2.2 Methylmercury speciation as function of pH and Cl^- concentration. Solid lines refer to the absence of Cl^- ; dashed lines denote a Cl^- concentration of 10^{-4} M

species. Tewari and Lee (1975) further observed that following the adsorption of MOH^+ , M(OH)_2 precipitate, which would not occur in bulk solution, formed on solid surface.

For a given pH value, increasing metal loading results in increases in sorption. The surface sorption energy, however, decreases with increasing surface coverage. This results in the fractional sorption of the added metal to decrease. The sorption behavior as a function of metal loading can usually be described by equation 2.1 (Sposito, 1985).

$$q(c) = \sum_{i=1}^n \frac{b_i k_i^{\beta_i} c^{\beta_i}}{1 + B_i C_i^{\beta_i}} \quad (2.1)$$

where $q(c)$ is the amount of solute adsorbed, c is the concentration of solute in solution, b_i , B_i , k_i , β_i ($i = 1, \dots, n$) and n are adjustable parameters.

Soil composition is also very important in determining the retention of metals on soils. Some ligands which are present in soil solution at certain environmental conditions, including hydroxide, carbonate, silicate, phosphate, and sulfide, are important to the precipitation of metal ions. Some inorganic ligands, such as Cl^- , and organic ligands can form soluble complexes with metals. The complexation of metals by ligands could increase, decrease or not change metal sorption (Vuceta, 1976). This is suggested to mainly depend on the adsorbability of the complexed metal ions (Elliott and Huang, 1979, 1980; Huang and Lin, 1981).

Soil 2:1 clay minerals, such as smectite and vermiculite, bear permanent charge in the interlayer and are important natural ion exchange materials. In surficial soils,

the clay minerals are generally coated with metal oxides (Jenne, 1988) and organic matter (Hart, 1982; Davis, 1984). These soil phases constitute the most important metal-binding components. For example, in a recent studies Lee et al. (1996) have shown that organic matter is the most important soil component controlling metal partitioning at fixed pH. The partitioning of Cd(II) to soil can be predicted to a very high degree ($r^2 > 0.9$) by considering the organic matter normalized partition coefficient (K_{om}) as a function of pH. This work suggests that soils are coated by organic matter and that other sorption phases, such as iron and manganese oxides, serve to store contaminants (Allen and Yin, 1996).

Background electrolyte in pore water can also affect the partition of metals to soil. Zachara *et al.* (1993) investigated Cd(II) sorption on specimen and soil smectites in sodium and calcium electrolytes and found that ion exchange dominated Cd sorption at low ionic strength in Na^+ electrolyte. Increasing Na^+ concentration to 0.1 M or changing the electrolyte to Ca^{2+} at ionic strength of 0.003 to 0.006 M suppressed Cd ion exchange.

The retention and release reactions of metals with soil or soil components have been frequently characterized by a fast step followed by a slow step (Sparks, 1989). The fast step usually involves the reaction on solid surfaces, while the slow reaction involves the penetration of metals into the mineral lattice (Kou, 1986; White and Yee, 1986; Bruemmer et al., 1988) or diffuse through intraparticle pores (Avotins, 1975; Sparks et al., 1980).

2.3.2 Sorption and Desorption of Hg(II) on Soils

Significant effort has been made to investigate the sorption behavior of Hg(II) on soils and soil components. A comprehensive review of the early knowledge about Hg in soils was given by Andersson in 1979. Recently, Schuster (1991) reviewed the literature regarding the behavior of Hg in soil with emphasis on complexation and adsorption processes. Another review dealing with the turnover and translocation of natural soil Hg and the Hg deposited from the atmosphere was given by Schlüter (1993). Both soil minerals, especially clay minerals and oxides (Fe, Al, and Mn oxides, hydroxides and oxihydroxides), and organic matter have been found to strongly adsorb Hg.

Obukhovskaya (1982) reported that the sorption of Hg(II) by kaolinite, vermiculite-chlorite, montmorillonite and iron oxide reached equilibrium within 10 to 30 minutes, and the increase in sorption within one month was insignificant. This suggested that Hg(II) mainly sorbed on mineral surface and practically did not penetrate into the mineral structure or interlayer. Compared to clay minerals, iron oxide has a higher sorption capacity. $\text{Hg}(\text{OH})_2(\text{aq})$ seems play the main role in Hg sorption on these minerals.

The relative sorption capacity of various clay minerals for Hg(II) is different for different studies (Schlüter, 1993). The capacity sequence does not follow the CEC. This might also be an indication that ion exchange does not dominate the sorption of Hg(II) on clay minerals. Typically, Hg(II) sorption on clay minerals is highly pH dependent. Obukhovskaya (1982) reported that sorption of Hg(II) on kaolinite, vermiculite-chlorite, and montmorillonite increased with pH and reached maximum at

pH above 6. Newton (1976) observed that Hg(II) sorption on bentonite reached a maxima in a pH range of 4 to 5. A further increase in pH decreased sorption. Varying the concentration of background electrolyte $\text{Ca}(\text{NO}_3)_2$ only slightly affected sorption.

Mercury(II) sorption on oxides usually reaches a maximum at low pH, in the range of 3 to 5, and then decreases with increasing pH. Kinniburgh and Jackson (1978) examined the sorption of Hg(II) on freshly prepared iron hydrous oxide gel and found that sorption maxima was attained at about pH 5. From pH 5 to 6.5, sorption remained constant at about 94%. Above pH 6.5 there is a slight decrease in sorption, for example from 95% at pH 6.45 to 91.6% at pH 8.6. Similar results were reported by Obukhovskaya (1982). He observed that Hg(II) sorption on iron hydroxide achieved a maximum value at pH about 6 and then slightly decreased. In a more recent study, Barrow and Cox (1992) reported that the maximum sorption of Hg(II) by goethite occurred at pH around 4. Further increases in pH decreased sorption to a small extent.

Manganese oxide also exhibits a large sorption capacity for Hg(II). Lockwood and Chen (1973) observed that Hg(II) sorption on MnO_2 remained constant between pH 4 and 10 with decreases in sorption at both ends of the 2 to 11 pH range used. $\text{Al}(\text{OH})_3$ seems to be a very inefficient Hg(II) sorbent (Andersson, 1979). Sand exhibits some weak sorption sites for Hg(II) (McNaughton and James, 1974; Lodenius *et al.*, 1987).

The reason for Hg(II) sorption maxima on oxides occurring in a low pH range was attributed to the formation of Hg hydroxides. The species $\text{Hg}(\text{OH})_2$ is believed to bind strongly with solid surfaces via double hydrogen bonding (Forbes *et al.*, 1974;

Obuskhovskaya, 1982). No satisfactory explanation for the decreases of sorption at higher pH has been presented. One possible reason could be the formation of $\text{Hg}(\text{OH})_3$. The dispersion of particles at higher pH could also retain some fine colloid ($< 0.45 \mu\text{m}$) - associated Hg in solution.

In the presence of Cl^- in solution, Hg-Cl complexes become predominant at low pH values. Unlike other metals, such as Cu, Pb, Zn, and Cd, whose sorption on oxides can be enhanced by the presence of Cl^- (Quirk and Posner, 1975; Kinniburgh and Jackson, 1978), the complexation of Hg by Cl^- significantly decreased Hg sorption (McNaughton and James, 1974; Kinniburgh and Jackson, 1978; Newton *et al.*, 1976; Barrow and Cox, 1992). This probably resulted from the linear configuration of Hg-Cl complexes which makes multidentate ligand bonding to solid surfaces difficult (Kinniburgh and Jackson, 1978). As pH increases to a value where Hg-OH species become predominant over Hg-Cl species, sorption increases significantly.

The evidence suggests that soil organic matter strongly sorbs Hg(II). The most importance sites on organic matter are $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, and $-\text{SH}$ groups. The amount of $-\text{NH}_2$ and $-\text{SH}$ groups are usually limited, however, their bonding with Hg is very strong (Bowen, 1979; Reimers and Krenkel, 1974). Carboxyl and phenolic groups constitute the majority of the binding sites on organic matter. Duffy *et al.* (1989) compared the binding ability of nine metals (Fe^{3+} , Hg^{2+} , Al^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Mg^{2+} , and Ca^{2+}) with the $-\text{COOH}$ groups of acetate and reported that Fe^{3+} and Hg^{2+} form the most stable complexes with $-\text{COOH}$. The interaction of Hg with carboxyl groups is believed to involve the formation of metal carboxylates via hydrogen bonding between HgOH^+ and $\text{Hg}(\text{OH})_2$ and $-\text{COOH}$ (Khan *et al.*, 1985).

Higher Hg concentrations are usually found in organic matter-rich soils (McKeague and Kloosterman, 1974). This may be an indication that organic matter has stronger sorption ability for Hg than soil minerals. Many researchers have investigated the mobility of Hg in soils. It seems that only rather concentrated chlorides or some strong ligands, such as EDTA, can efficiently extract sorbed Hg from soils (Dudas and Pawluk, 1976; Hogg et al., 1978; Harsh and Doner, 1981). However, in most cases, the experiments were conducted using a batch technique or column method, which could underestimate the leachability of Hg in the natural system. In batch desorption, the released solute can not be removed from the system, which could inhibit further release of the solute (Martin and Sparks, 1983). In column study, considerable diffusion is involved, and consequently the experimental time period may not be long enough to leach out the sorbed solute. As a matter of fact, transport of Hg from the top layer of soil to a lower layer and from soil to natural water systems have been observed (Lodenius et al., 1983; Lindqvist et al., 1991).

2.3.3 Sorption and Desorption of Methylmercury on Soils

Little information on the sorption of organo-mercurials to soils and soil components is available. Reimers and Krenkel (1974) observed that a considerable amount of methylmercury was sorbed by clay minerals and fine sands with a sequence of illite > montmorillonite > fine sands, whereas no sorption occurred on kaolinite and coarser sands. The fine sands sorbed methylmercury only at low Cl⁻ concentrations, but at all pH in the range from 5 to 9. This indicates that only CH₃HgOH is adsorbable to the sand surface. Both Cl⁻ concentration and pH affect the sorption of methylmercury on illite and montmorillonite. No satisfactory explanation is available

to explain these effects. Inoue and Aomine (1969) reported that phenylmercurials strongly sorb to montmorillonite, but they only weakly sorb to kaolinite and allophane. The maximum sorption occurred at pH around 6 and significantly decreased at both higher and lower pH values in the range of 4 to 8. This suggests that cation exchange may dominate the sorption of phenylmercurials on clay minerals. Unlike inorganic Hg which is strongly sorbed by all major functional groups of organic matter, methylmercury is only efficiently sorbed to sulfhydryl groups of organic matter. Amine and carboxyl groups are inefficient in binding with methylmercury (Reimers and Krenkel, 1974). In natural soils, sorption of organo-mercury seems to be dominant by clay and organic matter (Hogg *et al.*, 1978a, b).

2.3.4 Transformation of Hg(II) and Methylmercury in Soils

It has been found that some of the inorganic Hg(II) applied to soils can be reduced to Hg⁰ or transformed into methylmercury under suitable conditions. Alberts *et al.* (1974) and Miller (1975) suggested that the reduction of Hg(II) to Hg⁰ occurs chemically in the presence of humic and fulvic acid catalysts and is favored under slightly alkaline to slightly acid aqueous solutions. Skogerboe and Wilson (1981), however, observed that the reduction of Hg(II) to Hg⁰ mediated by fulvic acid decreased sharply above pH 4 when the formation of hydroxo Hg species became pronounced. This seems to indicate that only free Hg²⁺ is available for reduction. Other researchers suggested that the reduction of Hg²⁺ to Hg⁰ is also mediated by microorganisms as means of detoxification, even under aerobic conditions (Jonasson and Boyle, 1972; Landa, 1979; Waldron, 1980).

The transformation of Hg(II) to methylmercury has been reported by many researchers. Generally, the transformation increased with decreasing particle size (Rogers, 1976). Two pathways, an abiotic chemical process and a biological process, are responsible for the methylation of Hg(II) (Rogers, 1977; Tonomura *et al.*, 1972). The reaction largely depends on the availability of Hg(II). Higher concentrations of Hg(II) favor methylation. However, too high a concentration of Hg(II) could hinder the respective biological and abiological processes. In the presence of S²⁻, methylation of Hg(II) is reduced by formation of HgS (Bisogni and Lawrence, 1975; Wood, 1984). In most studies, the methylation reaction was found to be very slow. For example, Rogers (1976) reported that no more than 1% of the incubated Hg (as Hg(NO₃)₂) was methylated in soil in one week.

The methylmercury formed from Hg(II) in soils or applied directly to soils by mankind can disproportionate into Hg⁰ and Hg(II) (Rogers, 1976; Landa, 1979). The mechanisms responsible for demethylation are not well understood (Schlüter, 1993). Demethylation increases with temperature, which favors the microbial activity, and decreases at extreme moisture or dryness, which lowers microbial activity (Landa, 1979). This suggests that a biological process may be one of the pathways for demethylation.

2.4 Objectives of Research

From the above literature review, it is clear that different soil components have quite different sorption ability for Hg(II) and methylmercury. The sorption ability of the same component for Hg still could be different due to its different origin, which

affects the surface characteristics of soil minerals and the functional groups of humic substances. The retention and release behavior of Hg in natural soils, mixtures of these components, is even more complicated, which depends on the interactions among the soil components themselves and between these components and Hg. This behavior is subject to the simultaneous influences of soil composition and environmental conditions. Accordingly, the objectives of this research were:

- 1) To obtain quantitative information on the sorption and desorption of Hg(II) and methylmercury on fifteen representative New Jersey soils ranging in texture from sand to silty clay loam.
- 2) To examine the simultaneous effects of pH, Cl⁻, soil properties, and the Hg concentration levels on the sorption reaction.
- 3) To investigate the kinetics of Hg sorption and desorption on soils and discern the mechanisms controlling the rates of Hg retention on and release from soils.

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Chapter 3

EFFECTS of pH, CHLORIDE, ORGANIC MATTER, and CALCIUM on the SORPTION of MERCURY(II) by SOIL

3.1 Abstract

The effects of pH, Cl^- , and organic matter on Hg(II) sorption from a 1×10^{-7} and 1×10^{-7} M solution by fifteen New Jersey soils were examined to understand the factors responsible for Hg partitioning to soils under different environmental conditions. The maximum extent of sorption ranged from 86% to 98% of the added Hg and occurred in a pH range of 3 to 5 for all soils studied. Increasing the pH above this range significantly decreased the sorption of the added Hg, for example, from $89 \pm 8\%$ at pH 4.0 to $39 \pm 11\%$ at pH 8.5 for an initial Hg concentration of 1×10^{-7} M. An important factor was the complexation of Hg by the dissolved organic matter whose concentration increased with increasing pH. The presence of high concentration of Ca^{2+} (1×10^{-2} M) caused the coagulation of dissolved organic matter, which removed some Hg from solution. The effect of Cl^- on Hg(II) sorption by soil depended on both pH and the soil organic matter content. At circumneutral and higher pH, the addition of Cl^- did not affect the sorption by any soil. The standard deviation of Hg sorption for all soils was less than 4% for Cl^- concentrations from about 1×10^{-6} to 1×10^{-2} M. At about pH 3, the effect of Cl^- on Hg(II) sorption by soil depended on the soil organic matter content. When the Cl^- concentration increased from about 1×10^{-6} to 1×10^{-2} M, sorption by the lowest organic matter soil (1.2 g C kg^{-1}) decreased from 93% to

40% for an initial Hg concentration of 1×10^{-7} M, whereas sorption by the largest organic matter soil (49.9 g C kg⁻¹) decreased only from 95% to 91%.

3.2 Introduction

Sorption has been recognized as one of the important processes determining the fate of trace metal contaminants in soil. Among the factors controlling the sorption of trace metal contaminants, pH is one of the most important (Goldberg and Glaubig, 1987; Christensen, 1989; Zachara et al., 1989). Both the surface charge characteristics of soil particles and metal speciation in solution are affected by pH. Because of its strong affinity for Hg(II) (Baes and Mesmer, 1976), Cl⁻ also could be an important factor affecting the sorption of Hg(II).

MacNaughton and James (1974) found that Hg(II) sorption on SiO₂ increased abruptly in the pH range of 2 to 3 when Cl⁻ was not present in solution. Newton et al. (1976) reported that the maximum sorption of Hg(II) on bentonite clay occurred in the pH range of 4.5 to 5.5 regardless of the initial Hg concentration or the concentration of a Ca(NO₃)₂ electrolyte. Kinniburgh and Jackson (1978) examined Hg(II) sorption by freshly prepared iron hydrous oxide gel and reported that from pH 5 to 8.6, more than 90% of the Hg(II) was adsorbed. Sorption of Hg(II) by goethite was investigated by several researchers. In a recent study, Barrow and Cox (1992a) reported that in the absence of Cl⁻, the sorption maximum was just below pH 4. In all these studies with pure colloids as adsorbents, the addition of Cl⁻ to colloidal suspensions significantly reduced Hg(II) sorption in acidic solutions, and resulted in an increase in the pH at which the sorption maximum occurred.

Andersson (1979) suggested that in acidic soils (pH < 4.5 to 5), the only effective adsorbents for inorganic Hg(II) are organic substances, whereas in neutral soils iron oxides and clay minerals become much more effective. Semu et al. (1987) studied the effect of pH on Hg(II) sorption by tropical soils within a pH range of 5 to 8, and observed that the sorption increased with increasing pH. Barrow and Cox (1992b), however, reported that in the absence of Cl⁻, there was little effect of pH on Hg sorption between pH 4 to 6. Further increase in the pH resulted in a decrease in sorption. Little information on the effect of Cl⁻ on Hg(II) sorption by soils is available. Barrow and Cox (1992b) reported that addition of Cl⁻ decreased Hg(II) sorption on a loamy sand soil at low pH, but had little effect at high pH.

Another well-documented factor that significantly affects the sorption of trace metal contaminants is soil organic matter. Kerndorff and Schnitzer (1980) investigated the sorption of eleven metals (Hg, Fe, Pb, Cu, Al, Ni, Cr, Zn, Cd, Co, and Mn) by soil humic acid, and reported that among the eleven metals, Hg and Fe exhibited the strongest affinity for humic acid. Trost and Bisque (1970) examined the sorption capacity of various clay minerals and organic substances, and found that humus-rich materials had a far greater sorption capacity than did pure clays. Fang (1978) and Landa (1978) also reported similar results. Dissolved organic matter is expected to form very stable complexes with Hg(II). Peng and Wang (1982) reported that most of the Hg in river water may be present as organic complexes. The presence of organic matter in solution was reported to inhibit the sorption of Hg(II) on mineral surface (Schuster, 1991).

Often different factors can simultaneously affect the sorption of trace metal contaminants by soils. The purpose of this study was to investigate the simultaneous effects of pH, Cl⁻, organic matter and Ca²⁺ on the sorption behavior of small concentrations of Hg.

3.3 Materials and Methods

3.3.1 Materials

All solutions and suspensions were prepared using distilled deionized water and trace metal analytical-grade reagents. All standard solutions were prepared daily by diluting a 10 mg L⁻¹ Hg stock solution with 1% (v/v) HNO₃, and stabilized by addition of a few drops of 0.1% Na₂Cr₂O₇. Fifteen New Jersey soils, ranging from sand to loam, were used for this study. The soils were ground to pass a 2-mm sieve, and then air dried before use. The characteristics of the soils in terms of particle size distribution, Mn, Fe, and Al oxides, total organic carbon (OC), cation exchange capacity (CEC), and BET surface area (SA) are given in Table 3.1-3.3 (Lee, 1993).

3.3.2 Sorption Methods

A batch technique was used to perform all sorption experiments. A mass of 1 ± 0.01 g of each soil was immersed in 100 mL of 0.01 M NaNO₃ (an indifferent electrolyte) contained in a 125 mL Erlenmeyer flask. Mercury(II) (as Hg(NO₃)₂) was then added to each soil suspension to make the added Hg(II) concentration 1 × 10⁻⁷ or 1 × 10⁻⁶ M. The samples were shaken on a rotatory shaker (Orbit, No. 3590, Lab-Line

Instruments, Inc., Melrose Park, IL) at 100 rpm for 24 h at a room temperature of $25 \pm 2^\circ\text{C}$. Preliminary results had shown that Hg concentrations in solution stabilized within a 24-h reaction period. After 24 h of equilibration, the pH of each sample was determined and was used for data analysis. Following measurement of pH, the samples were filtered using a 10-mL plastic syringe connected to a filter holder containing a $0.45\text{-}\mu\text{m}$ Nuclepore membrane filter (Costar, Cambridge, MA). For each filtration, the syringe was washed twice using the sample solution and the first 10 mL of filtrate was discarded. An aliquot of each filtrate was then analyzed for Hg(II). Duplicate measurements were made for each filtrate, the average was taken to calculate Hg concentration. The difference between the initial Hg concentration and the amount remaining in solution at 24 h was considered to be sorbed by the soil. For the sorption of Hg(II) as a function of pH, the pHs of the soil samples prepared as described above were adjusted to range from 3 to 10 using 0.1 M HNO_3 or NaOH before the samples were shaken.

Three soils of different organic matter content, Freehold sandy loam (A horizon), Dunellen sandy loam, and Boonton Union loam, were used to study the effect of Cl^- concentration on Hg(II) sorption. The Cl^- concentrations were adjusted to range from the background concentration to 10^{-2} M by adding NaCl. The concentration of NaNO_3 was adjusted correspondingly to maintain a constant ionic strength of 0.01 M. The experiments were carried out at a fixed low pH (3), intermediate pH (6.5 - 7), or high pH (8.5 - 10).

Table 3.1 Soil particle size distribution

| Soil No. | Soil Name† | Particle Size Distribution | | |
|----------|------------------------------------|----------------------------|----------------------------|----------------------------|
| | | Sand g kg ⁻¹ | Silt g kg ⁻¹ | Clay g kg ⁻¹ |
| 1 | Sassafras sandy loam | 450 | 370 | 180 |
| 2 | Lakewood sand | 910 | 30 | 60 |
| 3 | Penn silt loam | 250 | 480 | 270 |
| 4 | Whippany silty clay loam | 490 | 160 | 370 |
| 5 | Washington loam | 200 | 490 | 310 |
| 6 | Freehold sandy loam (A horizon) | 920 | 20 | 60 |
| 7 | Freehold sandy loam (B horizon) | 370 | 420 | 210 |
| 8 | Rockaway stony loam | 540 | 300 | 160 |
| 9 | Fill materials from Delaware River | 850 | 50 | 100 |
| 10 | Downer loamy sand | 870 | 50 | 80 |
| 11 | Boonton Union loam | 490 | 350 | 160 |
| 12 | Dunellen sandy loam | 560 | 300 | 140 |
| 13 | Birdsboro silt loam | 500 | 320 | 180 |
| 14 | Hazen gravelly loam | 390 | 380 | 230 |
| 15 | Boonton Bergen loam | 600 | 270 | 130 |

† Soil No. 1, 6, 7, 10, 12, and 13 are Typic Hapludults; No. 2 is a Spodic Quartzipsamments; No. 3 and 5 are Ultic Hapludalfs; No. 4 is a Aquic Hapludalfs; No. 8, 11, and 15 are Typic Fragiudalfs; No. 9 is a loamy sand dredged from Delaware River; No. 14 is a Mollic Hapludalfs.

Table 3.2 Soil pH, CEC, organic C, and surface area

| Soil No. | Soil Name | pH [†] | CEC cmol kg ⁻¹ | Organic C [‡] g kg ⁻¹ | Surface Area m ² kg ⁻¹ |
|----------|------------------------------------|-----------------|------------------------------|--|---|
| 1 | Sassafras sandy loam | 5.78 | 3.10 | 3.5 | 5310 |
| 2 | Lakewood sand | 4.18 | 0.90 | 2.9 | 1100 |
| 3 | Penn silt loam | 4.67 | 3.80 | 7.5 | 8040 |
| 4 | Whippany silty clay loam | 6.17 | 9.50 | 13.3 | 5980 |
| 5 | Washington loam | 6.03 | 8.90 | 16.8 | 11590 |
| 6 | Freehold sandy loam (A horizon) | 5.22 | 0.80 | 1.2 | 2040 |
| 7 | Freehold sandy loam (B horizon) | 6.44 | 4.30 | 13.9 | 9010 |
| 8 | Rockaway stony loam | 4.69 | 2.70 | 28.4 | 8620 |
| 9 | Fill materials from Delaware River | 4.77 | 2.30 | 7.0 | 2370 |
| 10 | Downer loamy sand | 4.74 | 2.30 | 4.6 | 1150 |
| 11 | Boonton Union loam | 5.14 | 4.20 | 49.9 | 6540 |
| 12 | Dunellen sandy loam | 5.57 | 4.20 | 11.0 | 5210 |
| 13 | Birdsboro silt loam | 5.69 | 5.30 | 12.8 | 7060 |
| 14 | Hazen gravelly loam | 6.02 | 9.30 | 18.0 | 5900 |
| 15 | Boonton Bergen loam | 5.12 | 4.20 | 30.7 | 7200 |

[†] Determined in 1:1 soil/water.

[‡] Determined by the Walkley-Black wet combustion method (Sims and Heckendorn, 1991).

Table 3.3 Soil oxides contents

| Soil No. | Soil Name† | Total Oxides§ | | |
|----------|------------------------------------|--------------------------|--------------------------|--------------------------|
| | | Fe g kg ⁻¹ | Al g kg ⁻¹ | Mn g kg ⁻¹ |
| 1 | Sassafras sandy loam | 18.70 | 16.89 | 0.11 |
| 2 | Lakewood sand | 45.95 | 1.70 | 0.05 |
| 3 | Penn silt loam | 33.93 | 33.86 | 0.49 |
| 4 | Whippany silty clay loam | 22.96 | 26.71 | 0.15 |
| 5 | Washington loam | 38.86 | 37.43 | 0.86 |
| 6 | Freehold sandy loam (A horizon) | 14.44 | 6.17 | 0.27 |
| 7 | Freehold sandy loam (B horizon) | 10.86 | 10.63 | 0.18 |
| 8 | Rockaway stony loam | 24.75 | 26.71 | 0.61 |
| 9 | Fill materials from Delaware River | 24.75 | 19.57 | 0.23 |
| 10 | Downer loamy sand | 5.27 | 25.82 | 0.11 |
| 11 | Boonton Union loam | 19.82 | 20.46 | 1.54 |
| 12 | Dunellen sandy loam | 34.38 | 24.93 | 0.39 |
| 13 | Birdsboro silt loam | 33.03 | 19.57 | 0.49 |
| 14 | Hazen gravelly loam | 30.12 | 23.14 | 0.73 |
| 15 | Boonton Bergen loam | 26.99 | 24.03 | 0.36 |

§ Determined by extraction with perchloric - nitric acids.

The effect of dissolved organic matter on Hg(II) sorption was studied using organic matter that was extracted with dilute NaOH from Boonton Union loam. We added variable amounts of the organic matter (1.4 mg C L^{-1} - 61.1 mg C L^{-1}) to suspensions of Freehold sandy loam (A horizon) at pH 6.5. We also added the same amount of organic matter (43.7 mg C L^{-1}) to suspensions of Freehold sandy loam (A horizon), Dunellen sandy loam and Rockaway stony loam at variable pH (3 - 10). We also removed organic matter from these three soils by treatment with 30% H_2O_2 following the method of Jackson (1958). The H_2O_2 -treated soils were washed by repetitive mixing with distilled deionized water followed by centrifugation until no H_2O_2 in supernatants was detected using Quantofix Peroxide test paper, and then were air-dried prior to use. Treatment with H_2O_2 removed 86 to 97% of the organic matter from the three soils. Sorption of Hg by these organic matter - removed soils was then studied as a function of pH (3 to 10). These experiments were conducted in 0.01 M NaNO_3 .

To test the effect of Ca^{2+} on the sorption of Hg(II), we measured Hg(II) sorption on two soils, Freehold sandy loam (A horizon) and Boonton Union loam, in $\text{Ca}(\text{NO}_3)_2$ instead of NaNO_3 . The ionic strength was also maintained at 0.01 M. An initial Hg concentration of $1 \times 10^{-7} \text{ M}$ was employed. The tests were conducted at a pH range of 3 to 10.

3.3.3 Mercury Analysis

Mercury was determined by a flow injection analysis (FIA) system combined with atomic absorption spectrophotometric detection (Figure 3.1). The FIA system

consisted of a Ismatec pump (Cole-Parmer, No. 7332), a Rheodyne four-way rotary valve with a 500- μL sample loop, a gas-liquid separator of laboratory design and construction, a gas flow meter, a reaction coil of 450 mm \times 0.5 mm i.d., and an open ended quartz T-tube used as the absorbance cell. All transport tubing was Teflon of 0.5 mm i.d. In this system, Hg(II) was reduced to elemental form by Sn^{2+} , and then stripped by N_2 gas to the detection cell where the absorbance of Hg was measured. The linear range for this system was 1 $\mu\text{g L}^{-1}$ to 30 $\mu\text{g L}^{-1}$ with linear regression coefficient $r^2 = 0.9996$.

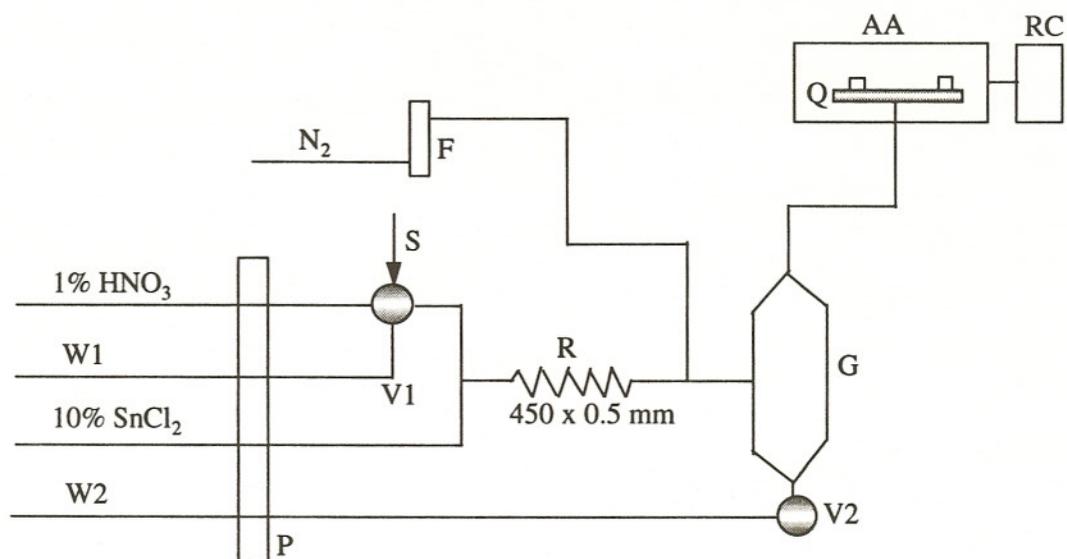


Figure 3.1 Schematic of flow injection system. P: Pump; V1: Six - way valve; V2: Two - way valve; R: Reaction coil; Q: Quartz tube; F: Flow meter; RC: Recorder; W1 and W2: Wastes; AA: Atomic absorption spectrophotometer; G: Gas-liquid separator.

Mercury(II) in solution-phase samples were digested following a modification of the method described by APHA (1992). For the digestions we placed a 5-mL aliquot of sample into a 10-mL glass vial; gently added 0.5 mL of each of concentrated HNO₃, H₂SO₄ and HCl; capped each vial tightly; and placed the vials into a water bath at 80 to 90°C for two hours. After cooling, the samples were analyzed for Hg. The digestion procedure was tested by standard addition using soil extracts as the matrix. Mercury(II) was added to nine soil extracts with dissolved organic C ranging from 16.5 to 98.8 mg organic C L⁻¹ to make the final Hg concentration be 20 µg L⁻¹. The mixtures were equilibrated for 24 hours on a on a reciprocating shaker, and then the Hg concentrations were determined. The recovery was 91.68 ± 6.80% (Table 3.4).

Table 3.4 Test of digestion method for determination of Hg

| Solution pH | Total Dissolved Organic C (mg L ⁻¹) | Mercury(II) Addition (µg L ⁻¹) | Recovery (%) |
|--------------------|---|--|--------------|
| 3.27 | 16.54 | 20 | 82.98 |
| 3.40 | 15.90 | 20 | 96.56 |
| 3.69 | 14.81 | 20 | 93.25 |
| 4.05 | 14.12 | 20 | 100.32 |
| 5.24 | 17.02 | 20 | 96.35 |
| 6.05 | 23.56 | 20 | 82.27 |
| 6.56 | 29.57 | 20 | 95.43 |
| 8.93 | 75.92 | 20 | 83.53 |
| 9.70 | 98.84 | 20 | 94.47 |
| Average | | | 91.68 |
| Standard Deviation | | | 6.80 |

Table 3.5 Mass recoveries of Hg from soil and solution phases

| Hg(II) Addition (μg) | pH | Total Mass Recovered (μg) | Recovery (%) |
|--|-------|---|-----------------|
| Freehold sandy loam (A horizon), organic matter content: 1.2 g kg^{-1} | | | |
| 0 | | 0.25 | |
| 10 | 3.00 | 8.77 | 85 |
| 10 | 6.58 | 8.50 | 83 |
| 10 | 10.83 | 8.34 | 81 |
| 5 | 11.15 | 4.27 | 80 |
| Rockaway stony loam, organic matter content: 28.4 g kg^{-1} | | | |
| 0 | | 0.29 | |
| 10 | 3.18 | 8.71 | 84 |
| 10 | 6.25 | 8.32 | 80 |
| 10 | 8.84 | 8.42 | 81 |
| 5 | 9.16 | 4.24 | 80 |

3.4 Results and Discussion

Before conducting further sorption experiments, a mass recovery test was first performed to see if any Hg evaporizes during sorption experiments. $1 \pm 0.01 \text{ g}$ of either Freehold sandy loam (A horizon) or Rockaway stony loam was mixed with $10 \mu\text{g}$ or $5 \mu\text{g}$ Hg in 100 ml of 0.01 NaNO_3 . The pH of each suspension was adjusted to range from 3 to about 11. After 24 hours of equilibration, the solids were separated from solution by filtration through a $0.45 \mu\text{m}$ membrane filter. The concentrations of Hg in both solution and solid phases were then analyzed following sample digestion. The solution digestion was performed according to the previously described procedure, and the soil digestion followed the method described in the Methods of Soil Analysis

(Page, 1982). The recoveries for both soils of different organic matter content at a variety of pHs are greater than 80% (Table 3.5). The unrecovered mass (15 - 20%) could result from evaporation and/or from irreversible sorption.

3.4.1 Effect of pH

As expected, the sorption of Hg(II) by the soils was pH dependent (Figure 3.2). At low pH, Hg(II) was extensively adsorbed by all soils. The maximum sorption of added Hg(II) occurred in the pH range of 3 to 5 for all soils. After sorption, the amount of Hg adsorbed ranged from 0.2 to 1.95 mg kg⁻¹ for an initial Hg concentration of 1× 10⁻⁷ M, which was within the concentration range of uncontaminated soils (0.005 - 4.6 mg kg⁻¹) (Steinnes, 1995). For an initial Hg concentration of 1× 10⁻⁶ M, the Hg sorbed ranged from 7.0 to 19.2 mg kg⁻¹, which is above the concentration range of uncomtaminated soils. This study mainly focused on the sorption of Hg from an 1× 10⁻⁷ M solution to understand the behavior of Hg that has been applied to soils.

We plotted the amount of Hg retained by soils from an 1× 10⁻⁷ M solution at pH 4 versus six soil parameters (OC, Al, Mn, and Fe oxides, CEC, and SA), and found that the sorption exponentially increased with increase of each of soil parameter. The correlation between Hg sorption (in g kg⁻¹) and each individual parameter was analyzed by linear regression (Wilkinson, 1988) after log transformation of the data. The correlation coefficient was 0.89 between Hg sorption and SA, and 0.67 to 0.75 between Hg sorption and the other parameters. Because all these parameters affected sorption, a multi-variant regression was performed. The correlation coefficient

obtained was 0.95. The standard regression coefficient ($b_{si} = b_i x_i/y_i$, where b_i is the coefficient of i th variable; x_i is the standard deviation of i th variable; y_i is the standard deviation of the dependent) was used to determine the relative importance of these parameters (Rosner, 1990). The greater the b_{si} , the more important the variable. Based on the calculated b_{si} values, the importance sequence was: SA ($b_{si} = 0.80$) > Al ($b_{si} = 0.42$) > OM ($b_{si} = 0.30$) > Mn ($b_{si} = 0.05$) > CEC ($b_{si} = -0.10$) > Fe ($b_{si} = -0.24$). When only the first three important parameters (SA, Al, OM) were included in regression, the correlation coefficient was 0.94 which was only 0.01 less than that obtained when six parameters were considered. The correlation equation was: $\log Ads = -3.090 + 0.013 \log OM + 0.035 \log Al + 0.077 \log SA$.

Besides the above soil properties, the sorption was also related to soil particle size distribution. Freehold sandy loam (A horizon), Lakewood sand, fill material from the Delaware River, and Downer loamy sand all contained a large portion of sand (850 - 920 g kg⁻¹) and had small organic matter contents (1.2 - 7.0 g C kg⁻¹). The mass of Hg(II) retained on these four soils was small over most of the experimental pH range (Figure 3.3). On the other hand, Sassafras sandy loam, which also was a low organic matter soil (3.5 g C kg⁻¹) but contained a larger portion of silt and clay (550 g kg⁻¹), adsorbed more Hg(II) over most of the experimental pH range.

Mercury(II) behaves differently from most other divalent heavy metals in that the extent of sorption is greatest in acidic media. For instance, the sorption of Cd on the same fifteen soils was less than 10% at pH below 5, but increased with increasing pH and reached a maximum of more than 90% (Allen et al., 1994). The greater sorption of Hg(II) at low pH was also reported for pure minerals such as silica,

hydrous iron oxide, bentonite and goethite (MacNaughton and James, 1974; Newton et al., 1976; Kinniburgh and Jackson, 1978; Barrow and Cox, 1992a). Both soil surface potential characteristics and Hg(II) speciation determined Hg sorption behavior in soil. In the soil solutions of this study, which had Cl^- concentrations of about 1×10^{-6} to 1×10^{-5} M, at low pH the major Hg(II) species were calculated to be positively charged Hg^{2+} and HgCl^+ and the neutral HgCl_2 species (Figure 3.4). The larger the Cl^- concentration, the larger the fraction of HgCl_2 and the higher the pH at which the hydroxyl-containing Hg species become predominant over Hg-Cl complexes. The species HgCl_2 has been found to be poorly adsorbed by most of the inorganic particles (MacNaughton and James, 1974; Newton et al., 1976; Kinniburgh and Jackson, 1978; Barrow and Cox, 1992a). The interactions of Hg^{2+} and HgCl^+ with soil surface largely depend on surface potential which is a function of pH. At very low pH (pH < 3), the surface had high positive potential, which resulted in strong repulsion of surface to these positively charged species. An increase in pH resulted in a decrease of surface potential, and the surface became more attractive (or less repulsive) to these species, which increased the sorption.

Because of the strong Lewis acid characteristics of Hg(II) which has hydrolysis constants of 3.87 for $\text{pK}_{\text{OH},1}$ and 2.77 for $\text{pK}_{\text{OH},2}$ the proportion of hydroxo-Hg species (including HgOH^+ , HgOHCl , and $\text{Hg}(\text{OH})_2$) increased exponentially over a narrow pH range of 3 to 5 (Figure 3.4). This is different from other metals and it is this behavior that resulted in the greater sorption of Hg(II) in acidic conditions. MacNaughton and James (1974) suggested that hydroxo Hg(II) species were more readily adsorbed than were Hg-Cl complexes. They reported that the maximum sorption of Hg(II) on SiO_2 occurred in the pH range in which the hydroxo mercury

species $\text{Hg}(\text{OH})_2$ was dominant over HgCl_2 . Many other researchers also suggested that the hydroxo metal species are equally or more readily adsorbed than are aquo metal species (James and Healy, 1972; Huang and Lin, 1981; Elliott et al., 1986; Huang et al., 1986). Therefore, as the concentration of hydroxo $\text{Hg}(\text{II})$ species significantly increased with increasing pH of 3 to 5, the sorption of $\text{Hg}(\text{II})$ increased (Figure 3.2-3.3).

As pH further increased, the sorption of added $\text{Hg}(\text{II})$ significantly decreased, for example, from $89 \pm 8\%$ at pH 4.0 to $39 \pm 11\%$ at pH 8.5 for an initial Hg concentration of 1×10^{-7} M. The existence of sorption maxima was also observed for the sorption of $\text{Hg}(\text{II})$ by soil components, such as goethite (Barrow and Cox, 1992a), bentonite (Newton et al., 1976), iron hydrous oxide (Kinniburgh and Jackson, 1978), and SiO_2 (MacNaughton and James, 1974), but the extent of the decrease in sorption by soil components at higher pH was much smaller than that observed in this study. Barrow and Cox (1992a) suggested that the decrease of the concentration of the positively charged species HgOH^+ resulted in the decrease of Hg sorption by goethite. Some researchers have suggested that the increase of the concentration in $\text{Hg}(\text{OH})_2$ relative to that of $\text{Hg}(\text{OH})\text{Cl}$ at a pH greater than the pH at which maximum sorption occurs may be responsible for the decrease in sorption. At these pH values, the increase in the activity of $\text{Hg}(\text{OH})\text{Cl}$ as a function of increasing concentration of OH^- is greater than that of $\text{Hg}(\text{OH})_2$ (Kinniburgh and Jackson, 1978; Newton et al., 1976). Any of these reasons could contribute to the decrease in Hg sorption by soils as pH increased. As shown below, the dissolution of soil organic matter, however, may be the most important factor causing the significant decrease of $\text{Hg}(\text{II})$ sorption by soils at high pH.

3.4.2 Effect of Organic Matter

We noted that the amount of dissolved soil organic matter increased significantly as the solution pH was raised (Figure 3.5). One consequence of the increase in dissolved organic matter is a corresponding decrease in organic-based surface sorption sites which may contribute to the decrease in Hg(II) sorption. The complexation of Hg by the dissolved organic matter, however, was probably more important in decreasing the Hg sorption by soil. We tested this hypothesis by adding organic matter to soil suspensions at both constant pH and variable pH. We found that the Hg(II) sorption at pH 6.5 decreased from approximately 60% to 28% of the added Hg when the added dissolved organic matter increased from 1.4 to 61.1 mg C L⁻¹ (Figure 3.6). When 43.7 mg organic C L⁻¹ was added to soil suspensions at pH values ranging from 2.5 to 10, the Hg(II) sorption generally decreased over most of the pH range for all soils except at very low pH (Figure 3.7a-c). At pH less than 4, more than 50% of the added organic matter was retained by Rockaway sandy loam or precipitated (Figure 3.7d), and the Hg(II) sorption was not affected or only slightly increased (Figure 3.7b). At pH greater than 4, more than 50% of the added organic C remained in solution and the Hg(II) sorption decreased. For Freehold sandy loam (A horizon) and Dunellen sandy loam, only near pH 3 was more than 50% of the added organic C retained by soil particles or precipitated (Figure 3.7d). In this pH region the addition of organic matter had no effect on Hg(II) sorption (Figure 3.7a, c). At higher pH, more than 50% of the added organic C remained in solution at equilibrium and the sorption of Hg(II) decreased.

The efficacy of the dissolved organic matter in decreasing Hg sorption may depend on the amount of Hg present. Barrow and Cox (1992b) also observed that Hg sorption on a loamy sand soil decreased at higher pH. The extent of the decrease in sorption in their study, however, was less than we observed for the soils in this study. It is likely that this resulted from the Hg concentration used in their study (greater than 10^{-4} M) being much larger than that in this study (1×10^{-7} and 1×10^{-6} M). For a given amount of dissolved organic matter, at low Hg loading, a large amount of Hg could be complexed by dissolved organic matter. Increasing the Hg loading resulted in more amount of inorganic Hg to be available for sorption by soil solids, and the extent of the decrease in sorption caused by dissolved organic matter eventually decreased. Comparison of Hg sorption by soils for two initial concentrations used in this study supported this hypothesis. For most soils, the fractional sorption of Hg at pH above 5 increased with initial Hg(II) concentration (Figure 3.2).

The effect of soil organic matter on Hg(II) sorption was further studied by removal of soil organic matter. When soil was treated by H_2O_2 for the removal of organic matter, the sorption of Hg(II) was significantly reduced at low pH (Figures 3.7a-c). Two hypotheses seemed reasonable for this decrease. First, organic matter generally has stronger affinity for Hg(II) than do soil inorganic components. Removal of organic matter contributed to the decrease of Hg(II) sorption. Second, when soil organic matter was removed, some inorganic surface areas were exposed. Compared with organic matter, soil inorganic components usually have smaller surface areas. Therefore the total soil surface area was expected to have decreased. This may have also contributed to the observed decrease of Hg(II) sorption. After H_2O_2 treatment for the removal of organic matter, for Dunellen sandy loam (No. 12), as pH was increased,

the sorption increased and reached a maximum at pH 7 to 8 (Figures 3.7c). For Freehold surface sandy loam (No. 6) and Rockaway sandy loam (No. 8), the sorption increased and reached a maximum at about pH 4 (Figures 3.7a-b). Further increases in pH resulted in a decrease of the Hg(II) sorption. The extent of the decrease was much smaller than that for the sorption of Hg(II) by soils without changes in organic matter. This also suggested that the complexation of Hg(II) by dissolved organic matter was the major factor resulting in Hg(II) sorption by soils to significantly decrease in alkaline systems.

The difference in pH at which the maximum sorption of Hg(II) on soils from which the organic matter had been removed probably resulted from a difference in soil composition. Two types of components may be responsible for this difference. One is clay minerals. Freehold sandy loam contains 920 g sand kg⁻¹ and has a very small CEC (0.8 cmol kg⁻¹). This soil only contains a small amount of clay minerals. Dunellen sandy loam contains almost the same amount of sand (560 g kg⁻¹) as Rockaway sandy loam (540 g kg⁻¹) does, but has a much larger CEC (4.2 cmol kg⁻¹) and smaller organic matter content (11.0 g C kg⁻¹) than Rockaway sandy loam (CEC = 2.7 cmol kg⁻¹; organic matter = 28.4 g C kg⁻¹). Because soil CEC is largely derived from clay minerals and organic matter (Bohn et al., 1985), the larger CEC in Dunellen sandy loam must have resulted from a larger fraction of clay minerals. The sorption of Hg(II) on clay minerals has been reported to increase up to pH 8 to 9 (Andersson, 1979). Therefore, a greater clay mineral content in Dunellen sandy loam may have resulted in the maximum sorption occurring at a higher pH range. Another component possibly responsible for the difference was iron oxide. Andersson (1979) reported that Hg(II) sorption by Fe₂O₃·nH₂O increased with increasing pH up to pH 6.2 to 8.5.

Barrow and Cox (1992a) showed that the sorption of Hg(II) by goethite reached a maximum at pH about 4, and then only slightly decreased from pH 4 to 7. The Dunellen sandy loam contained more total iron oxide than did the other two soils (Table 1). This may have also shifted the maximum sorption of Hg(II) by Dunellen sandy loam to higher pH.

3.4.3 Effect of Chloride

In this study, we chose three soils of different organic matter content to investigate the effect of Cl⁻ on Hg sorption at different pH values and soil organic matter content. At neutral or higher pH, only very small amount of Hg-Cl complexes can be formed, and the extent of sorption largely depends on the balance between the interaction of other forms of Hg with soil surface and the complexation of Hg by dissolved organic matter. An increase in Cl⁻ concentration was expected to have little effect on sorption by any of the soils. This was verified by the experimental results (Figures 3.8a-c). At pH ≥ 6.5, when Cl⁻ was increased from about 1 × 10⁻⁶ M to 1 × 10⁻² M, there was almost no change in the Hg sorption by any of the three soils. Similar results were reported by Barrow and Cox (1992b) who observed that the sorption of Hg by a loamy sand was not affected by addition of Cl⁻ at pH 6.7 to 7.4. They also reported that the addition of Cl⁻ decreased Hg sorption at low pH. We found that this was not always the case. The effect of Cl⁻ on Hg sorption by soil at low pH depended on the soil organic matter content.

Under acidic conditions, there was a very small amount of dissolved organic matter in the soil solutions. Thus, Hg speciation in different soil solutions was similar.

Sorption largely depended on the interaction of Hg species with different soil surfaces. For the soil with a low organic matter content (1.2 g C kg^{-1} ; Freehold sandy loam, A horizon), the addition of Cl^- significantly reduced sorption at pH 3. When Cl^- concentration was increased from about $1 \times 10^{-6} \text{ M}$ to $1 \times 10^{-2} \text{ M}$, sorption decreased from 93% to 40% of the total added Hg(II). The predominant sorption sites on this soil were inorganic. In the soil solutions, most of the Hg(II) was calculated to be present as the HgCl_2 complex (Figure 3.9) which is poorly adsorbed by inorganic surfaces (MacNaughton and James, 1974; Newton *et al.*, 1976; Kinniburgh and Jackson, 1978; Barrow and Cox, 1992a). Therefore, as the concentration of Cl^- was raised, the fraction of HgCl_2 increased, whereas the fraction of HgCl^+ , Hg^{2+} , and $\text{Hg}(\text{OH})\text{Cl}$ decreased (Figure 3.9), which resulted in the decrease of Hg(II) sorption (Figure 3.7a).

For the soil of intermediate organic matter content (11.0 g C kg^{-1} ; Dunellen sandy loam), the addition of Cl^- slightly reduced sorption. When Cl^- concentration was increased from about $1 \times 10^{-6} \text{ M}$ to $1 \times 10^{-2} \text{ M}$, sorption decreased from 95% to 81% of the total added Hg(II). For the soil with the largest organic matter content (49.9 g C kg^{-1} ; Boonton Union loam), the addition of Cl^- had almost no effect on the sorption of Hg(II). When Cl^- was increased from about $1 \times 10^{-5} \text{ M}$ to $1 \times 10^{-2} \text{ M}$, sorption decreased only from 95% to 91% of the total added Hg(II). The decrease of the effect of Cl^- on Hg sorption by organic matter probably resulted from the competitive binding of organic matter for Hg. Many evidences have suggested that there were different energy of sites on organic matter (Purdue *et al.*, 1984). It is expected that the binding of Hg with some of the sites on organic matter is stronger than that with Cl^- . For a given Hg concentration, the effect of Cl^- on Hg sorption

depends on the concentration of the high energy sites on particulate organic matter. Increases in organic matter content could increase the amount of high energy sites, which sorb more Hg and eventually decreases the effect of Cl^- . For a given soil, the binding sites on organic matter are fixed, the effect of a certain amount of Cl^- on Hg sorption may depend on Hg concentration. Increasing Hg concentration could result in more Hg to be available for Cl^- binding.

3.4.4 Effect of Calcium

It has been found that background cations can affect heavy metal sorption to soils via competitive binding for the available binding sites (Zachara *et al.*, 1993). Ca^{2+} is one of the common cations that are present in soil solution. The effect of Ca^{2+} on Hg(II) sorption was investigated in this study. If there is competitive binding between Ca^{2+} and Hg(II), the sorption of Hg(II) in $\text{Ca}(\text{NO}_3)_2$ ($I = 0.01 \text{ M}$) should be smaller than that in NaNO_3 , which is an indifferent electrolyte and has been found to exhibit no competitive binding at a concentration level of 0.01 M (Zachara *et al.*, 1993).

As shown in Figures 3.10 - 3.11, the sorption of Hg(II) in both electrolytes at pH less than about 4 was similar. At higher pH, Hg(II) sorption in $\text{Ca}(\text{NO}_3)_2$ was even higher than that in NaNO_3 . This probably resulted from the coagulation of organic matter by Ca^{2+} , which removed some of the dissolved organic matter - associated Hg from solution. Similar results were reported by Thanabalasingam and Pickering (1985) for the sorption of Hg(II) on humic acid. They observed that sorption at pH 3 to 5 was similar for all electrolytes used. As pH further increased, the sorption in Na^+

and 0.01 M NH_4^+ electrolytes decreased but remained unchanged in 0.01 M Ca^{2+} or Mg^{2+} or 0.0001 M NH_4^+ .

It is speculated that the organic matter coagulated by Ca^{2+} in this study was mainly humic acid, since fulvic acid - metal complexes have been shown to be fairly soluble at a fulvic acid/metal weight ratio of > 2 (which is the case of this study) (Schnitzer and Kerndorff, 1981). This was tested by acidifying the filtrates to pH about 1. No precipitates were found in solution, indicating almost all humic acid being removed from solution. Since there was still dissolved fulvic acid whose concentration increased with increasing pH (Figure 3.12), the complexation of Hg by the the fulvic acid may result in the decrease of sorption. Furthermore, the increasing dispersion of particles at higher pH could also retain some fine colloid ($< 0.45 \mu\text{m}$) - associated Hg in solution.

3.5 Summary and Conclusions

The sorption of Hg(II) to soils was highly pH dependent. The maximum sorption occurred in a pH range of 3 to 5 for all soils studied. Above pH 5, the sorption significantly decreased. Increasing the pH resulted in an increase of the amount of dissolved organic matter. Because of the complexation of Hg by the dissolved organic matter, sorption decreased significantly as pH was raised. The importance of the release of organic matter in decreasing Hg sorption by soil may depend on both Hg loading levels and the environmental conditions which determine the amount of organic matter that can be dissolved. Consequently, performing studies

at environmental Hg levels is very important to understand the behavior of Hg that has already been released to the environment.

The presence of Cl^- in soil had no effect on Hg(II) sorption by any soil under alkaline conditions because only a small amount of Hg-Cl complexes were present. Under acidic conditions, the effect of Cl^- on Hg sorption depended on the soil organic matter content and possible Hg level. For soils with a small organic matter content, the presence of Cl^- could significantly reduce Hg(II) sorption; for soils with a very large organic matter content, the presence of Cl^- may have almost no effect on Hg(II) sorption. For a given soil, increasing Hg loading level could result in more Hg available for binding by Cl^- .

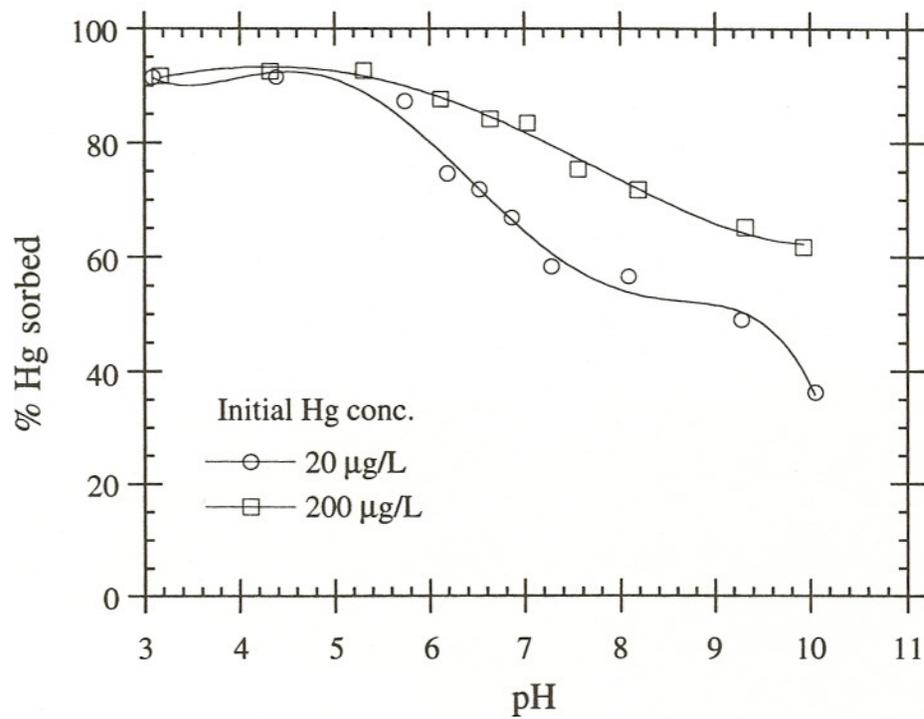


Figure 3.2 Sorption of Hg(II) on the Washington loam as a function of pH. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

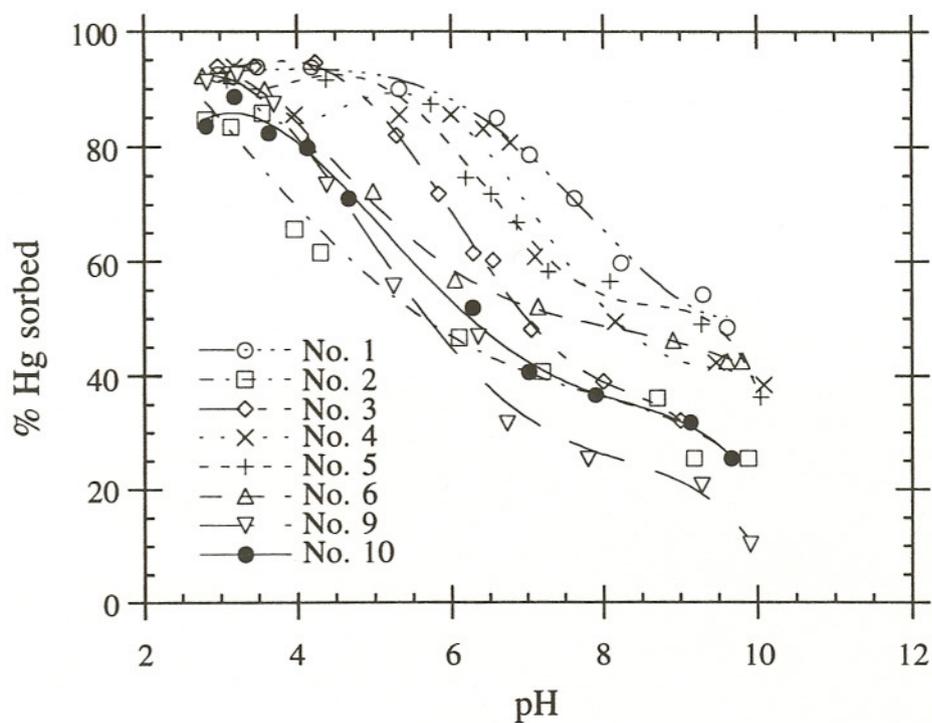


Figure 3.3 Comparison of Hg(II) sorption on different properties of soils as a function of pH. Initial Hg(II) concentration = 1×10^{-7} M; Soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C. See Table 3.1 for soil identification.

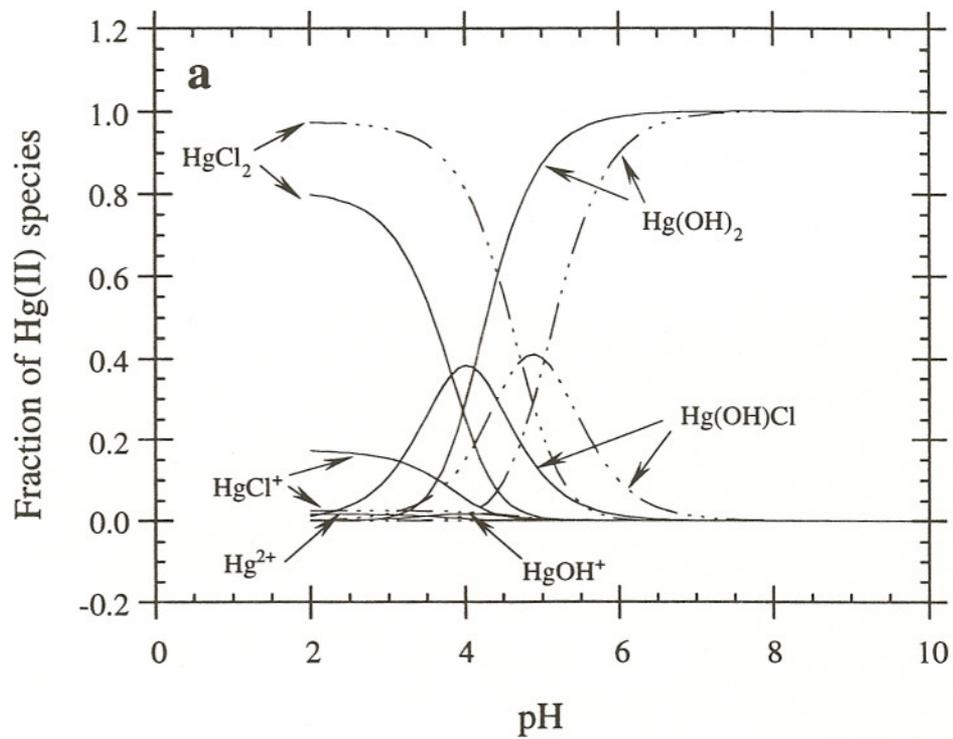


Figure 3.4 Hg(II) speciation as a function of pH and Cl^- concentration. Dashed lines denote the case of $\text{Cl}^- = 1 \times 10^{-5} \text{ M}$ and solid lines denote the case of $\text{Cl}^- = 1 \times 10^{-6} \text{ M}$.

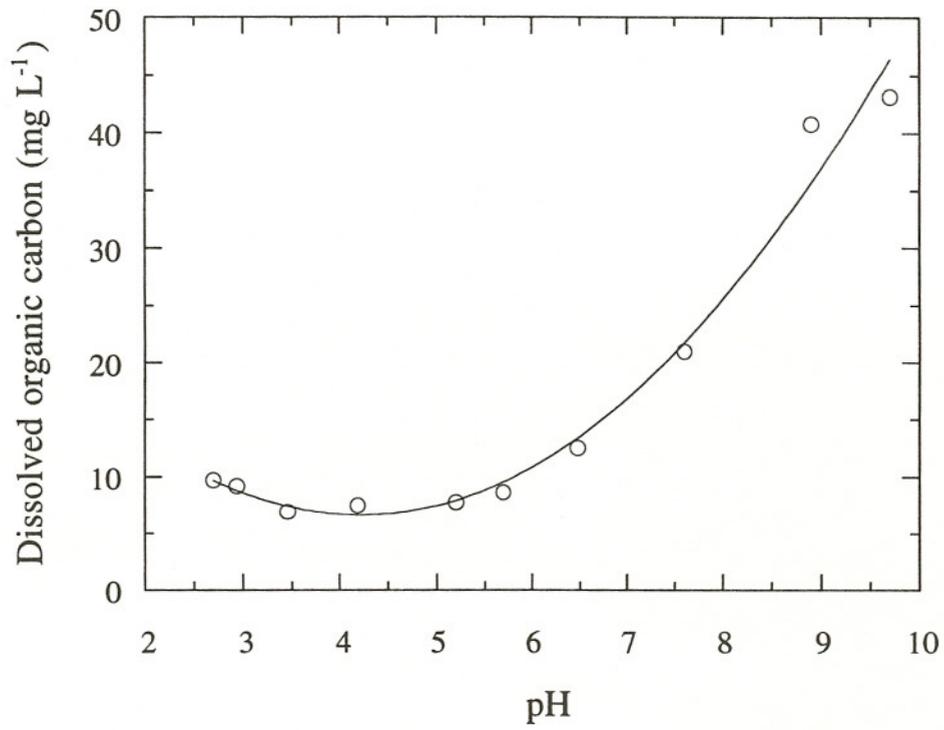


Figure 3.5 Dissolution of soil organic carbon as a function of solution pH for the Freehold sandy loam (B horizon).

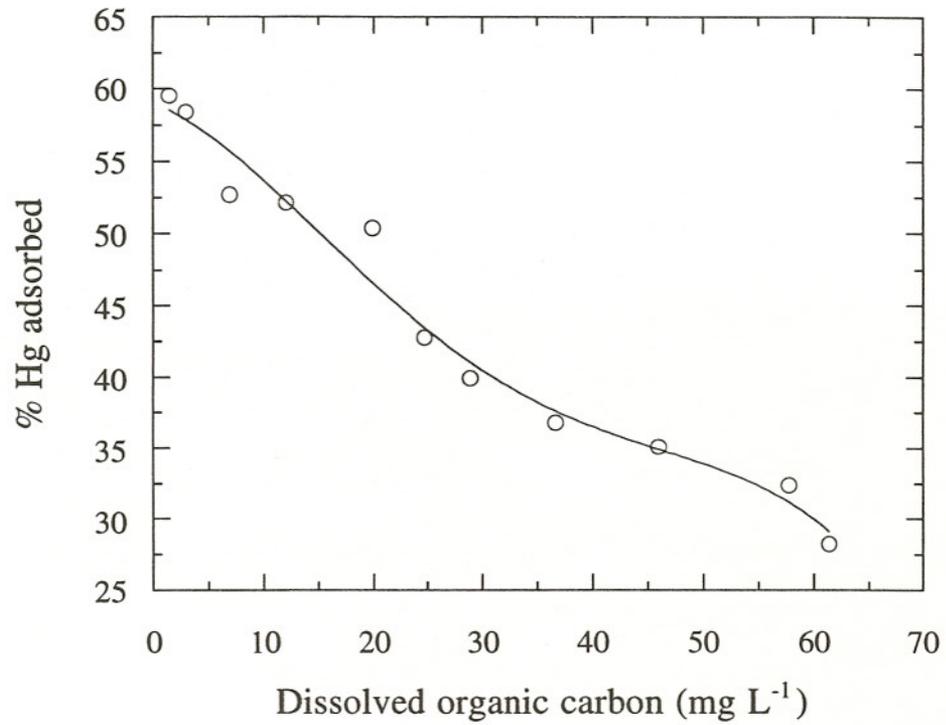


Figure 3.6 Effect of dissolved organic carbon on Hg(II) sorption by the Freehold sandy loam (A horizon) at pH 6.5.

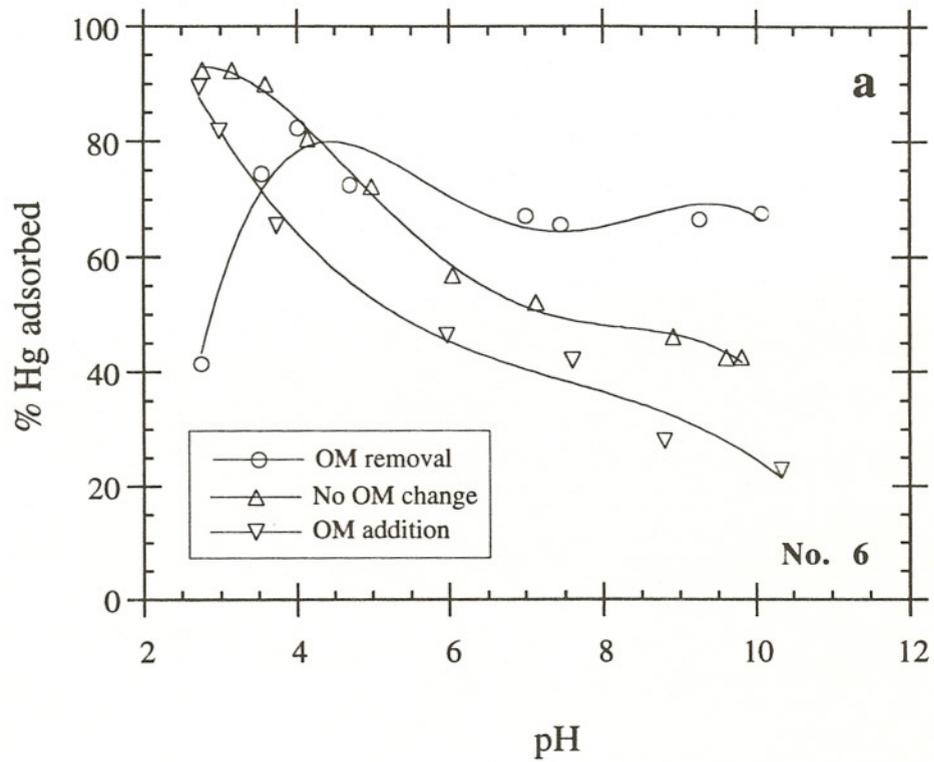


Figure 3.7a Comparison of Hg(II) sorption by the Freehold sandy loam (A horizon) with hydrogen peroxide treatment for organic matter removal, addition of organic matter, and no change as a function of pH.

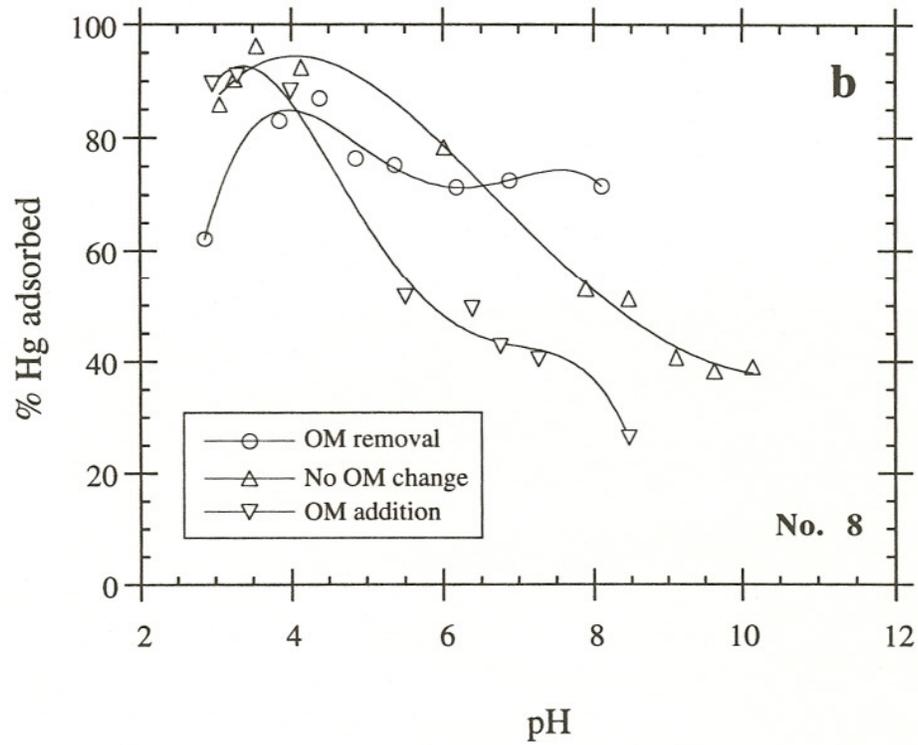


Figure 3.7b Comparison of Hg(II) sorption by the Rockaway stony loam with hydrogen peroxide treatment for organic matter removal, addition of organic matter, and no change as a function of pH.

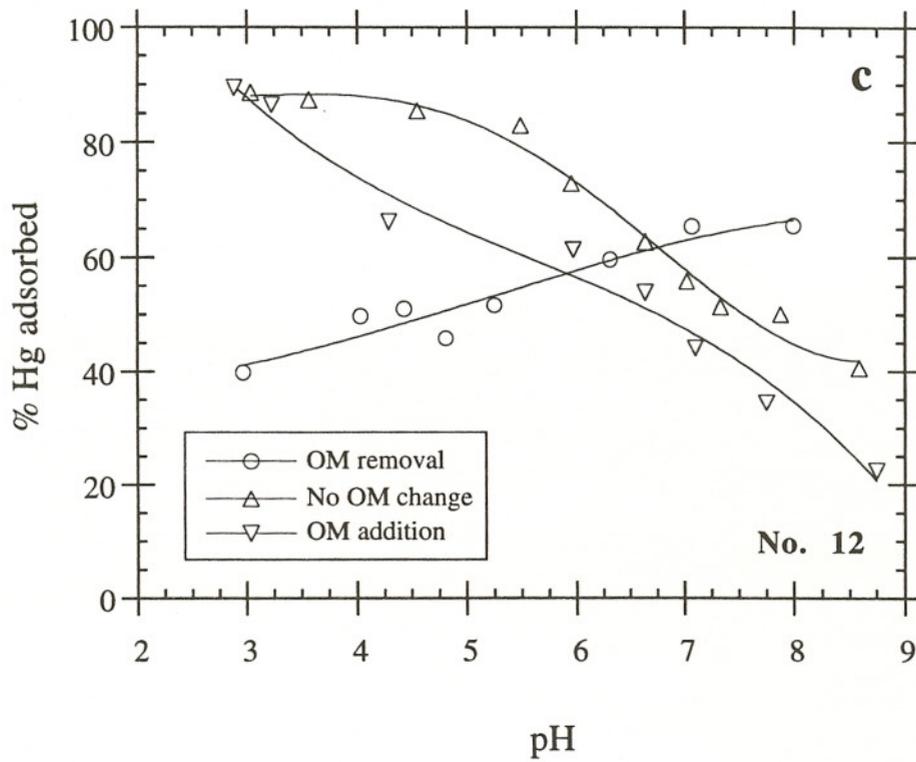


Figure 3.7c Comparison of Hg(II) sorption by the Dunellen sandy loam with hydrogen peroxide treatment for organic matter removal, addition of organic matter, and no change as a function of pH.

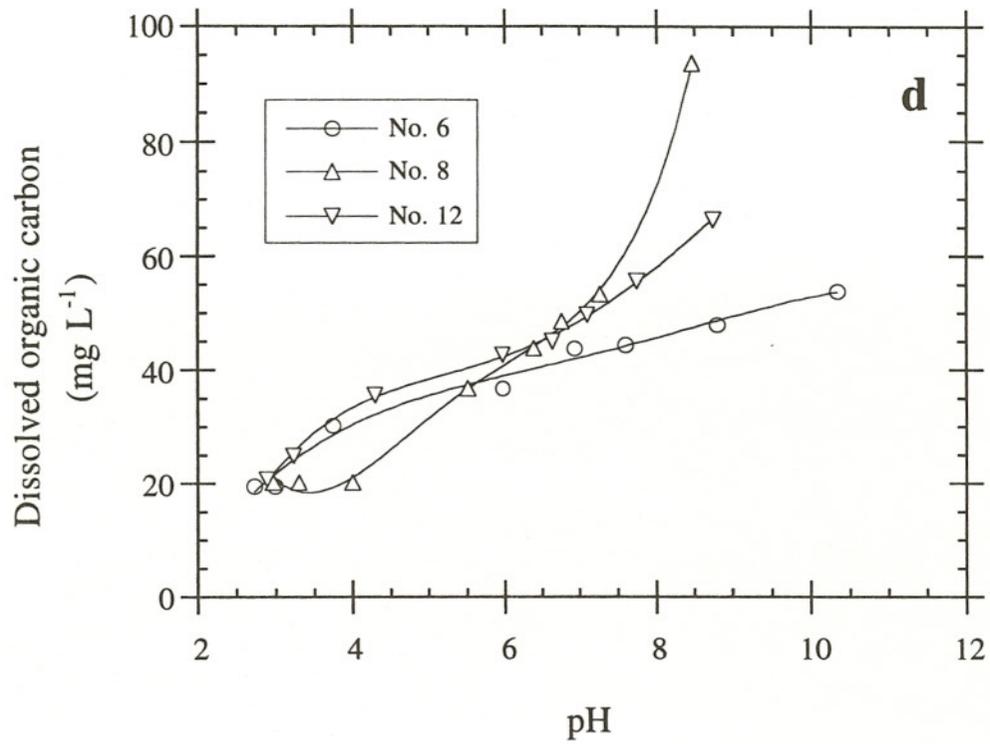


Figure 3.7d Final concentration of dissolved organic carbon in solution as a function of pH. See Table 3.1 for soil identification.

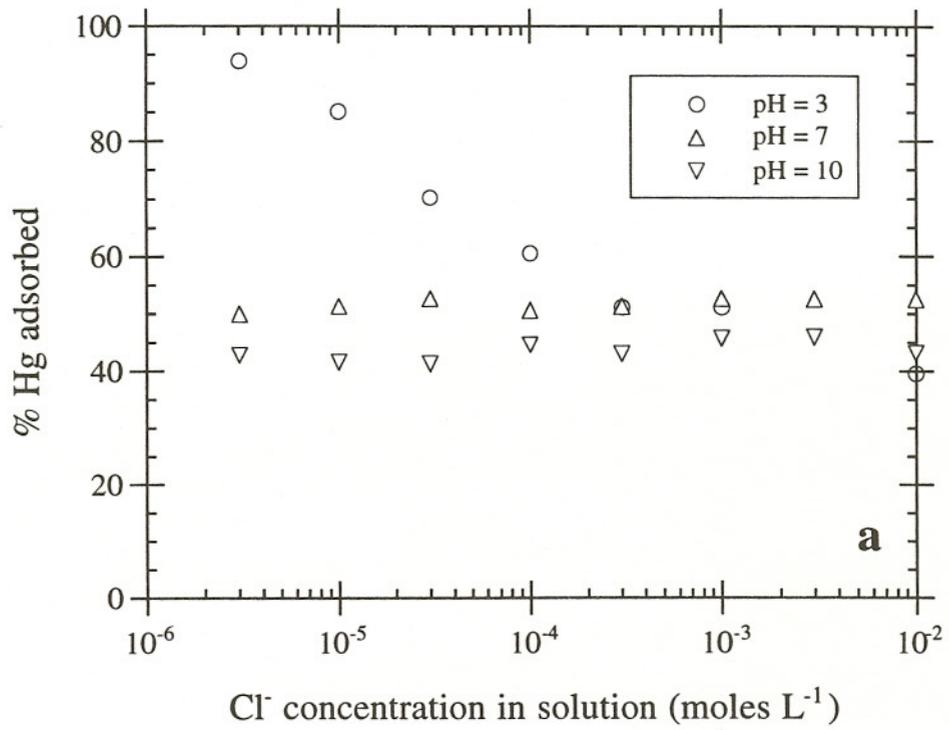


Figure 3.8a Sorption of Hg(II) on the Freehold sandy loam (A horizon) as a function of pH and chloride concentration.

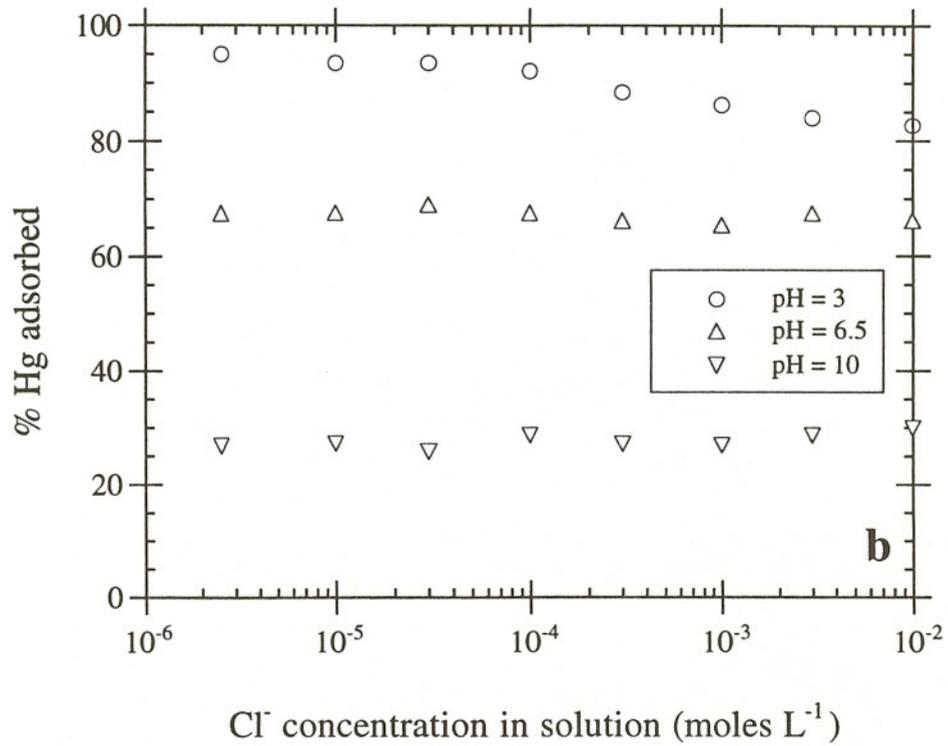


Figure 3.8b Sorption of Hg(II) on the Dunellen sandy loam as a function of pH and chloride concentration.

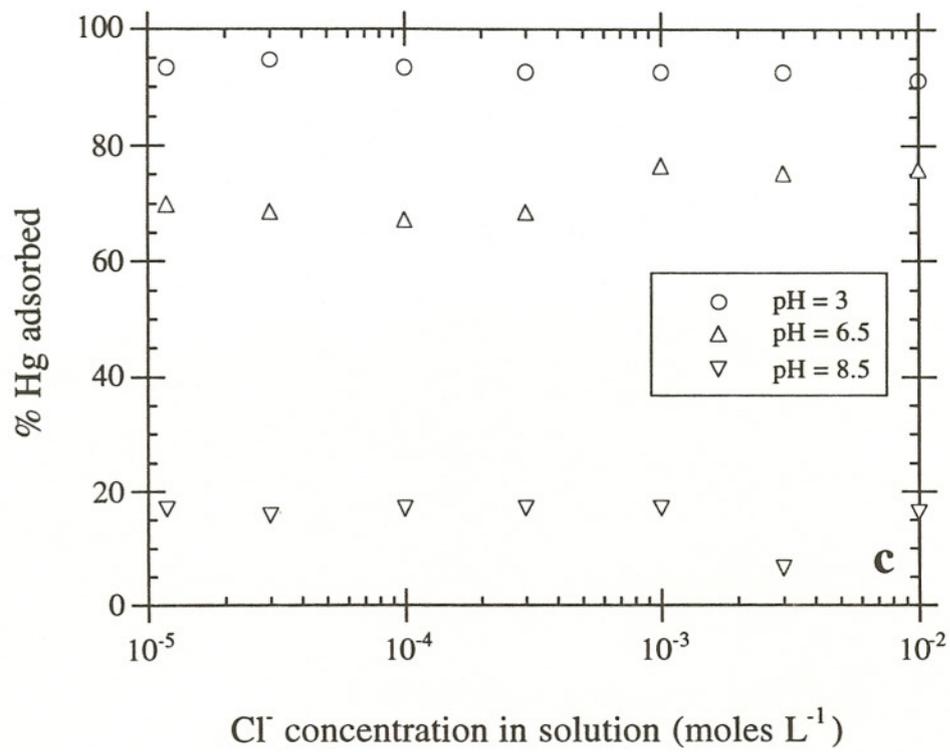


Figure 3.8c Sorption of Hg(II) on the Boonton Union sandy loam as a function of pH and chloride concentration.

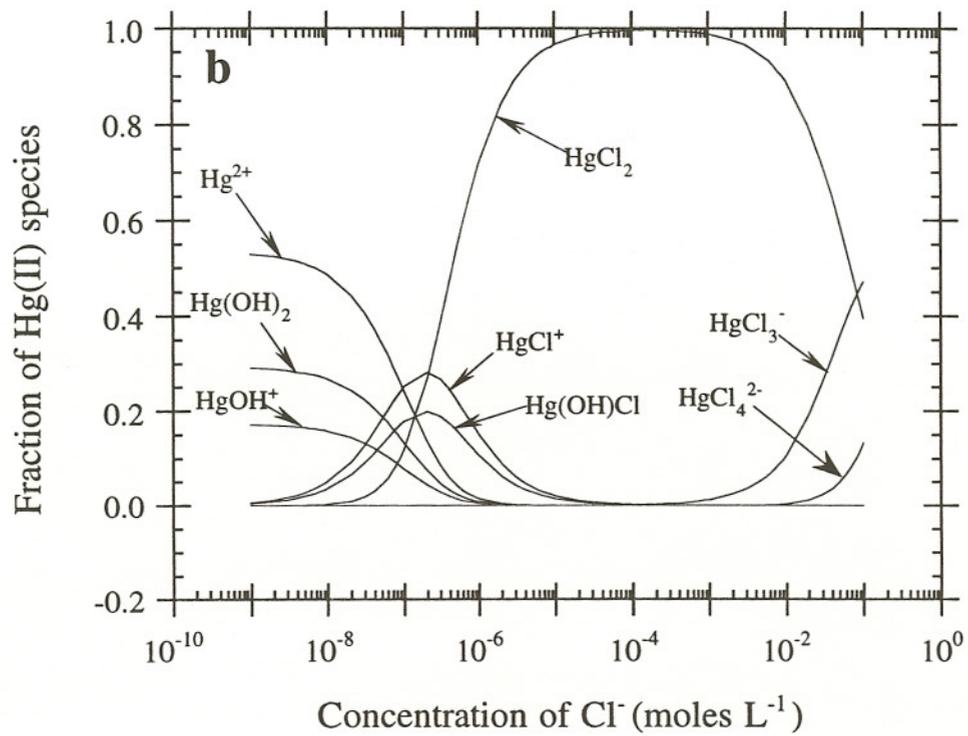


Figure 3.9 Hg(II) speciation as a function of Cl⁻ concentration at pH 3.

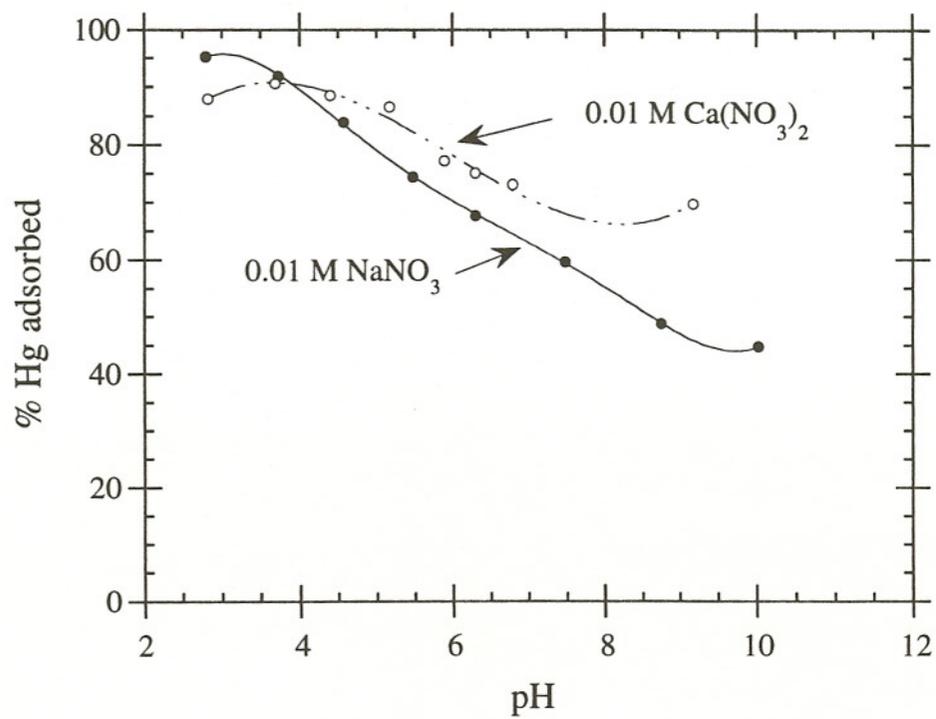


Figure 3.10 Comparison of the sorption of Hg(II) on the Freehold sandy loam (A horizon) in NaNO₃ and Ca(NO₃)₂. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO₃; T = 25 ± 2°C.

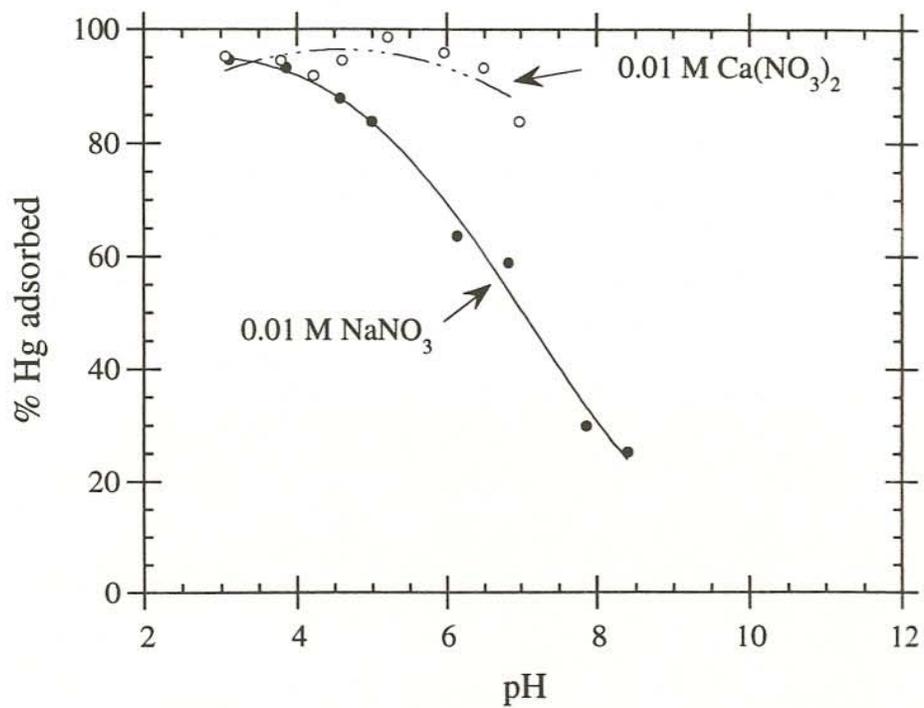


Figure 3.11 Comparison of the sorption of Hg(II) on the Boonton Union loam in NaNO_3 and $\text{Ca}(\text{NO}_3)_2$. Soil:water = 1 g 100 mL⁻¹; I = 0.01 M NaNO_3 ; T = 25 ± 2°C.

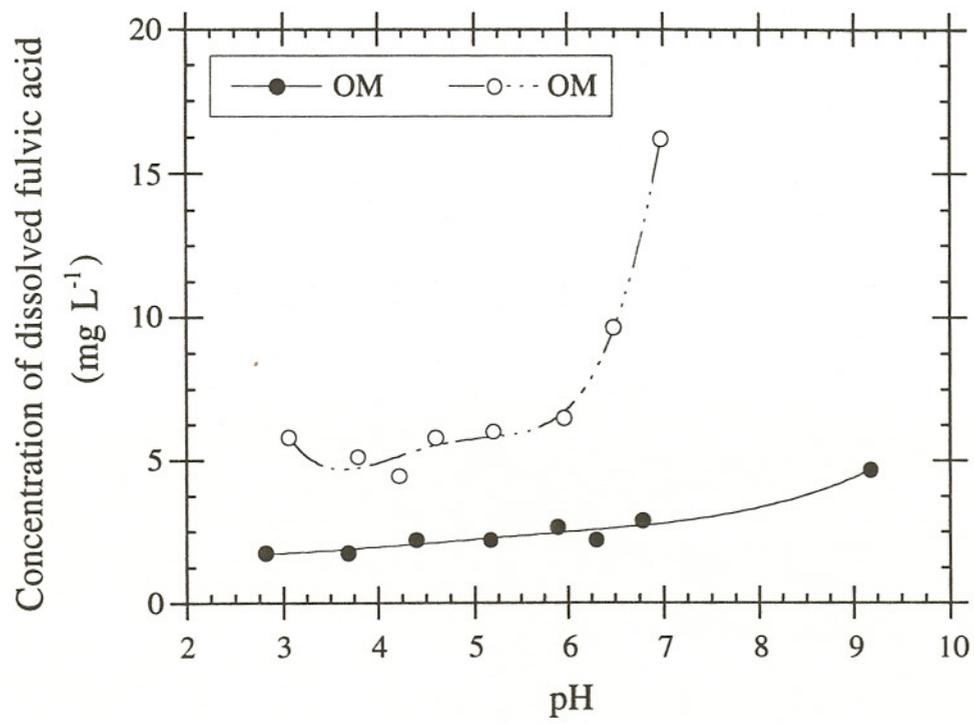


Figure 3.12 Concentration of dissolved fulvic acid as a function of pH.

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Chapter 4

SORPTION and DESORPTION of MERCURY(II) by SOIL: ISOTHERMS and MECHANISMS

4.1 Abstract

Mechanisms of Hg(II) sorption and desorption by 15 soils were investigated. Within an initial Hg solution concentration range of 1.0×10^{-7} to 1.1×10^{-4} M, all soils with a large organic matter content (> 11.0 g C kg⁻¹) had an S-type isotherm, whereas all soils with a low organic matter content (< 7.5 g C kg⁻¹) had an L-type isotherm. Changing the concentration of NaNO₃ background electrolyte had no effect on sorption, suggesting that sorption was predominantly inner-sphere complexation. This was supported by the Hg solution speciation characteristics. A model which incorporated the interactions of aqueous Hg with both dissolved organic matter and soil solids was developed to describe the isotherms and to evaluate the sorption capacities of soils. The sorption capacities correlated with the soil organic carbon content ($R^2 = 0.92$). The extent of hysteresis for Hg desorption was more significant for soils with high organic matter content and low sand content. This is probably because organic matter contains a greater number of high affinity sites and some of the adsorbed Hg may be entrapped in the organic matter structure.

4.2 Introduction

Sorption and desorption are important processes that affect the mobility and fate of contaminants in soil. An understanding of these processes and their mechanisms is crucial to the assessment of potential groundwater contamination and to the development of cost-effective soil remediation strategies.

A number of factors, including soil properties, environmental conditions, and the amount of contaminants in soil, affect sorption (Goldberg and Glaubig, 1987; Christensen, 1989; Sposito, 1989; Zachara et al., 1989; Schuster, 1991; Lee, et al., 1995). Among these factors, the dependence of sorption on the amount of contaminant present has often been studied in terms of an sorption isotherm to understand the sorption process involved and to evaluate soil sorption capacity. Because of the heterogeneity of soils, sorption isotherms are typically different for different soils and contaminants. Based on the shape of sorption isotherms, Sposito (1989) classified them into four types, i.e., S-type, L-type, H-type and C-type. The L-type isotherm is frequently observed for the sorption of heavy metals by soil. It is usually described by either the Langmuir equation or Freundlich equation, or the Langmuir two site equation (Travis and Etnier, 1981). An universal expression of this equation is (Sposito, 1985):

$$q(c) = \sum_{i=1}^n \frac{b_i k_i^{\beta_i} c^{\beta_i}}{1 + B_i C_i^{\beta_i}} \quad (4.1)$$

where $q(c)$ is the amount of solute adsorbed, C is the concentration of solute in solution, b_i , B_i , k_i , β_i ($i = 1, \dots, n$) and n are adjustable parameters.

It has often been observed that not all of the adsorbed contaminants can be desorbed, i.e., the reactions are not completely reversible (Di Toro et al., 1986; Schultz et al., 1987). This is commonly referred to as sorption/desorption hysteresis. The ease of the release of contaminants from soil largely depends on the mechanisms through which sorption occurred. Both inner-sphere and outer-sphere complexation could be operational for metal sorption by soil. An inner-sphere surface complex is more stable than is an outer-sphere surface complex. In an inner-sphere complex the metal ion binds directly with the surface functional group (Sposito, 1984). No coordinated waters lie between these two units, and the surface complex bond can be either covalent or ionic. On the other hand, an outer-sphere complex is coulombic in nature, with at least one of the metals' coordinated waters interposed between it and the surface functional group (Sposito, 1984). In addition to the chemical reaction between contaminants and the soil solid surface, the physical contact of contaminants with soil particles is also very important in determining desorption. Bruemmer et al. (1988) studied the sorption/desorption of Ni, Zn, and Cd by goethite and suggested that the diffusion of trace metals into the mineral structure may in part explain the sorption/desorption irreversibility. Avotins (1975) showed that the desorption of Hg from hydrous ferric oxide was characterized by both a fast and a slow process. They attributed the slow process to the diffusion of Hg from the hydrous ferric oxide interior back to the surface. Dong et al. (1994) described Zn desorption from vertisols by a parabolic diffusion model and found that the overall diffusion constant was significantly correlated with organic C and clay content.

The purpose of the present study was to examine the effect of the amount of Hg present on sorption and to investigate the mechanisms controlling Hg sorption and

desorption by soil. A model which incorporated the interactions of aqueous Hg with both dissolved organic matter and soil solids was proposed to describe the sorption isotherms and to evaluate the sorption capacities of soils in relation to soil properties.

4.3 Materials and Methods

4.3.1 Sorption Experiments

Fifteen New Jersey soils listed in Table 3.1 - 3.3 were used to perform this study. A batch technique was used to perform all studies. Distilled, deionized water was used to prepare all reagents and soil suspensions. Aliquots of 0.4 g of soil were mixed with 40 ml 0.01 M NaNO₃ in 50-ml glass centrifuge tubes. The soil suspensions were allowed to stand overnight to hydrate before adding Hg. The pH of the suspensions were then determined and the average was used as the experimental pH. Upon hydration, Hg(II) was added to each soil suspension from a 40 mg L⁻¹ or a 400 mg L⁻¹ Hg(NO₃)₂ stock solution which was kept in 0.1 M HNO₃. The amount of Hg added was varied in order to make the initial Hg solution concentration in the samples range over three orders of magnitude from 1.0 × 10⁻⁷ M to 1.1 × 10⁻⁴ M (at greater concentrations, precipitation was calculated to occur). The pH of each sample was then adjusted to the initial value by adding 0.1 M NaOH. The centrifuge tubes were capped with Teflon caps and shaken endwise on a reciprocating shaker at 60 strokes per minute for 24 hours at room temperature (25 ± 2°C). During the shaking, the pH was checked and adjusted if necessary. A preliminary study indicated that the Hg concentrations in solution were stable after 24 hours of shaking. After 24 hours of equilibration, the final pH values of the samples were measured. The pH variation

from the initial value was ± 0.3 pH units. The samples were then centrifuged at 1300 g for 30 min. The Hg concentration in the supernatants were analyzed by the flow injection analysis system. The difference between the initial Hg concentration and the amount remaining in the solution was considered to be adsorbed by soil.

In another series of experiments, the effect of the concentration of the electrolyte on sorption was studied following the same procedure described above. Two soils with different properties, Freehold sandy loam (A horizon) and Boonton Union loam, were used. For each soil, three sets of 8 soil samples were prepared in 0.001 M NaNO₃, 0.01 M NaNO₃, and 0.1 M NaNO₃. The initial Hg(II) concentrations for each set of samples were adjusted to cover a range of 1.0×10^{-7} to 1.1×10^{-4} M. The pH of all samples for each soil were adjusted to the pH of the soil - 0.01 M NaNO₃ suspension before shaking.

4.3.2 Desorption Experiments

Desorption was conducted following sorption for two soils, Freehold sandy loam (A horizon) and Boonton Union loam. Three different adsorbed Hg concentrations were used for each soil. At the end of sorption, 3/4 of the supernatant of each sample was replaced by the same volume of 0.01 M NaNO₃ whose pH had been adjusted to that of the samples. The samples were vortex mixed and then returned to the shaker to shake for an additional 24 hours. Following the same procedure as for sorption, the samples were centrifuged and the Hg concentrations analyzed. The desorption step was repeated four times. The concentration of Hg

retained by the soil in the suspension after each desorption step was calculated according to the following equation:

$$q_i = q_{i-1} - (C_i - C_{i-1} / 4) / W \quad (4.2)$$

where q_i is the concentration of Hg remaining in the soil at the end of i th desorption step ($\mu\text{mol g}^{-1}$); q_{i-1} is the concentration of Hg remaining in the soil at the end of $(i-1)$ th desorption step ($\mu\text{mol g}^{-1}$); C_i is Hg concentration in the solution at the end of i th step ($\mu\text{mol L}^{-1}$); C_{i-1} is Hg concentration in the solution at the end of $(i-1)$ th desorption step ($\mu\text{mol L}^{-1}$), and W is the solid concentration in the suspension (g L^{-1}).

4.4 Results and Discussion

4.4.1 Sorption Isotherms

Sorption isotherms for Hg on 15 soils were constructed by plotting the amount of Hg adsorbed versus the concentration of Hg remaining in solution. All soils with an organic carbon content greater than 11.0 g kg^{-1} had an S-type isotherm (Figure 4.1a), whereas all soils with an organic carbon less than 7.5 g kg^{-1} had an isotherm similar to the L-type isotherm classified by Sposito (1989) (Figure 4.1b).

The S-type isotherm has rarely been observed for the sorption of heavy metals. It has only been reported for Cu and Hg sorption by soils (Sposito, 1989; Barrow and Cox, 1992). The slope of this type of isotherm initially increases with increasing solute concentration, then decreases as surface site coverage increases and eventually becomes zero when surface sites are filled. It is believed that this type of isotherm

results from the complexation of metals by dissolved organic matter. As metal concentration exceeds the complexation capacity of dissolved organic matter, sorption increases greatly (Sposito, 1989). We found that within the experimental Hg concentration range of this study, the shape of sorption isotherms at the water-soil pH depended on both the amount of dissolved organic matter in the solution and the sorption capacity of soil for Hg. Generally, in the solutions of soils which had an S-type isotherm, the amount of dissolved organic matter was greater ($\geq 4.0 \text{ mg C L}^{-1}$); whereas in the solutions of soils which had an L-type isotherm, the amount of dissolved organic matter was smaller ($\leq 3.8 \text{ mg C L}^{-1}$) (Table 4.1). This, however, was not true for all soils. For example, the isotherm of Rockaway sandy loam was S-shaped, but the concentration of dissolved organic matter in the solution of this soil was only 2.2 mg C L^{-1} . On the other hand, fill material from Delaware river had an L-type isotherm, but the concentration of dissolved organic matter in its solution was 4.1 mg C L^{-1} . This probably resulted from the different sorption capacity of these two soils for Hg (as shown later). Since dissolved organic matter has a strong sorption affinity for Hg (Yin et al., 1996), it was expected that at low Hg concentrations, a large amount of Hg was complexed by dissolved organic matter in the solutions of both soils. As the Hg concentration increased, more Hg became available for sorption by soil solids. This resulted in increased sorption. When sorption reached a critical value, the fractional sorption (the amount of Hg adsorbed /the total added Hg) began to decrease, which resulted in a decrease in the slope of the isotherm. For Rockaway sandy loam (Figure 4.1a), fractional sorption increased with increasing added Hg until the concentration of the added Hg reached the midpoint ($8 \times 10^{-5} \text{ M}$) of the experimental Hg range, and then it slightly decreased. Therefore, this soil had an S-

type isotherm. For fill material from the Delaware River (Figure 4.1b), on the other hand, Hg fractional sorption increased only when the initial Hg concentration was less than 7.5×10^{-6} M because of its low sorption capacity (as shown later). Further increases in the initial Hg concentration resulted in a decrease in the fractional sorption. As a result, the L-shaped part of the isotherm whose slope decreased with increasing Hg concentration was predominant.

Table 4.1 Concentration of dissolved organic carbon

| Soil No. | Concentration of Dissolved Organic Carbon (mg L ⁻¹) | Type of Isotherm |
|----------|--|------------------|
| 1 | 2.2 | L |
| 2 | 3.6 | L |
| 3 | 3.8 | L |
| 4 | 5.3 | S |
| 5 | 9.1 | S |
| 6 | 1.6 | L |
| 7 | 7.5 | S |
| 8 | 2.2 | S |
| 9 | 4.1 | L |
| 10 | 3.5 | L |
| 11 | 9.1 | S |
| 12 | 4.0 | S |
| 13 | 5.4 | S |
| 14 | 7.0 | S |
| 15 | 10.0 | S |

We further studied the effect of organic matter on the sorption isotherm shape and the soil sorption capacity by removal of organic matter from Rockaway stony

loam. The organic matter was removed by treatment of soil with H_2O_2 following the procedure described by Yin et al. (1996). The H_2O_2 treatment removed 86% of organic matter from soil. As shown in Figure 4.1c, when organic matter was removed, the sorption capacity of Rockaway stony loam significantly decreased. Hg fractional sorption by this organic matter-removal soil decreased with increasing added Hg concentration within the entire experimental Hg concentration range. Consequently, sorption took on a L-type isotherm.

4.4.2 Sorption Mechanisms

Sorption mechanisms of heavy metals by soil solids have been studied by a number of methods. Microscopic and spectroscopic methods can be used to obtain direct information about the binding characteristics (Hawthorne, 1988; Hochella and White, 1990; Fendorf et al., 1994a, b). These methods, however, are usually limited to the pure mineral-metal system because of the difficulty in interpretation of data for heterogeneous system such as soil. Indirect information about sorption mechanisms can be obtained by both equilibrium and kinetic studies. In this study, we employed an equilibrium method to extract sorption information. At equilibrium, sorption is not affected by the concentrations of electrolyte if sorption occurs by inner-sphere complexation (Zhang and Sparks, 1989; Grossl et al., 1994). For outer-sphere complexation, an increase in the concentration of electrolyte may decrease sorption. Figure 4.2 indicates that there was no significant difference in sorption isotherms for three different concentrations of NaNO_3 (0.001M, 0.01M and 0.1 M) for the two soils with different properties, suggesting Hg sorption by the soils was predominantly by inner-sphere complexation. The inner-sphere complexation was also suggested by Hg

speciation characteristics in the solution. In the soil solutions of this study, Cl^- concentrations ranged from 1×10^{-6} to 1×10^{-5} M, and pH ranged from 4.9 to 6.5. The inorganic Hg species were calculated as a function of the Hg concentration using MINEQL+ (Schecher and McAvoy, 1991) with boundary conditions of pH = 4.9, $\text{Cl}^- = 1 \times 10^{-5}$ M and pH = 6.5, $\text{Cl}^- = 1 \times 10^{-6}$ M. The thermodynamic constants used were corrected to 0.01 M NaNO_3 from those of Baes and Mesmer (1976). From Figure 4.3, for Hg concentrations used in this study, the major Hg species were the neutral species $\text{Hg}(\text{OH})_2$, $\text{Hg}(\text{OH})\text{Cl}$, and HgCl_2 , which accounted for more than 95% of the total soluble Hg. As Cl^- concentration decreased or/and pH increased, the fraction of $\text{Hg}(\text{OH})_2$ relative to HgCl_2 and $\text{Hg}(\text{OH})\text{Cl}$ increased. For $\text{Cl}^- = 10^{-6}$ M and pH = 6.5, almost 100% of the inorganic Hg was present as $\text{Hg}(\text{OH})_2$ within our experimental Hg concentration range. These neutral Hg species were not likely to form outer-sphere complexes with soil solids because of the electrostatic nature of the outer-sphere complex. James and Healy (1972) suggested that a decrease in the charge of species decreased the solvation energy and favored chemical sorption. Based on thermodynamic calculations according to a surface complexation model, Huang and Lin (1981), Huang et al. (1986), and Corapcioglu and Huang (1987) suggested that, through chemical bonding, hydroxymetal species, including MOH^+ and $\text{M}(\text{OH})_2$, were equally or even more adsorbable than were aquo ions. The sorption of Hg by soil at water-soil pH was probably completed by hydrogen bonding between coordinated H_2O (or OH^-) of Hg and the solid surface or by covalent bonding between Hg and surface coordinated O.

4.4.3 Modeling Sorption Isotherms

A number of equations, including the Langmuir equation, Freundlich equation and Langmuir two-site equation, have frequently been used to describe sorption isotherm of heavy metals (Travis and Etnier, 1981). They are not capable of describing the S-type isotherm which was a result of the interaction of inorganic Hg with both dissolved organic matter and soil solids. Barrow and Cox (1992) presented an empirical model ($S = ax^{bc}$, where S is the amount of Hg adsorbed; x is the concentration of Hg species considered; and a , b , c are adjustable parameters) to describe Hg sorption by a loamy sand. This model can be thought of as a modification of the Freundlich equation in which the exponent is not a constant but is itself a function of concentration. Only one Hg species HgOH^+ was assumed to be involved in sorption, which was calculated by assuming a constant dissolved organic matter (DOM) concentration and variable DOM-Hg stability constants which changed with both pH and the amount of postulated DOM-Hg complex. By adjusting the values of a , b , c , the authors showed that the experimental data could be described by the proposed model. However, this model is virtually a parameter-optimization method. The obtained parameters have no physical significance. Furthermore, as shown above, the fraction of HgOH^+ accounted for less than 5% of the total soluble Hg. It is not likely that the sorption of Hg by soil is due to the single HgOH^+ species. In this study, we developed a model in which the reactions of soluble inorganic Hg(II) with both dissolved organic matter and soil solids were considered to describe the sorption isotherm. The obtained parameters were used to evaluate soil sorption capacity and binding strength for Hg.

If 1:1 metal-ligand complexation is considered, the reaction between aqueous inorganic Hg and dissolved organic matter can be expressed by the following equations in which charges on chemical species are omitted for simplicity:



$$K_{OM} = \frac{[HgL]}{[Hg][L]} = \frac{[HgL]}{[Hg](C_L - [HgL])} \quad (4)$$

$$[HgL] = \frac{K_{OM}[Hg]C_L}{1 + K_{OM}[Hg]} = C_w - [Hg] \quad (5)$$

where $[HgL]$ is the concentration of aqueous organically complexed Hg ($\mu\text{mol L}^{-1}$); $[Hg]$ is the concentration of aqueous inorganic Hg ($\mu\text{mol L}^{-1}$); C_w is total aqueous mercury concentration ($\mu\text{mol L}^{-1}$); $[L]$ is the concentration of free ligand in solution ($\mu\text{mol L}^{-1}$), C_L is total ligand in solution ($\mu\text{mol L}^{-1}$), K_{OM} is the overall stability constant ($\text{L } \mu\text{mol}^{-1}$).

At natural soil pH, soil solids are negatively charged, and a surface site can be represented as $\equiv\text{SO}^-$. The reaction between Hg and $\equiv\text{SO}^-$ can be expressed as:



$$K_S = \frac{[\equiv\text{SOHg}]}{[Hg][\equiv\text{SO}^-]} \quad (7)$$

where K_S is the stability constant ($L \mu\text{mol}^{-1}$); $[\equiv \text{SO}^-]$ is the density of free surface negative sites ($\mu\text{mol g}^{-1}$), and $[\equiv \text{SOHg}]$ is the concentration of mercury adsorbed by soil ($\mu\text{mol g}^{-1}$), which can be calculated by:

$$[\equiv \text{SOHg}] = (C_T - C_W) / W \quad (8)$$

where C_T is the added Hg concentration ($\mu\text{mol L}^{-1}$), and W is the soil concentration in the suspension (g L^{-1}).

The density $\equiv \text{SO}^-$ of free can be calculated by:

$$[\equiv \text{SO}^-] = (N_t - [\equiv \text{SOHg}]) \alpha_- \quad (9)$$

where N_t is Hg sorption capacity of soil ($\mu\text{mol g}^{-1}$); α_- is fractional negative surface sites which was obtained by acid-base titration.

We define $[\equiv \text{SOHg}] = C_S$, and equation (7) is then rewritten as:

$$K_S = \frac{C_S}{[\text{Hg}] [\equiv \text{SO}^-]} = \frac{C_S}{[\text{Hg}] (N_t - C_S) \alpha_-} \quad (10)$$

Equation (10) can be rearranged to give:

$$C_S = \frac{K_S [\text{Hg}] N_t \alpha_-}{1 + K_S [\text{Hg}] \alpha_-} \quad (11)$$

From equation (5), we have

$$K_{\text{OM}} [\text{Hg}]^2 + (K_{\text{OM}} C_L - K_{\text{OM}} C_W + 1) [\text{Hg}] - C_W = 0 \quad (12)$$

which can be solved for the concentration of aqueous inorganic Hg

$$[Hg] = \frac{K_{OM}C_W - K_{OM}C_L - 1 + ((K_{OM}C_L + 1 - K_{OM}C_W)^2 + 4K_{OM}C_W)^{1/2}}{2K_{OM}} \quad (13)$$

Finally we solve for the concentration of sorbed Hg by Substitute (13) to (11):

$$C_S = \frac{K_S N_t \alpha_- (K_{OM}C_W - K_{OM}C_L - 1 + ((K_{OM}C_L + 1 - K_{OM}C_W)^2 + 4K_{OM}C_W)^{1/2})}{2K_{OM} + K_S \alpha_- (K_{OM}C_W - K_{OM}C_L - 1 + ((K_{OM}C_L + 1 - K_{OM}C_W)^2 + 4K_{OM}C_W)^{1/2})} \quad (14)$$

When $[Hg] \cong C_W$, equation (14) is approximated to:

$$C_S = \frac{K_S C_W N_t \alpha_-}{1 + K_S C_W \alpha_-} \quad (15)$$

We used a non-linear program (Wilkinson, 1988) to fit the experimental data according to equations (14) and (15). The results indicated that equations (14) and (15) respectively described the S-type and L-type isotherms shown in Fig. 1. The parameters, regression coefficients, and the residual sums of squares between experimental and predicted values are listed in Table 4.2. The regression coefficient squares are greater than 0.990 for all soils studied.

Table 4.2 Model fitting parameters

| Soil No.† | Log K _S L mol ⁻¹ | N _t μmol g ⁻¹ | Log K _{OM} L mol ⁻¹ | C _L μmol L ⁻¹ | Residual Sum of Squares μmol g ⁻¹ | R ² |
|-----------|---|--|--|--|---|----------------|
| 1 | 5.52 | 7.79 | | | 0.94 | 0.990 |
| 2 | 5.33 | 10.33 | | | 0.27 | 0.996 |
| 3 | 5.97 | 10.99 | | | 0.23 | 0.998 |
| 4 | 5.54 | 17.09 | 8.24 | 0.33 | 0.16 | 0.998 |
| 5 | 5.73 | 17.59 | 7.00 | 0.72 | 0.16 | 0.998 |
| 6 | 5.16 | 3.73 | | | 0.28 | 0.992 |
| 7 | 5.57 | 16.11 | 6.64 | 0.76 | 0.90 | 0.994 |
| 8 | 6.03 | 19.03 | 7.51 | 0.18 | 0.63 | 0.996 |
| 9 | 5.25 | 12.80 | | | 0.55 | 0.995 |
| 10 | 5.37 | 9.05 | | | 0.47 | 0.995 |
| 11 | 5.71 | 22.80 | 7.78 | 0.23 | 0.20 | 0.998 |
| 12 | 5.75 | 13.03 | 5.69 | 0.49 | 0.38 | 0.996 |
| 13 | 5.80 | 14.78 | 7.28 | 0.46 | 0.43 | 0.998 |
| 14 | 5.69 | 18.46 | 6.76 | 1.56 | 0.30 | 0.998 |
| 15 | 5.80 | 19.69 | 7.17 | 0.89 | 1.97 | 0.995 |

†See Table 1.

4.4.4 Correlations of Sorption Capacity and Binding Strength with Soil Properties

The sorption capacities of the fifteen New Jersey soils for Hg ranged from 3.73 μmol g⁻¹ to 22.8 μmol kg⁻¹. We analyzed the correlation between sorption capacity and soil properties, including organic carbon (OC), Al, Mn, Fe, surface area (SA), and CEC, by a multi-variant regression. The relative importance of these parameters was evaluated according to the standard regression coefficient ($b_{si} = b_i x_i / y_i$, where b_i is the coefficient of i th variable; x_i is the standard deviation of i th variable; y_i is the standard

deviation of the dependent) (Rosner, 1990). The greater the b_{si} , the more important the parameter. Based on the b_{si} values, the relative importance of these parameters in contributing soil sorption capacity was OC ($b_{si} = 0.72$) > CEC ($b_{si} = 0.45$) > SA ($b_{si} = 0.08$) > Mn ($b_{si} = 0.02$) > Fe ($b_{si} = -0.01$) > Al ($b_{si} = -0.11$). Both OC and SA had significant correlation with soil sorption capacity. Compared with SA (significant at < 0.05), OC is more important (significant at < 0.01). By plotting the sorption capacity versus the soil organic carbon content, we noticed that the sorption capacity was highly correlated with OC except for three data points whose OC contents were the highest (Figure 4.4). These three data points correspond to soil Nos. 8, 11 and 15. Because of the high sorption capacities of these three soils, within the experimental initial Hg concentration range we could observe only the initial and middle parts of the S-isotherms. As a result, the estimated sorption capacity of these three soils may not be accurate (Harter, 1984). When only the remaining 12 soils were considered, a regression coefficient (R^2) of 0.92 was obtained between the sorption capacity and the soil OC content. The standard deviation of the predicted value of the sorption capacity from experimental data was $1.15 \mu\text{mol g}^{-1}$.

We compared the K_s values of the soils that are given in Table 3 to evaluate those factors responsible for the difference in the relative binding strengths. The log K_s values of soils with a high proportion of sand (including soil Nos. 2, 6, 9, 10) were small ($\log K_s < 5.37$). We determined the relative importance of soil parameters for Hg binding by a multi-variant regression. The sequence obtained for relative importance was OC ($b_{si} = 0.68$) > SA ($b_{si} = 0.39$) \cong Al ($b_{si} = 0.37$) > Fe ($b_{si} = 0.27$) > CEC ($b_{si} = -0.38$) > Mn ($b_{si} = -0.57$).

4.4.5 Desorption

Two soils were used for the desorption study. One was a high organic matter (49.9 g C kg⁻¹ loam (Boonton Union loam) with silt plus clay content of 510 g kg⁻¹; the other was a low organic matter (1.2 g C kg⁻¹) sandy soil (Freehold sandy loam, A-horizon) with a sand content of 920 g kg⁻¹. For each soil, a series of different adsorbed Hg concentrations was tested. Desorption isotherms are shown in Figures 4.5a-b. Sorption/desorption hysteresis was evident for both soils. The hysteresis for Boonton Union loam was more significant than was that for Freehold sandy loam (A horizon). After 4 steps of desorption, more than 12% of the adsorbed Hg was desorbed from Freehold sandy loam (A horizon), whereas less than 2% of the adsorbed Hg was desorbed from Boonton Union loam. One factor contributing to the hysteresis may be the inner-sphere complexation that controlled sorption. The difference in hysteresis between the two soils probably resulted from Hg binding to different affinity sites on two soils. For Freehold sandy loam (A horizon), as the initial Hg concentration in the soil increased from 2.42 to 3.66 $\mu\text{mol g}^{-1}$, desorption increased from 12.0% to 21.2%, implying a large amount of Hg being bound by low affinity sites at a higher Hg level. For Boonton Union loam, as initial Hg concentration in soil increased from 3.94 to 10.80 $\mu\text{mol g}^{-1}$, desorption decreased from 1.6% to 0.9%. This suggested that at the experimental sorption level, most of the Hg was bound by high affinity sites. Consequently, although the absolute desorption increased (from 0.06 $\mu\text{mol g}^{-1}$ to 0.09 $\mu\text{mol g}^{-1}$) with the increase in the concentration of adsorbed Hg, the fractional desorption decreased. Since the initial Hg concentrations on Boonton Union loam were higher than those on Freehold sandy loam (A horizon), whereas the fractional desorption was in reverse order, it is obvious that Boonton Union loam had

more high affinity sites than did Freehold sandy loam (A horizon). This was also suggested by the higher K_s values of Boonton Union loam. In addition to the chemical binding, the physical entrapment of Hg in the soil organic matter structure could also contribute to the difficulty in the desorption of Hg from the high organic matter soil, Boonton Union loam.

4.5 Summary and Conclusions

The shape of sorption isotherms of Hg largely depended on the soil organic matter content. Within the experimental initial Hg concentration range, which covered three orders of magnitude (1.0×10^{-7} M to 1.1×10^{-4} M), all soils with organic carbon content greater than 11.0 g kg^{-1} had an S-type isotherm, whereas all soils with organic carbon content less than 7.4 g kg^{-1} had an L-type isotherm. Organic matter affected the sorption isotherm by affecting the amount of Hg complexed by dissolved organic matter and affecting the sorption capacity of soil for Hg. None of the traditional sorption equations were capable of describing the S-type isotherm. The S-type isotherm, however, can be described by a model developed in this study which considered the interaction of Hg(II) with both dissolved organic matter and soil solids. The sorption capacity of soil for Hg obtained via model fitting was correlated with the organic matter content ($R^2 = 0.92$).

Both the fact that the concentrations of background electrolyte did not affect sorption and the calculated Hg speciation characteristics in the soil solution suggested that the sorption of Hg by soil at soil-water pH occurred mainly by inner-sphere complexation reactions. This may in part explain the observed

sorption/desorption hysteresis. Compared with the soil which contained higher proportion of sand and smaller amount of organic matter, the hysteresis for the soil with a larger amount of organic matter and a small proportion of sand was more significant. This probably resulted from the binding of Hg to a greater number of high affinity sites in the high organic matter soil and the entrapment of Hg in the soil organic matter structure.

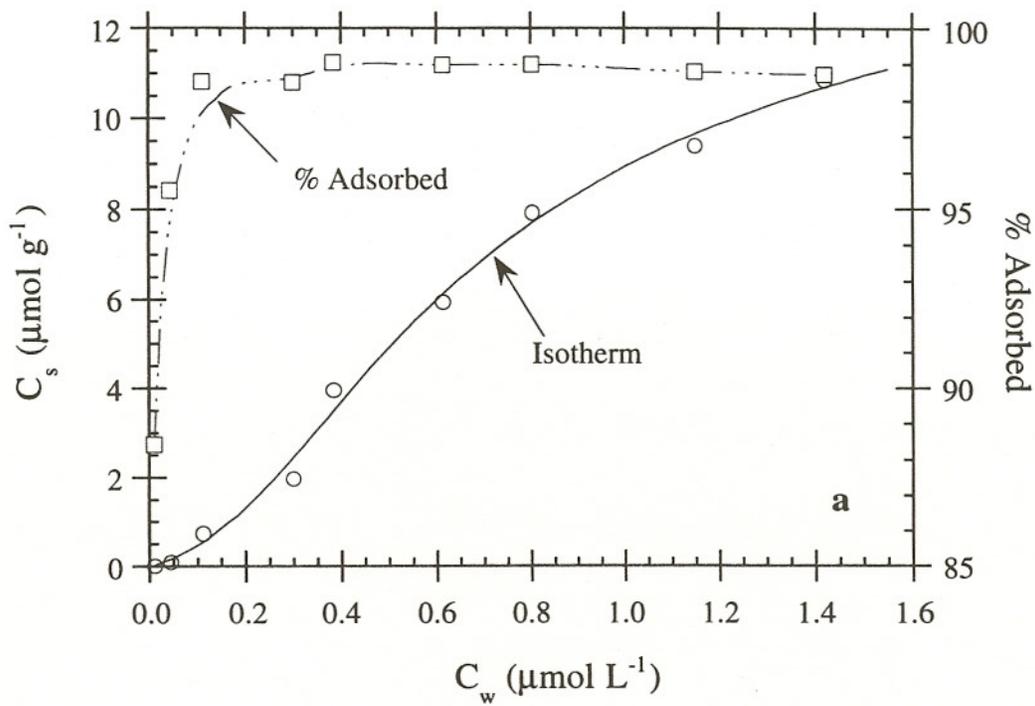


Figure 4.1a S-type sorption isotherms of Hg(II) on Rockaway sandy loam. Solid lines represent model-predicted isotherms. Soil : water = 0.4 g/40 mL; I = 0.01 NaNO₃; T = 25°C.

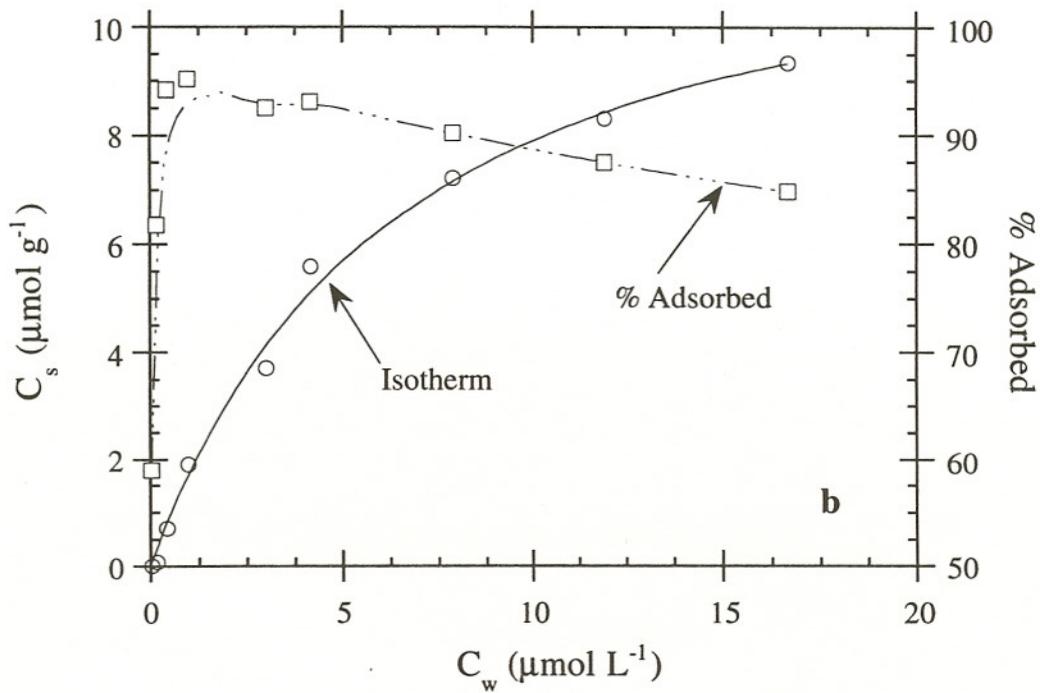


Figure 4.1b L-type sorption isotherm of Hg(II) on fill material from Delaware river. Solid lines represent model-predicted isotherms. Soil : water = 0.4 g/40 mL; I = 0.01 NaNO₃; T = 25°C.

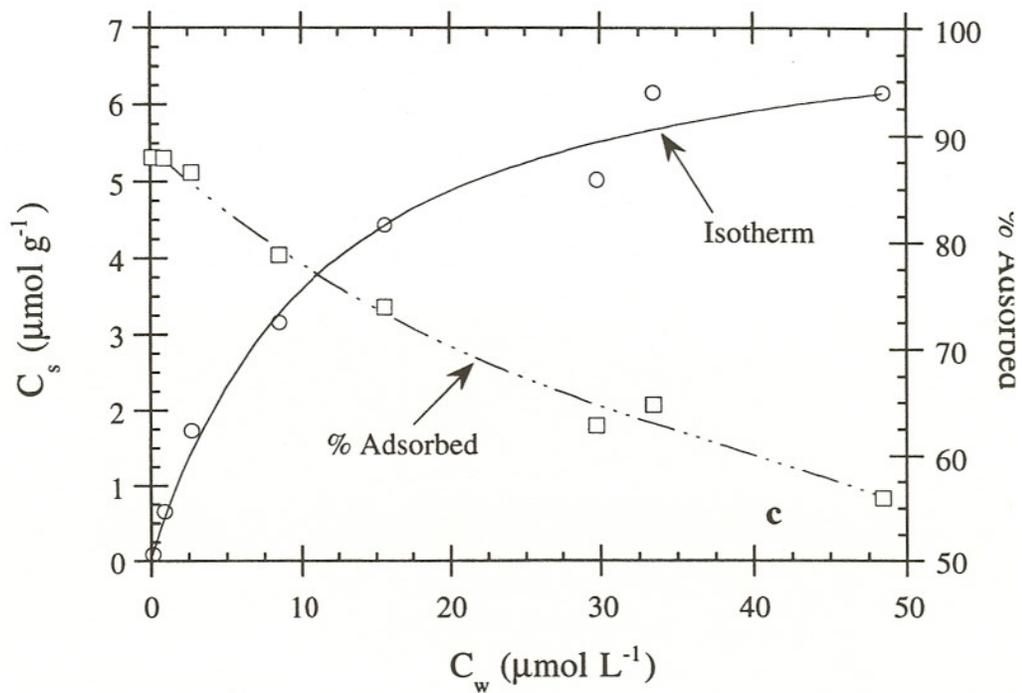


Figure 4.1c Sorption isotherm of Hg(II) on Rockaway sandy loam from which organic matter was removed. Solid lines represent model-predicted isotherms. Soil : water = 0.4 g/40 mL; I = 0.01 NaNO₃; T = 25°C.

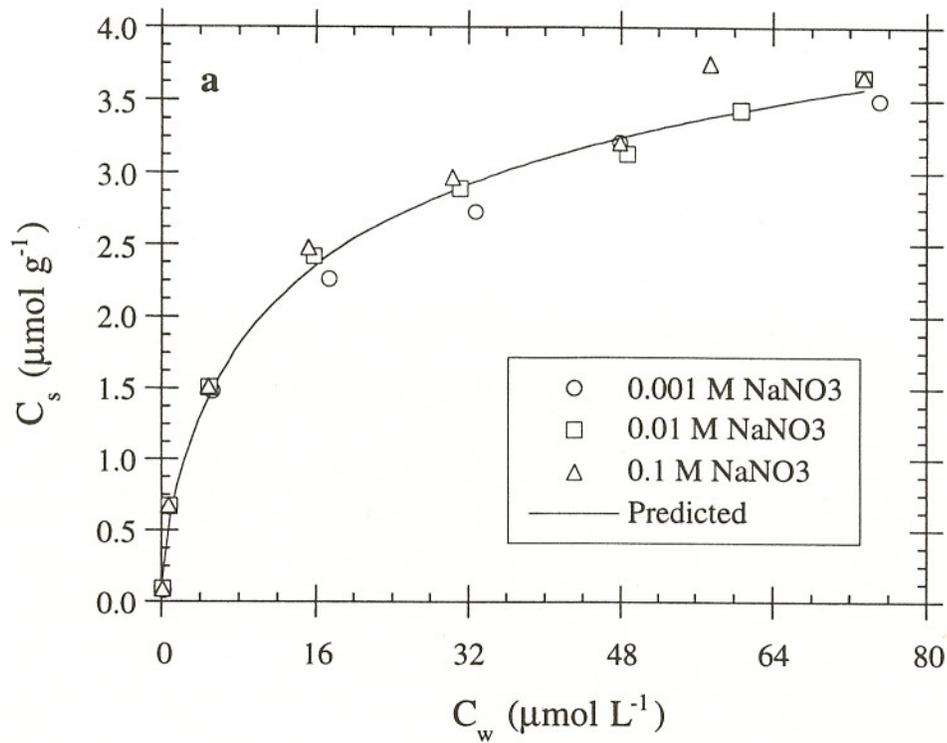


Figure 4.2a Comparison of sorption isotherms of Hg on Freehold sandy loam (A horizon) in different concentrations of electrolyte. Solid lines represent the model-predicted isotherms in 0.01 M NaNO₃.

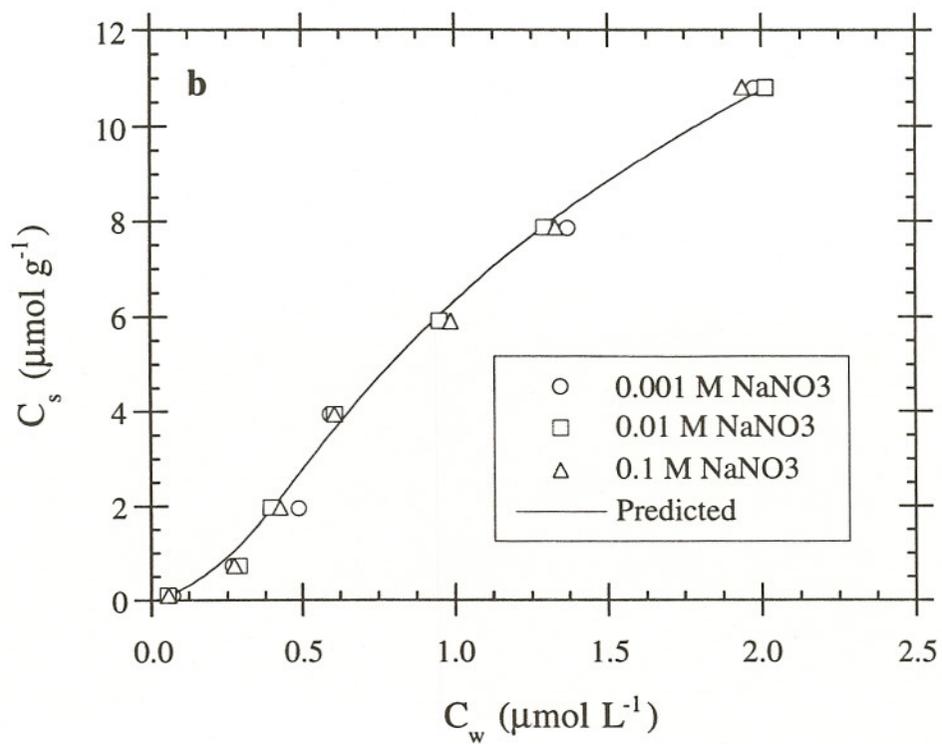


Figure 4.2b Comparison of sorption isotherms of Hg on Boonton Union loam in different concentrations of electrolyte. Solid lines represent the model-predicted isotherms in 0.01 M NaNO₃.

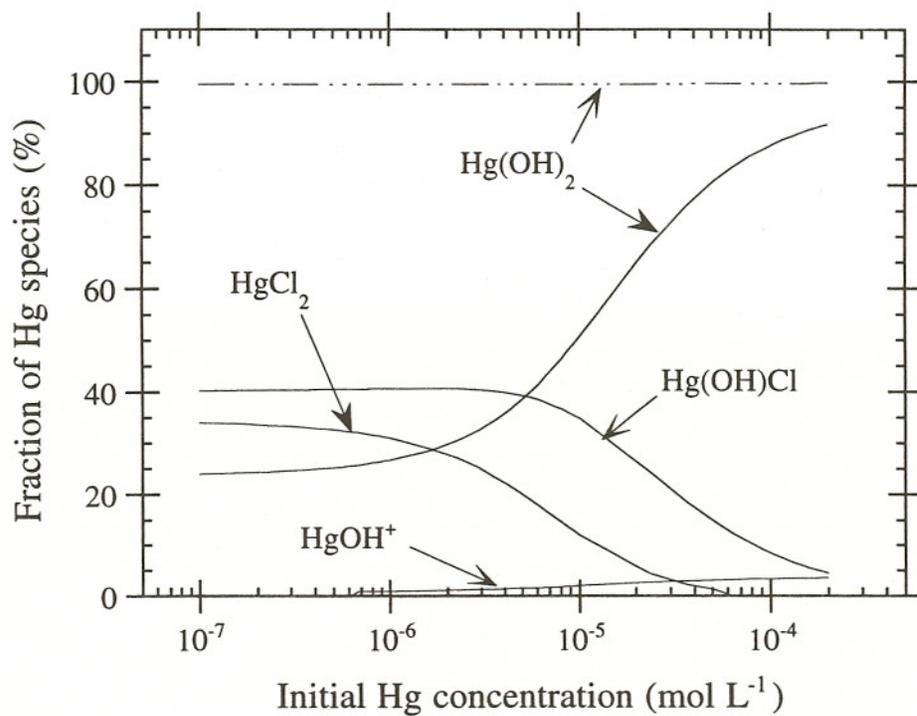


Figure 4.3 Mercury speciation as a function of initial Hg concentration. Solid lines: Cl⁻ = 10⁻⁵ M, pH = 5; dashed line: Cl⁻ = 10⁻⁶ M; pH = 6.5.

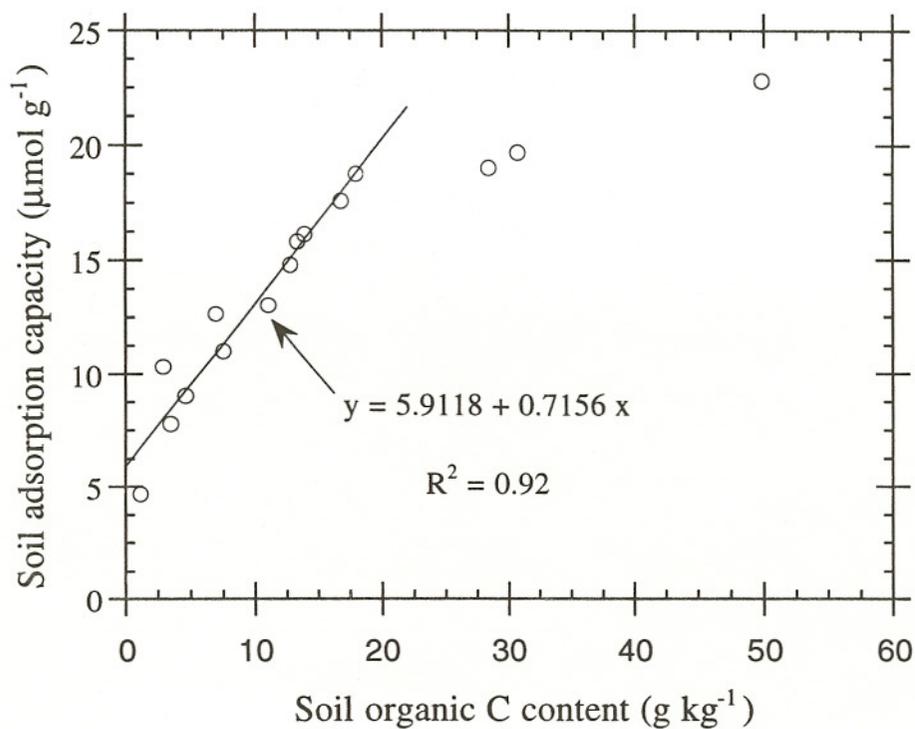


Figure 4.4 Correlation between soil adsorption capacity for Hg and the soil organic carbon content. Regression did not include the three soils having the greatest organic carbon content.

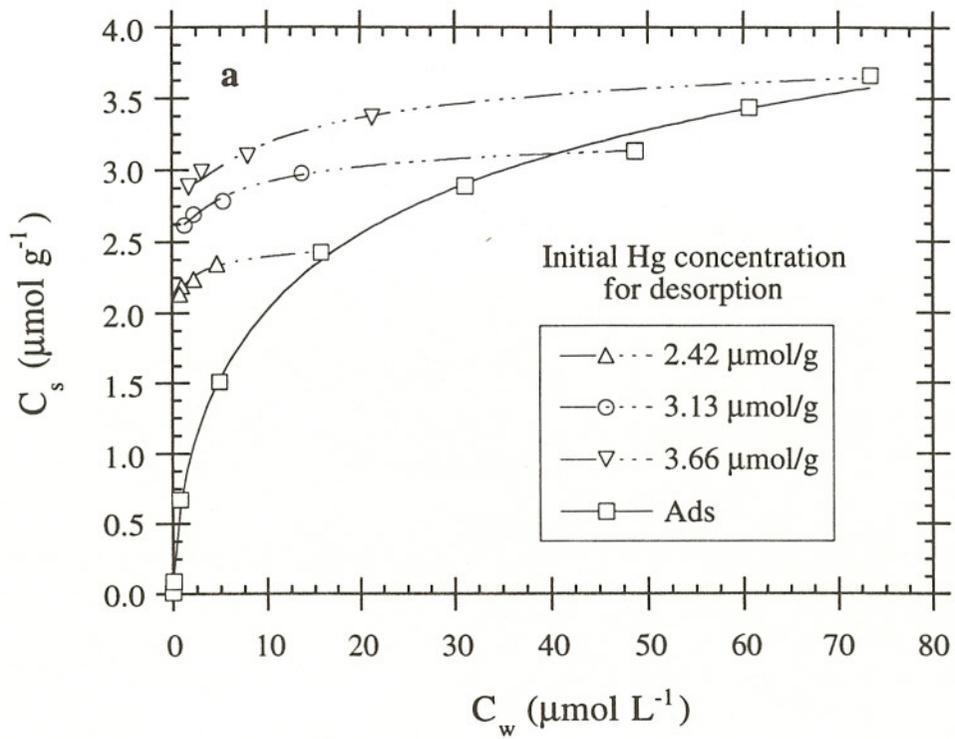


Figure 4.5a Desorption isotherms of Hg on Freehold sandy loam (A horizon). Solid lines represent adsorption; dashed lines represent desorption.

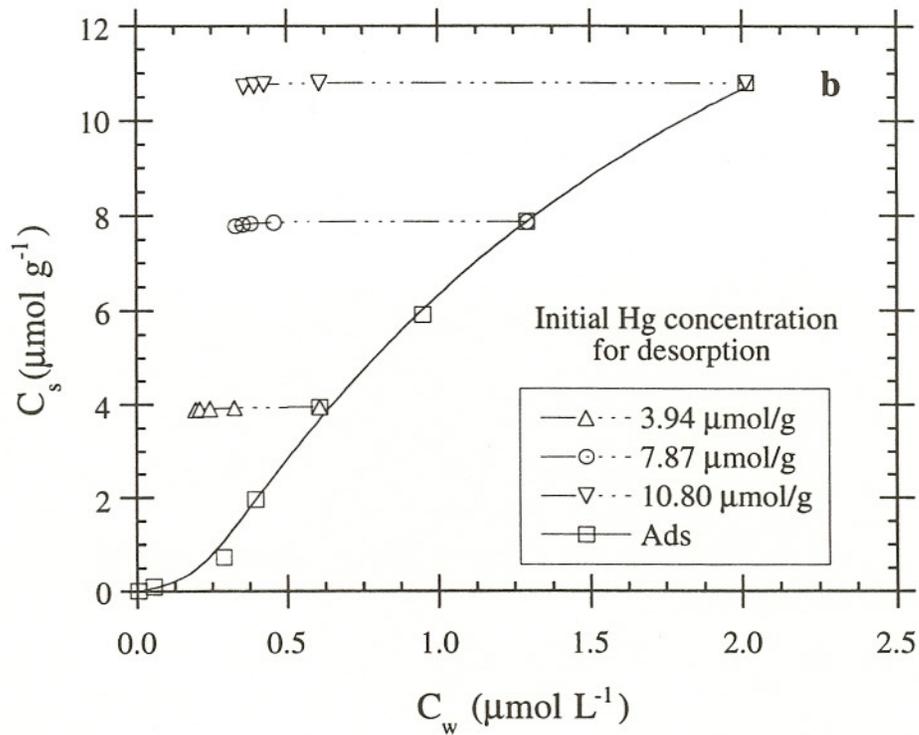


Figure 4.5b Desorption isotherms of Hg on Boonton Union loam.. Solid lines represent adsorption; dashed lines represent desorption.

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Chapter 5

KINETICS of MERCURY(II) SORPTION and DESORPTION on SOIL

5.1 Abstract

Sorption and desorption kinetics of Hg(II) on four soils at pH 6 were investigated using a stirred-flow reactor to discern the mechanisms controlling the retention and release reaction rates of Hg on soil. Sorption was very fast at the beginning for all soils. After 2 min, the Hg adsorbed ranged from 96 - 180 $\mu\text{g g}^{-1}$ for an influent concentration of 8 mg L^{-1} , and accounted for 4 - 38% of the total Hg adsorbed within 5 h. As the soil organic matter and silt and clay contents increased, so did sorption of Hg and the time required for attainment of equilibrium. Mercury desorption was characterized by a fast phase followed by a slow phase. Not all adsorbed Hg was readily released. Organic matter was found to be the major component responsible for Hg persistence in soil. Lower initial Hg concentrations in soil resulted in higher fractions that were resistant to desorption, implying that Hg preferentially bound to high energy sites. Apparent sorption and desorption rate coefficients were determined using a simplified multi-sites model. Both rate coefficients were inversely correlated with soil organic C content and the Hg partition coefficient.

5.2 Introduction

Equilibrium reactions between Hg(II) and soils have been extensively studied (Schuster, 1991; Barrow and Cox, 1992; Yin, et al., 1995a, b). Little, however, has appeared in the literature concerning the kinetics of these reactions. Due to the mobility of soil solution, the retention and release reactions of soluble contaminants with soil, in most cases, are time-dependent rather than instantaneous equilibrium processes. A knowledge of the reaction rates is therefore necessary in order to predict the transport and fate of contaminants in soil and provide cost-effective soil remediation strategies.

The reactions of contaminants with soil involve both chemical reaction and diffusion processes. Diffusion has often been reported to be the rate limiting step (Sparks, 1989). Both penetration into the mineral lattice (Kou, 1986; White and Yee, 1986; Bruemmer et al., 1988) and diffusion through intraparticle pores (Avotins, 1975, Sparks et al., 1980) have been suggested to be responsible for the slow reactions of metals with soil or soil components. These diffusion processes were often considered as the cause of the observed sorption/desorption hysteresis which increases with time of aging (Ainsworth et al., 1994). Some researchers suggested that hysteresis resulted from the binding of metals to different sites. Di Toro et al. (1986) modeled the sorption - desorption of Co and Ni on montmorillonite and quartz by assuming the sorbed chemical to be the sum of a reversibly sorbed component and a resistant component. Amacher et al. (1988, 1990) proposed a multi-reaction model to describe the reactions of several metals with soil. They assumed that sorption/desorption processes involved three concurrent reactions with three different kinds of sites on

soil, i.e., a rapid and reversible reaction, a slow and reversible reaction, and an irreversible reaction.

In most cases, kinetic information has been obtained using either batch or miscible displacement techniques. Both methods suffer from pronounced diffusion effects (Ogwada and Sparks, 1985).

The purpose of this study was to examine the rates of Hg retention and release on soil and to understand the mechanisms controlling the reaction rates. In this study, we used a stirred-flow method to perform experiments. The soil suspension in the reaction chamber was well mixed (Seyfried, et al, 1989) which significantly reduced diffusion (Amacher, 1991). The desorbed solute was continuously removed from the reactor, therefore, further release of Hg was not prohibited by the soluble Hg as was observed in batch experiments (Martin and Sparks, 1983). We investigated Hg sorption/desorption kinetics on four soils with different properties. We also removed organic matter from soils to evaluate the importance of soil components and porosity in determining the reaction rates. Apparent Hg sorption and desorption rate coefficients were determined using a simplified multi-sites model.

5.3 Materials and Methods

5.3.1 Kinetic Experiments

Four soils, Freehold sandy loam (A horizon), Sassafras sandy loam, Dunellen sandy loam, and Rockaway stony loam, listed in Table 3.1 - 3.3 were used to perform studies. The stirred-flow reaction chamber used was a modification of that developed

by Carski and Sparks (1985). It was made of Plexiglas and consisted of two units, a reaction cell (6.7 cm^3) with an inlet side port near the bottom, and a cover with an outlet port on the top. The reaction cell was thread sealed by the cover. A 25-cm in diameter, $0.45\text{-}\mu\text{m}$ pore size Nuclepore membrane filter (Costar, Cambridge, MA) was fitted just below the outlet port of the cover to retain the soil in the chamber. Both influent and effluent were transported by 0.89 mm i.d. Teflon tubing. For sorption studies, 0.3 g soil samples and a Teflon-coated magnetic stirrer were placed into the reaction cell. The soil was wetted with 0.5 mL of 0.01 M NaNO_3 and allowed to hydrate for 1 hour. The reaction cell was then filled with 8 mg L^{-1} or 4 mg L^{-1} Hg influent (prepared in 0.01 M NaNO_3 at pH 6) and sealed with the cover. The same influent solution was then pumped into the chamber using an Ismatec pump (Cole-Parmer, No. 7332) at a rate of 1 mL min^{-1} , and the effluent was collected with an automatic fraction collector after the first 2 minutes and then at 5-min intervals. Hg concentrations in the effluent samples were then determined by a cold vapor Hg analyzer (Perkin Elmer MHS 10) coupled with an atomic absorption spectrophotometer (Perkin Elmer Zeeman model 5000). The sorption experiment was continued until equilibrium, which was judged by equivalence of influent and effluent concentrations, was achieved. Following sorption, desorption was initialized by passing 0.01 M NaNO_3 (pH = 6) through the chamber.

To account for the dilution effect and the amount of Hg adsorbed by the reaction chamber, we measured blank curves for sorption and desorption without soil in the chamber following the same procedure as described above. 23% of the input Hg was initially adsorbed by the reactor for an influent Hg concentration of 8 mg L^{-1} , and 38% for an influent concentration of 4 mg L^{-1} . The reactor was saturated in 30

minutes and 60 minutes for an influent Hg concentration of 8 mg L⁻¹ and 4 mg L⁻¹, respectively. Duplicate experiments were run and the variance of effluent concentrations at each time point was less than 6%.

The flow rate was monitored during the entire experiment, and the change of the flow rate was less than 5%. A magnetic stirrer was used to ensure adequate mixing in the reaction chamber, and the stirring speed was maintained at a minimum to reduce abrasion of the soil. After each run either with or without soil present, the transport tubing was washed by passing 15% HNO₃ followed by distilled deionized water, and the reaction chamber was cleaned by soaking in 15% HNO₃ overnight followed by washing with distilled deionized water.

5.3.2 Data Analysis

The amount of Hg adsorbed or released from soil can be calculated from the difference in solution concentrations with and without soil in the reaction chamber (Schnabel and Fitting, 1988; Sparks, 1989). The adsorbed or released quantity is the sum of the concentration differences in both effluents and the solutions in the chamber with and without soil. For sorption, it can be expressed as:

$$q_a(t_i) = \frac{\sum[(\bar{C}_{ib} - \bar{C}_{is}) J \Delta t_i] + [C_b(t_i) - C_s(t_i)]}{W} \quad (1)$$

in which $q_a(t_i)$ is the cumulative sorption at time t_i , $\mu\text{g g}^{-1}$; J is flow rate; L min^{-1} ; Δt_i is sampling time interval, min; \bar{C}_i is the effluent concentration for the i th sampling period, $\mu\text{g L}^{-1}$; $C(t_i)$ is the concentration in the chamber at time t_i , $\mu\text{g L}^{-1}$; and W is soil

concentration in the chamber, g L^{-1} . Subscripts s and b refer to the cases with and without soil in the chamber, respectively.

The quantity desorbed is given by:

$$q_d(t_i) = \frac{\sum[(\bar{C}_{is} - \bar{C}_{ib}) J \Delta t_i] + [C_s(t_i) - C_b(t_i)]}{W} \quad (2)$$

where $q_d(t_i)$ is the cumulative desorption at time t_i , $\mu\text{g g}^{-1}$.

For equations (1) and (2), effluent Hg concentrations can be determined directly. The concentration in the chamber at the end of a specific sampling period, however, needs to be estimated. This was approximated by averaging the effluent concentrations for that time period and the succeeding one.

5.4 Results and Discussion

5.4.1 Sorption Kinetics

Before running complete sorption and desorption kinetic experiments, we conducted a preliminary study following the method of Bar-Tal et al. (1990) to ascertain whether the reactions of Hg with soil were instantaneous or kinetically controlled. The assumption of this method is that if a non-equilibrium condition exists in the reaction chamber, stopping the flow of adsorptive for a sufficient time period before equilibrium is established should result in a noticeable drop in effluent concentration when flow is restarted. If the reaction is instantaneous, the plot of effluent concentrations versus time should be continuous. Although not presented in

It is speculated that soil particle size may also be important to the reaction rate. This hypothesis was tested by removal of organic C from Freehold sandy loam (A horizon) and Dunellen sandy loam. The organic C was removed by treatment of soils with H_2O_2 following the method described by Yin et al. (1996b). This procedure removed 96% and 88% of the soil organic C from Freehold sandy loam (A horizon) and Dunellen sandy loam, respectively. If micropore diffusion contributed to the slow reaction rate, it will take a longer time for sorption to reach equilibrium on Dunellen sandy loam than on Freehold sandy loam (A horizon) after removal of organic C from both soils, because the former soil contains much more silt and clay which have more micropores than does sand. As shown in Figure 5.1, after removal of organic C, Dunellen sandy loam adsorbed more Hg and required longer time for reaction to reach equilibrium than Freehold sandy loam (A horizon) did. This suggests that micropore diffusion was probably involved in the sorption.

The effect of influent Hg concentration on the reaction was tested on Freehold sandy loam (A horizon) and Dunellen sandy loam. The results are represented in Figure 5.2. A decrease in influent concentration decreased sorption, indicating that the reaction was reversible or partially reversible. The decrease in influent concentration also resulted in an increase in the equilibrium time. The influent Hg concentrations used in this study resulted in the soil being nearly saturated (Yin et al., 1996b). It is expected that for a lower Hg influent concentration level, the effect of influent concentration on the sorption kinetics would be more significant. The dependence of the sorption rate on Hg influent concentration suggested that diffusion was probably involved in the reaction. Diffusion has frequently been reported to be the rate limiting step for metal sorption and desorption (Sparks et al., 1980; Jardine and Sparks, 1983;

Bruemmer, et al., 1988). Diffusion controlled processes often follow parabolic kinetics, which are characterized by a linear relationship between fractional sorption (q/q_{∞} , where q is the solute adsorbed at time t , and q_{∞} is the solute adsorbed at equilibrium) and $t^{1/2}$. Although not shown, plots of Hg fractional sorption versus $t^{1/2}$ for all soils studied are curvilinear, implying that parabolic diffusion was not predominant for the reactions of this study.

5.4.2 Desorption Kinetics

Desorption experiments were conducted following sorption studies for which equilibrium was achieved within the experimental sorption time period. As shown in Figure 5.3, Hg removal rate profiles on all soils were characterized by two desorption regimes, a fast regime followed by a slow regime. The fast desorption regime occurred during the first 100 min, and the desorption rate related to the initial Hg concentration in soil. After 8 h of desorption, the desorption rate was less than $0.6 \mu\text{g g}^{-1} \text{min}^{-1}$ for all soils. However, $2000 \mu\text{g g}^{-1}$ Hg still remained on the Dunellen sandy loam, $446 \mu\text{g g}^{-1}$ on the Sassafras sandy loam, and $50 \mu\text{g g}^{-1}$ on the Freehold sandy loam (A horizon) (Figure 5.4). The fractional removal (q/q_0) profiles for all soils are similar in shape, but the quantity is different (Figure 5.5). At the end of 8-h of desorption, of the Hg retained 79% was released from the Freehold sandy loam (A horizon), 62% was released from the Sassafras sandy loam, and 43% was released from the Dunellen sandy loam.

One well-documented factor responsible for the persistence of metals in soil or soil components is diffusion into the mineral lattice (Kou, 1986; White and Yee 1986;

Bruemmer et al., 1988) or into intraparticle pores (Avotins, 1975, Sparks et al., 1980). We speculated that the interaction of metals with soil organic matter may also contribute to the observed sorption/desorption hysteresis. Although few attempts have been made to study the importance of soil organic matter to metal persistence in soil, it has been reported that restricted diffusion in organic matter was responsible for the persistence of many organic chemicals in soil (Bouchard et al., 1988; Nkedi-Kizza et al., 1989; Carroll et al., 1994). To ascertain the soil components responsible for Hg persistence in soil, we compared Hg desorption on Freehold sandy loam (A horizon) and Dunellen sandy loam with and without removal of organic matter. After removal of organic matter, the predominant portion of Freehold sandy loam (A horizon) was sand, whereas there was nearly 50% silt and clay in Dunellen sandy loam. If the interaction of Hg with soil organic matter is responsible for the observed hysteresis, then the removal of organic matter should significantly increase Hg fractional release. If diffusion through intra or/and inter mineral micropores is responsible for Hg slow release, then Hg fractional release should be much higher for Freehold sandy loam (A horizon) than for Dunellen sandy loam after removal of organic matter. As shown in Figure 5.5, removal of organic C significantly increased fractional release of Hg from both soils. At the end of 8-h desorption, the fractional release from Dunellen sandy loam (OC removal) was 95%, which was slightly lower than the 99% from Freehold sandy loam (A horizon). This suggested that organic matter was the major component responsible for Hg persistence in soil. Diffusion through mineral micropores may contribute to hysteresis, but the contribution was much smaller than that by organic matter. This was probably because the experimental time period was not long enough

for Hg to penetrate into the mineral structure, and the diffusion within mineral micropores may also be significantly reduced by continuous stirring.

Comparison of Hg desorption on Sassafras sandy loam and Dunellen sandy loam also suggested that organic matter was the most important component responsible for Hg persistence in soil. As shown in Table 3.1 and Table 3.2, Sassafras sandy loam has a similar surface area and higher silt and clay content than does Dunellen sandy loam, however, Hg fractional desorption from this soil was much higher (62%) than that from Dunellen sandy loam (42%) (Figure 5.4). This probably resulted from the higher organic matter content in Dunellen sandy loam.

We plotted the fraction of Hg remaining ($F = q_a/q_0$) in soil after 8 h of desorption versus the soil organic C (OC) content, and found that the F values proportionally increased with OC. Upon log transformation of OC values, a linear correlation between F and log OC was obtained. The regression equation is: Fractional Hg remaining = $0.179 + 0.374 \log \text{OC}$ with a regression coefficient of 0.999.

We speculated that the slow release resulted from Hg preferentially bonding to high energy sites. Because these high energy sites have limited sorption capacity, lower concentration may result in higher fractional sorption to these high energy sites, and consequently cause lower fraction of release from soil. This hypothesis was tested on Freehold sandy loam (A horizon). As shown in Figure 5.6, 60% Hg retained was released within nearly 2 h for an initial concentration of $254 \mu\text{g g}^{-1}$, whereas 55% Hg retained was released for an initial concentration of $214 \mu\text{g g}^{-1}$. Fig. 6 also indicated that after 50 min of desorption, the Hg remaining on the soil for two initial concentrations was almost the same. This can only be explained by the preferential

distribution of adsorbed Hg among soil sites. Although the initial concentrations were different, the amount of Hg adsorbed on high energy sites could be similar. As a result, after the Hg on the low energy sites was quickly released, the Hg remaining on soil (high energy sites) was similar for different initial concentrations.

5.4.3 Modeling Sorption and Desorption Kinetics

A number of models have been postulated to describe metal sorption and desorption kinetics. Early attempts mainly focused on one-site kinetic equations (Travis and Etnier, 1981). The rate coefficient obtained using these equations is usually an apparent coefficient which changes with flow rate and initial solute concentration. In many cases, a deviation of experimental data from the simple one-site kinetic equations was observed. Accordingly, two-site or two-region models, with two classes of sites either in series or parallel, were proposed to describe non-equilibrium sorption (Selim et al., 1976; Nkedi-Kizza et al., 1989). Selim and co-workers (Amacher et al., 1990; Selim, 1992) also proposed a multireaction model, with sorption sites ranging from 3 to 5 types, to simulate metal sorption on soil. Because this model involves so many adjustable parameters, its usefulness was limited.

Due to the heterogeneous nature of soil, there are virtually a continuum of sites on soil. Assume there are totally n type of sites on soil. The sorption reaction between Hg and the i th type of site can be expressed as:



The reaction rate is assumed to be a function of the density of unoccupied *i*th surface sites:

$$\frac{dq_i}{dt} = k_i (q_{i\infty} - q_i) \quad (4)$$

where dq_i/dt is the reaction rate ($\mu\text{g g}^{-1} \text{min}^{-1}$); k_i is rate coefficient (min^{-1}); q_i is the concentration of Hg on the *i*th sites at time *t* ($\mu\text{g g}^{-1}$); and $q_{i\infty}$ is the concentration of Hg on the *i*th site at equilibrium ($\mu\text{g g}^{-1}$). Integration of equation (4), with initial condition $t = 0, q = 0$, yields:

$$q_i = q_{i\infty} - q_{i\infty} \exp(-k_i t) \quad (5)$$

The total Hg ($q_a, \mu\text{g g}^{-1}$) adsorbed by soil at time *t* is:

$$\begin{aligned} q_a &= \sum_{i=1}^{i=n} q_i = \sum_{i=1}^{i=n} (q_{i\infty} - q_{i\infty} \exp(-k_i t)) \\ &= q_{\infty} - \sum_{i=1}^{i=n} q_{i\infty} \exp(-k_i t) \end{aligned} \quad (6)$$

where q_{∞} is Hg concentration on soil at equilibrium ($\mu\text{g g}^{-1}$). The second term in equation (6) can be approximated as:

$$\sum_{i=1}^{i=n} q_{i\infty} \exp(-k_i t) \cong \alpha \exp(-k_a t) \quad (7)$$

where α relates to the sum of Hg concentration on all soil sites at equilibrium; k_a is an overall sorption rate coefficient whose value is in between the rate coefficient for the fastest reaction sites and that for the slowest reaction sites.

Substitution of (7) into (6) gives:

$$q_a = q_\infty - \alpha \exp(-k_a t) \quad (8)$$

Assume Hg reactions with m types of sites of the total n types of soil sites are reversible. The desorption reaction of Hg from the j th type of reversible sites can be expressed as:



$$\frac{dq_j}{dt} = -k_j q_j \quad (10)$$

where dq_j/dt is the desorption rate ($\mu\text{g g}^{-1} \text{min}^{-1}$); q_j is Hg concentration on the j th site at time t ($\mu\text{g g}^{-1}$); and k_j is the desorption rate coefficient for the j th site (min^{-1}).

Integration of equation (10), with initial condition at $t = 0$, $q_j = q_{j0}$, yields:

$$q_{dj} = q_{j0} - q_{j0} \exp(-k_j t) \quad (11)$$

where q_{dj} is the concentration of Hg desorbed from j th sites at time t ($\mu\text{g g}^{-1}$). The total Hg desorbed from all sites is:

$$q_d = q_0 - \sum_{j=1}^{j=m} q_{j0} \exp(-k_j t) \quad (12)$$

where q_d is the accumulative concentration of Hg released from all sites ($\mu\text{g g}^{-1}$); q_0 is the concentration of Hg retained on all reversible sites at the beginning ($\mu\text{g g}^{-1}$). The second term in equation (12) can be approximated as:

$$\sum_{j=1}^{j=m} q_{j0} \exp(-k_j t) \cong \beta \exp(-k_d t) \quad (13)$$

where β is a constant related to q_0 ; and k_d is an overall desorption rate coefficient whose value is in between the rate coefficient for the fastest desorption sites and that for the slowest desorption sites.

Substitution of equation (13) to (12) gives:

$$q_d = q_0 - \beta \exp(-k_d t) \quad (14)$$

Equation (8) and (14) were used to fit sorption and desorption kinetics respectively. Parameters were determined with a non-linear least-square optimization program (Wilkinson, 1988). The results are summarized in Table 5.1. The large regression coefficients (r^2), small values of standard deviation (SE) for estimated parameters, as well as the magnitude of root mean squares (RMS) indicated that the fit of experimental data was good. An example is shown in Figure 5.7. There is a small deviation between the predicted values and the experimental data when the reaction is close to equilibrium. This is due to the reverse reaction which was not considered in the model.

As indicated in Table 2, the amount of Hg adsorbed on reversible sites (q_0) is much smaller than the total retained Hg (q_∞), suggesting that not all adsorbed Hg can be readily desorbed. Both k_a and k_d were found to inversely correlate with the soil organic C content and the Hg partition coefficient (K_p). By plotting $\log k_a$ and $\log k_d$ versus $\log OC$ and $\log K_p$, linear relationships were obtained as indicated in Table 3. The regression coefficients (r^2) for all regressions are 0.939 or greater.

Table 5.1 Model fitting parameters

| Soil No. | Influent Hg Conc. $\mu\text{g L}^{-1}$ | Sorption | | | | | | | |
|----------|---|--------------------------------------|---|----------------------------------|----------------------------|----------------------------|-------------------------|-------|--|
| | | q_{∞} $\mu\text{g g}^{-1}$ | SE [†] $\mu\text{g g}^{-1}$ | α $\mu\text{g g}^{-1}$ | SE $\mu\text{g g}^{-1}$ | k_a min^{-1} | SE min^{-1} | r^2 | RMS [‡] $\mu\text{g g}^{-1}$ |
| 6 | 4000 | 214 | 1 | 195 | 3 | 0.0529 | 0.0019 | 0.991 | 4 |
| | 8000 | 257 | 1 | 239 | 5 | 0.1167 | 0.0057 | 0.987 | 6 |
| 1 | 8000 | 1204 | 4 | 1132 | 10 | 0.0219 | 0.0004 | 0.996 | 18 |
| 12 | 4000 | 4341 | 88 | 4381 | 80 | 0.0037 | 0.0001 | 0.999 | 32 |
| | 8000 | 3935 | 27 | 3986 | 27 | 0.0098 | 0.0002 | 0.997 | 56 |
| 8 | 8000 | 5714 | 58 | 5748 | 49 | 0.0059 | 0.0001 | 0.999 | 49 |

| Soil No. | Influent Hg Conc. $\mu\text{g L}^{-1}$ | Desorption | | | | | | | |
|----------|---|-------------------------------|----------------------------|---------------------------------|----------------------------|----------------------------|-------------------------|-------|-----------------------------|
| | | q_0 $\mu\text{g g}^{-1}$ | SE $\mu\text{g g}^{-1}$ | β $\mu\text{g g}^{-1}$ | SE $\mu\text{g g}^{-1}$ | k_d min^{-1} | SE min^{-1} | r^2 | RMS $\mu\text{g g}^{-1}$ |
| 6 | 4000 | 127 | 2 | 124 | 2 | 0.0221 | 0.0011 | 0.996 | 2 |
| | 8000 | 196 | 1 | 165 | 3 | 0.0138 | 0.0005 | 0.977 | 6 |
| 1 | 8000 | 745 | 4 | 640 | 10 | 0.0100 | 0.0003 | 0.980 | 22 |
| 12 | 4000 | | | | | | | | |
| | 8000 | 1554 | 7 | 1453 | 13 | 0.0085 | 0.0002 | 0.992 | 35 |
| 8 | 8000 | | | | | | | | |

[†] SE is standard deviation of the estimated parameter.

[‡] RMS is the root mean square which is defined by $[\text{RSS}/(n-p)]^{0.5}$, where RSS is residual sum of square; n is the number of data points; and p is the number of parameters.

Table 5.2 Linear relationships between rate coefficients and soil organic C (OC) content as well as Hg partition coefficient (K_p)

| | Log k_a (min^{-1}) | | | | Log k_d (min^{-1}) | | | |
|------------------------------------|---------------------------------|--------|-------|-----------------|---------------------------------|--------|-------|------|
| | Intercept | Slope | r^2 | SD [†] | Intercept | Slope | r^2 | SD |
| Log OC (g kg^{-1}) | -0.989 | -0.921 | 0.939 | 0.17 | -1.856 | -0.219 | 0.958 | 0.03 |
| Log K_p (L g^{-1}) | -2.372 | -0.946 | 0.991 | 0.08 | -2.141 | -0.185 | 0.993 | 0.01 |

[†] Standard deviation of predicted values.

5.5 Summary and Conclusions

Hg sorption and desorption on soils were kinetically controlled and not completely reversible. Sorption was initially very fast. At the end of the first 2 min, the adsorbed Hg was 96 - 180 $\mu\text{g g}^{-1}$, which accounted for 4 - 38% of the total Hg that was adsorbed within 5 h. Soils with higher organic matter and higher silt and clay contents had greater sorption of Hg and took a longer time to reach equilibrium. Hg desorption was characterized by a biphasic pattern, a slow desorption followed an initial fast phase. The fractional Hg release depended on soil properties. Among soil components, organic matter is the major component responsible for Hg persistence in soil. Low initial Hg concentration in soil resulted in a higher resistant fraction, which is a result of Hg preferential bonding to high energy sites.

Kinetics of Hg sorption and desorption on soils can be described by the simplified multi-sites model. Both apparent sorption and desorption rate coefficients were found to inversely relate to the soil organic C content and Hg partition coefficient

(K_p). Linear relationships between $\log(k_a$ or $k_d)$ and $\log OC$ and $\log K_p$ were obtained with regression coefficient $r^2 > 0.939$.

An implication of the results is that the application of Hg to a low organic matter sandy soil could eventually result in groundwater contamination. On the other hand, the contamination of a high organic matter soil with Hg, especially for low concentration of Hg and after long contact time, may not pose serious groundwater problem. However, the decontamination of the latter soil using some methods, such as in-situ washing with water, may not be effective.

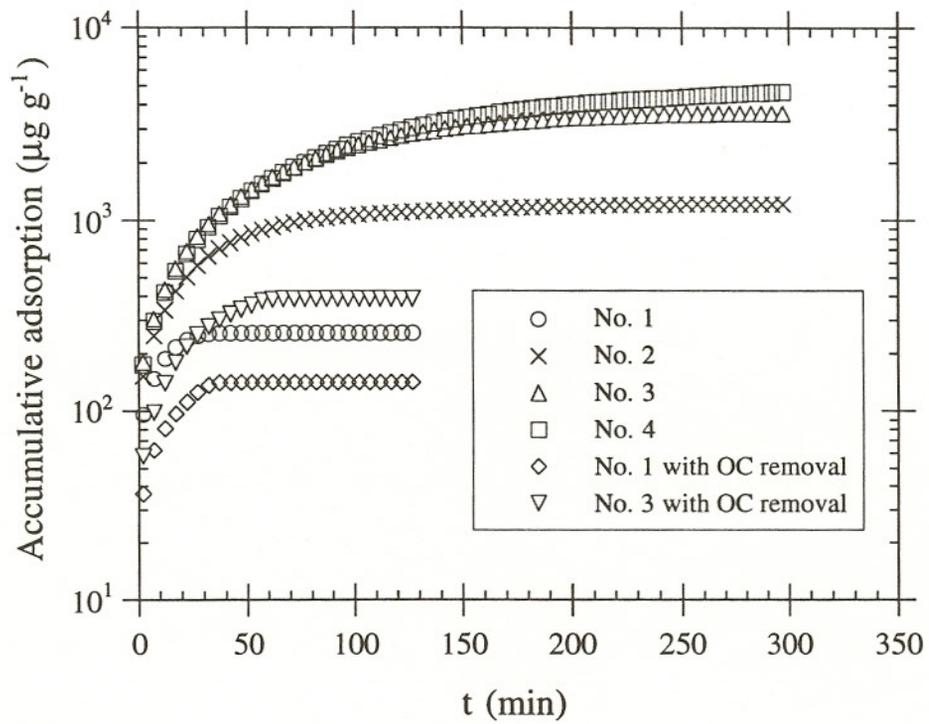


Figure 5.1 Kinetics of Hg sorption on soils at an influent concentration of 8 mg L⁻¹. See Table 3.1 for soil identification.

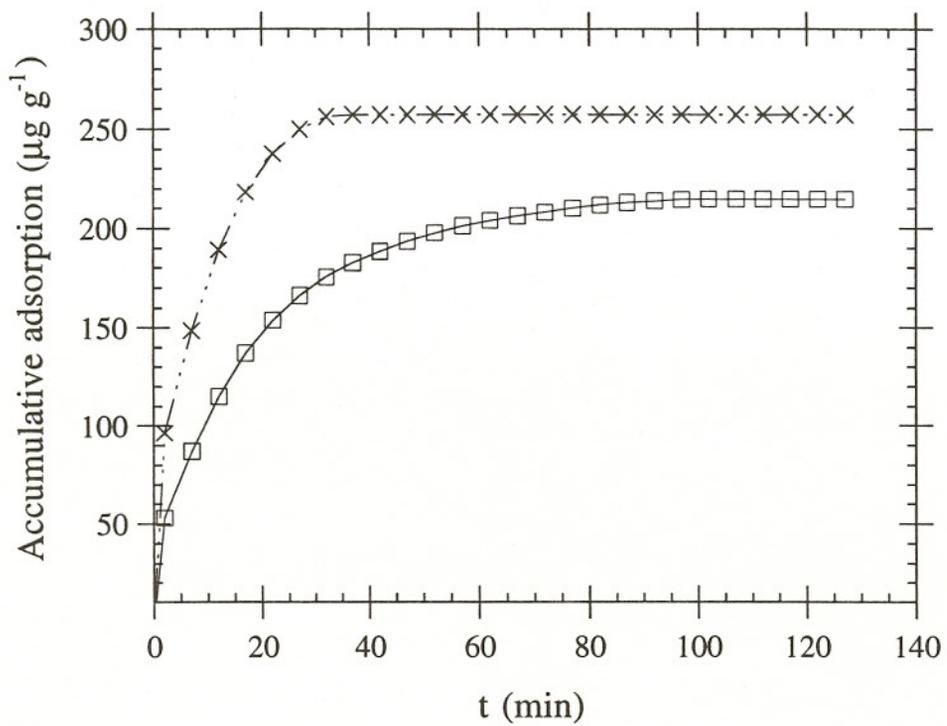


Figure 5.2 Comparison of Hg sorption kinetics on Freehold sandy loam (A horizon) at different influent concentrations. Solid line refers to an influent concentration of 4 mg L⁻¹; dashed line denotes an influent concentration of 8 mg L⁻¹.

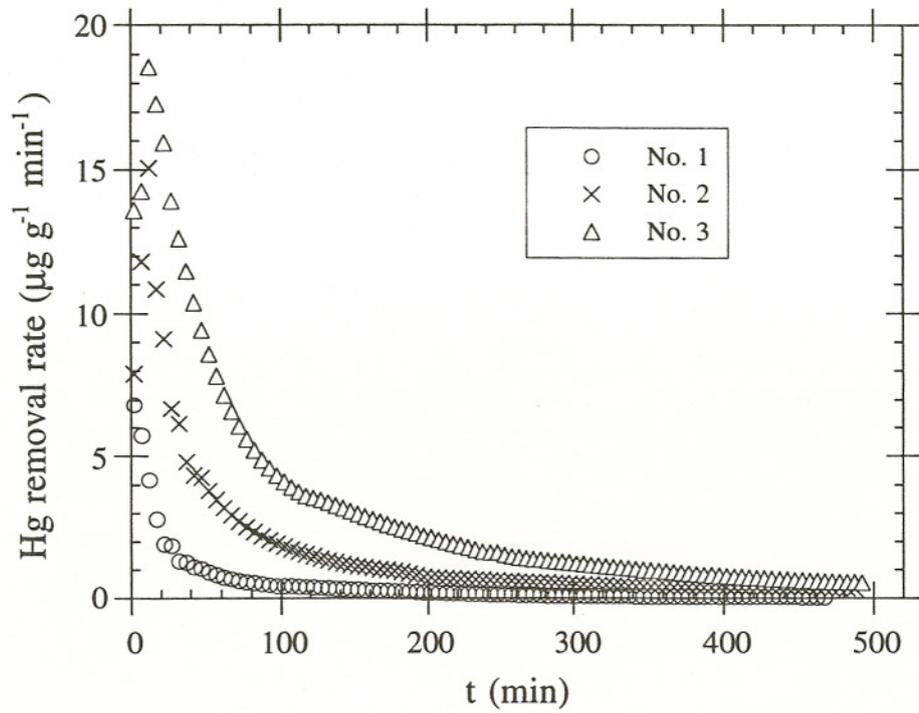


Figure 5.3 Rate of Hg removal from three soils following sorption at an influent concentration of 8 mg L^{-1} . See Table 3.1 for soil identification.

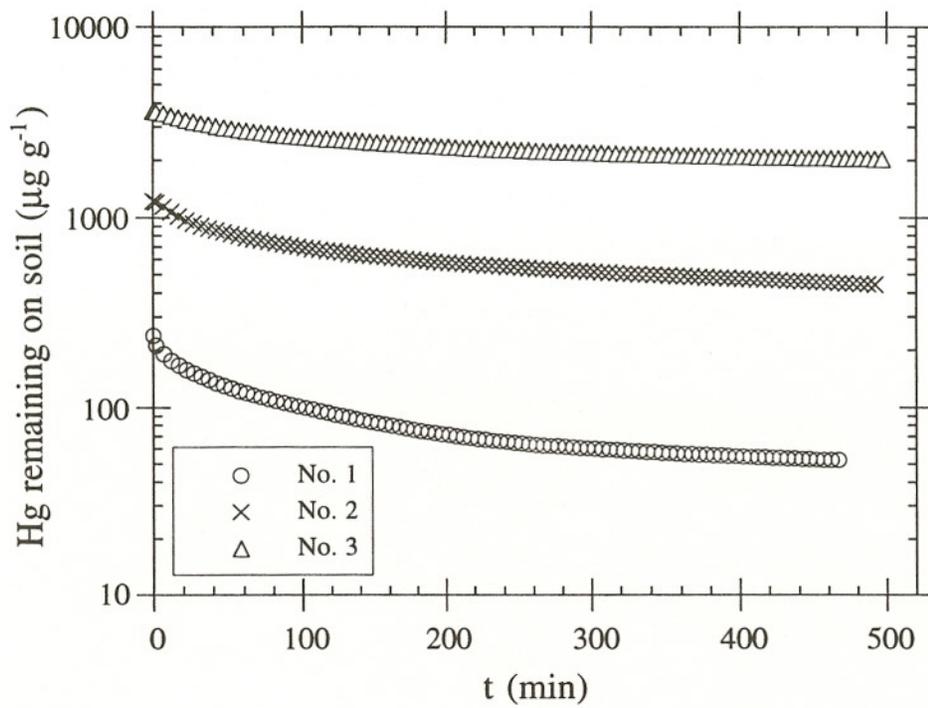


Figure 5.4 Hg remaining in soil during desorption process following sorption at an influent concentration of 8 mg L^{-1} .

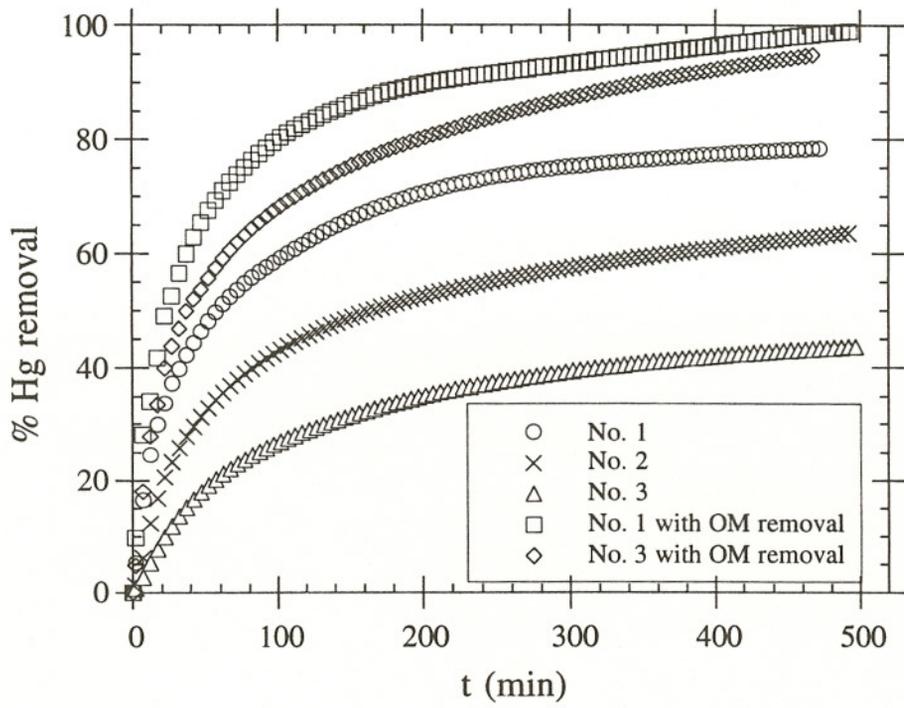


Figure 5.5 Fractional Hg removal as a function of time. See Table 3.1 for soil identification.

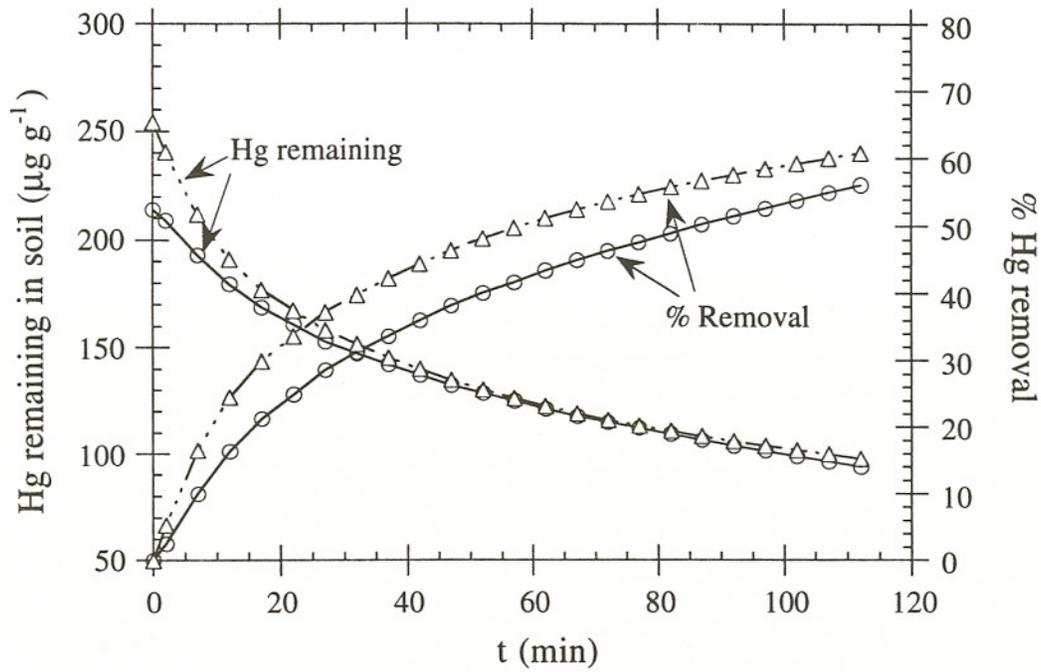


Figure 5.6 Comparison of Hg remaining and removal profile on Freehold sandy loam (A horizon) for two initial concentrations. Solid lines refer to an initial concentration of 214 $\mu\text{g g}^{-1}$; dashed lines denote an initial concentration of 254 $\mu\text{g g}^{-1}$.

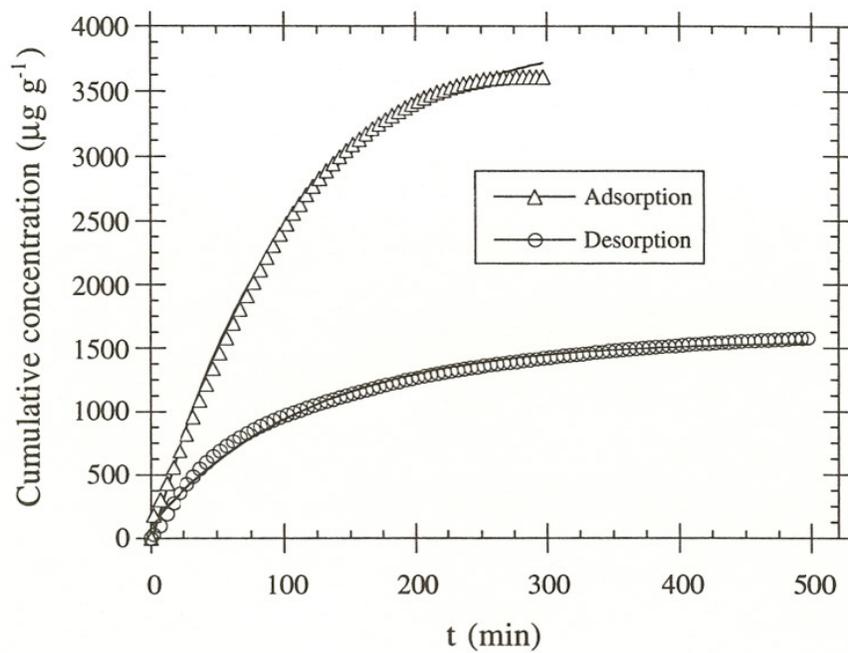


Figure 5.7 Comparison of the observed and predicted sorption and desorption kinetics. Solid lines represent predicted values.

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Chapter 6

ARSENIC

6.1 Introduction

During the past two years, we mainly focused on the development of a method for the determination of arsenic. We first tested a colorimetric method developed by Johnson (1971) and Johnson and Pilson (1972). This method is simple to operate and allows simultaneous determination of both As(V) and As(III). For low As concentrations, however, we found that it is significantly affected by naturally occurring phosphate. Alternatively, ion chromatography (IC) can be used to determine As(V) and As(III). The main advantage of this analytical method is that phosphate interference is avoided. However, due to its high pK_a , As(III) could not be analyzed, even when oxidized to As(V).

Finally, we developed a hydride generation system for the determination of As by absorption spectroscopy. The preliminary results have indicated that the detection limit for this system is as low as $10 \mu\text{g L}^{-1}$. The limitation of this method is that As(V) and As(III) cannot be determined simultaneously. However, they are possibly differentiated by using different reductants.

6.2 Development of a Method for the Determination of Arsenic

6.2.1 Colorimetric Method

Arsenic is considered analytically difficult to measure. A relatively simple colorimetric method modified from the work of Johnson (1971) and Johnson and Pilson (1972) was tested for arsenic determination. The colorimetric method was described as efficient in natural water systems: 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 complex. The samples were subsequently determined using a spectrophotometer at a wavelength of 865 nm for maximum absorbance. This maximized the sensitivity for arsenate determination and only slightly reduced the sensitivity for phosphate, a known interferent in arsenic determinations using spectrophotometric methods.

6.2.1.1 Calibration

All reagents were prepared with distilled, deionized water. All glass and plastic containers used were cleaned by soaking in 10 % HNO₃ for 24 hours and then washed with distilled water followed by DI water.

1000 mg L⁻¹ As(III) and As(V) stock solutions were prepared from NaAsO₂ and NaHAsO₄ · 7 H₂O 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⁻¹ were prepared by dilution from 1000 mg/L As(III) and As(V) stock 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. The mixed reagent is prepared fresh for use.

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 solutions were subsequently added to each vial to oxidize As(III) to As(V). In the case of As(V) this procedure was also followed ensure that all As was in +5 oxidation form, 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 wavelength of 865 nm.

As expected, the calibration curves for As(V) and As(III) are almost identical as is shown in Figure 6.1 and Figure 6.2. The correlation coefficients greater than 0.999. The linear range extends to 10 mg L⁻¹.

6.2.1.2 Recovery Test

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% OM) and Boonton Union soil (8.6% OM). 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 6.1, the recoveries of arsenic(V) were more 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 As(III) sometimes varied randomly and was always less than 90%, especially when the initial As(III) concentration was low. It was concluded that the colorimetric method is not suitable for arsenic determinations mainly to phosphate interference, as shown in Table 6.3. The recoveries of arsenic(III) are shown in Table 6.2.

As a result of the failure of the spectrophotometric method, ion chromatography and hydride generation atomic absorption have been tested for the determination of As(III) and As(V).

6.2.2 Ion Chromatography

Ion chromatography (IC) has attained the stature of a standardized method for determination of a wide variety of inorganic and organic ions (Mehra and Frankenberger, 1988). With this method, one can differentiate chemical species without or with little interference of other ions present in solution. Arsenic determination by ion chromatography has not yet been demonstrated with complex matrices such as soils or sediments, however.

The greatest number of species currently separable by IC are anionic. Arsenic can be detected under the form AsO_4^{3-} at trace level in soil samples. However, As(III) cannot be detected due to its high pK_a , around 9.2. Although ions with pK_a greater than 7 may be eluted under IC conditions, they cannot be detected by conductivity detection

as they pass through the cell. The poor ionization of these species results in weak signals. However As(III) can be oxidized to arsenic(V) prior to injection, as was described earlier using KIO_3 .

A IC 2mm system with automated sampler, conductivity detector, eluent degas module and gradient pump was used. Two concentrations of sodium hydroxide, 5 mM and 200 mM, were used as eluents. The eluents were kept under an inert helium atmosphere to avoid carbonate contamination. The eluent going through the column had a final ratio of 95% DI water: 5% 5 mM NaOH.

An Ionpac AS 11 analytical column was employed with an Ionpac AG 11 guard column. Since NaOH is converted to water in the anion micromembrane suppressor, the concentration of hydroxide in the eluent will have only a small effect on the background conductivity.

Figure 6.3 shows the calibration curve for arsenic(V). A standard addition method was used to test the accuracy of the IC with soil extract as matrix (Hazen loam, 3.1% organic matter). The recoveries of added As(V) were greater than 90%.

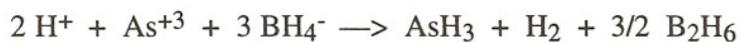
Arsenic(III) could not be recovered in soil extract or in water. Several oxidant reagents were tested in acidic medium: 0.04 M KIO_3 , 0.08 M KIO_3 , 0.18 M $\text{K}_2\text{S}_2\text{O}_8$ and 0.21 M $\text{Na}_2\text{S}_2\text{O}_8$. The percent recovered varied from 10% to 75% (shown in Table 6.2). Due to the low recovery, it was concluded that IC was not a suitable method for arsenic determination in soils extracts.

6.2.3 Hydride Generation Atomic Absorption

Hydride generation atomic absorption spectrometry is a simple method to analyze aqueous inorganic arsenic in the $\mu\text{g L}^{-1}$ range (Glaubig and Goldberg, 1988). The detection limit for As(V), however, is much higher than that for arsenic(III). This analysis is therefore possible by determining total arsenic, As(III) plus As(V). As(V) can be determined by reducing As(V) to As(III) prior to hydride generation.

In this study, we developed a hydride generation system simulating the commercial MHS-10 system (Perkin Elmer). This system is coupled with a Perkin Elmer atomic absorption spectrophotometer (Model 560) for As determination. The quartz cell is electrically heated by a 4 meter Niquel-Cromium wire wrapped around the cell using an electrical isolated material (with braided ceramic sleeving). 3% NaBH₄ in 1% of NaOH is used as reductant, and Ar or N₂ is used as AsH₃ vapor carrier.

This system is currently employed for determinations of mercury and hydride forming elements. The sodium borohydride reducing agent liberates hydrogen on contact with acids. The reaction mechanism involved in the reduction of metal ions are complicated and take place via the formation of intermediate radicals. For arsenic the following reaction represents simplifications of the reduction process:



For arsenic, the sample solution is first treated so that arsenic is present in ionic form in acid solution. Reductant is added to the sample solution where it reacts 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 700 °C). Where the hydride is decomposed. The absorption due to As(0) is measured.

Preliminary results indicated that this method can detect As at concentrations as low as 10 µg L⁻¹ (Figure 6.4). With NaBH₄ as the reductant, As(III) is determined. The reaction between NaBH₄ and As(V) is slow. However As(V) can be reduced by KI prior to analysis, as mentioned before. This will be tested next. Furthermore, the hydride generation system needs to be optimized, and the accuracy of this system and the interferences of the matrix on the measurement will also be tested.

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Table 6.1 Recovery test for As(V)

| Equilibrium pH | Arsenic Added (mg L ⁻¹) | As(V) Recovered (mg L ⁻¹) | As(V) recovered (%) |
|----------------|--|--|---------------------|
| | Lakewood sand | | |
| 4.74 | 0 | 0 | 0 |
| 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 | | |
| 5.9 | 0 | 0 | 0 |
| 4.14 | 4.24 | 4.08 | 96.2 |
| 5.9 | 4.24 | 3.88 | 91.5 |
| 9.62 | 4.24 | 3.89 | 91.7 |
| | Boonton Union loam | | |
| 4.58 | 0 | 0 | 0 |
| 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 6.2 Recovery test for As(III) with Boonton Union loam extract at natural pH

| Sample No. | Arsenic(III) added (mg L ⁻¹) | As(III) recovered (mg L ⁻¹) | As(III) recovered (%) |
|------------|--|---|-----------------------|
| Blank | 0 | 0 | |
| 1 | 0.46 | 0.31 | 67.4 |
| 2 | 0.46 | 0.34 | 74.4 |
| 3 | 0.46 | 0.32 | 69.1 |
| 4 | 0.46 | 0.27 | 59.8 |
| 5 | 0.46 | 0.35 | 75.6 |
| 6 | 0.46 | 0.35 | 77.3 |
| Average | | | 70.6 |
| Blank | 0 | 0 | |
| 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 6.3 Effect of phosphate on the measurement of As in water

| Sample No. | Phosphate (mg L ⁻¹) | Arsenic(III) added (mg L ⁻¹) | As(III) Recovered (mg L ⁻¹) | As(III) recovered (%) |
|------------|---------------------------------|--|---|-----------------------|
| | 0.43 | 0 | 0 | |
| 1 | 0.43 | 0.43 | 0.27 | 63.3 |
| 2 | 0.43 | 0.43 | 0.27 | 62.4 |
| 3 | 0.43 | 0.43 | 0.28 | 64.1 |
| 4 | 0.43 | 0.43 | 0.25 | 59.1 |
| 5 | 0.43 | 0.43 | 0.26 | 59.9 |
| 6 | 0.43 | 0.43 | 0.27 | 62.4 |
| Average | | | | |
| | 4.26 | 0 | 0 | |
| 1 | 4.26 | 4.26 | 4.08 | 95.8 |
| 2 | 4.26 | 4.26 | 4.12 | 96.7 |
| 3 | 4.26 | 4.26 | 4.11 | 96.5 |
| 4 | 4.26 | 4.26 | 4.14 | 97.1 |
| 5 | 4.26 | 4.26 | 4.17 | 97.9 |
| 6 | 4.26 | 4.26 | 4.19 | 98.3 |
| Average | | | | |

Table 6.4 Recovery of As(III) by IC

| Sample No. | Oxidant | Arsenic (III) added (mg L ⁻¹) | As(III) Recovered (mg L ⁻¹) | As(III) recovered (%) |
|------------|-----------------------------|---|---|-----------------------|
| | | 0 | 0 | |
| 1 | Potassium iodate 0.04 M | 5.00 | 3.88 | 77.5 |
| 2 | Potassium persulfate 0.18 M | 5.00 | 1.27 | 24.8 |
| 3 | Sodium persulfate 0.21 M | 5.00 | 0.52 | 10.4 |

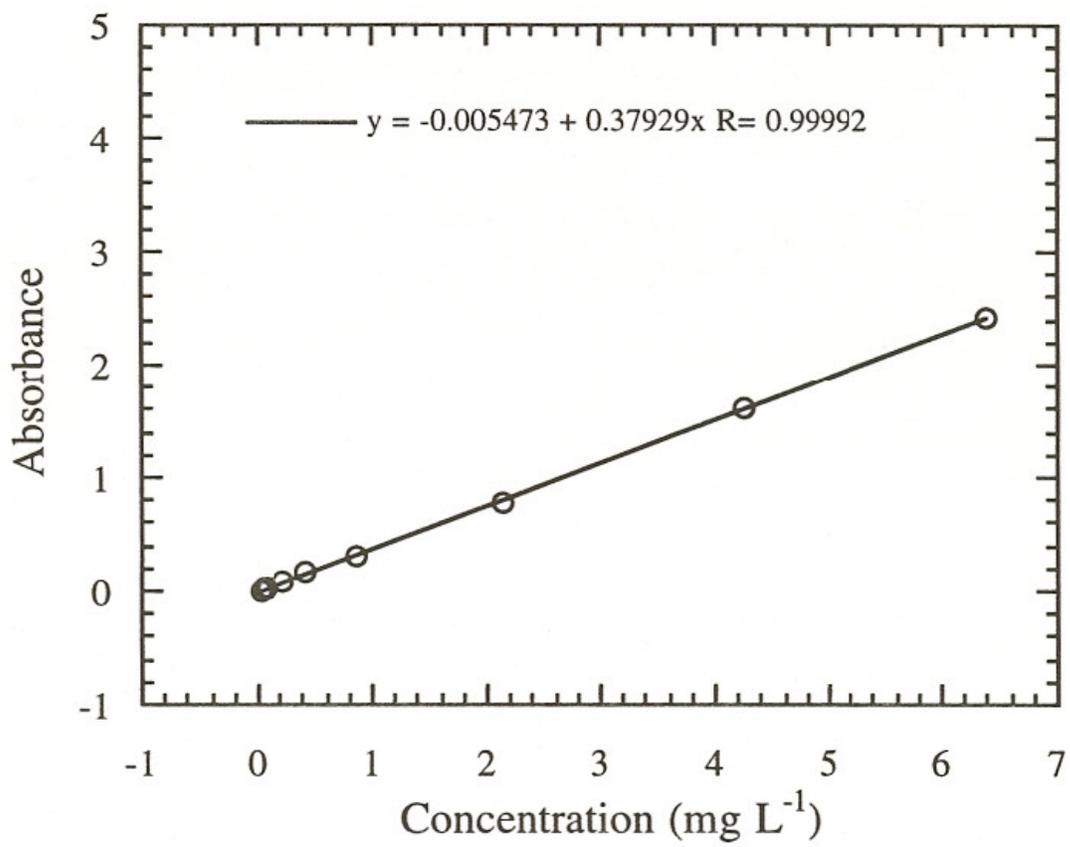


Figure 6.1. Calibration curve for As(V) by the heteropoly blue colorimetric procedure

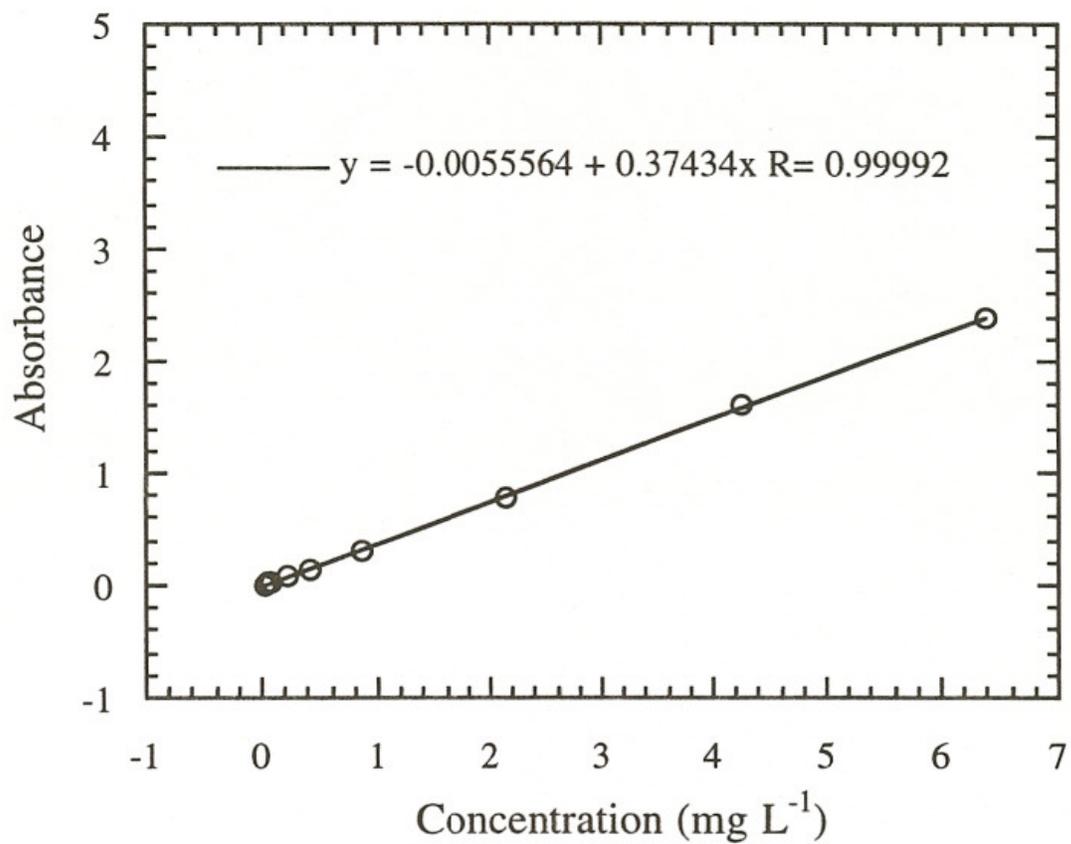


Figure 6.2. Calibration curve for As(III) by the heteropoly blue colorimetric procedure

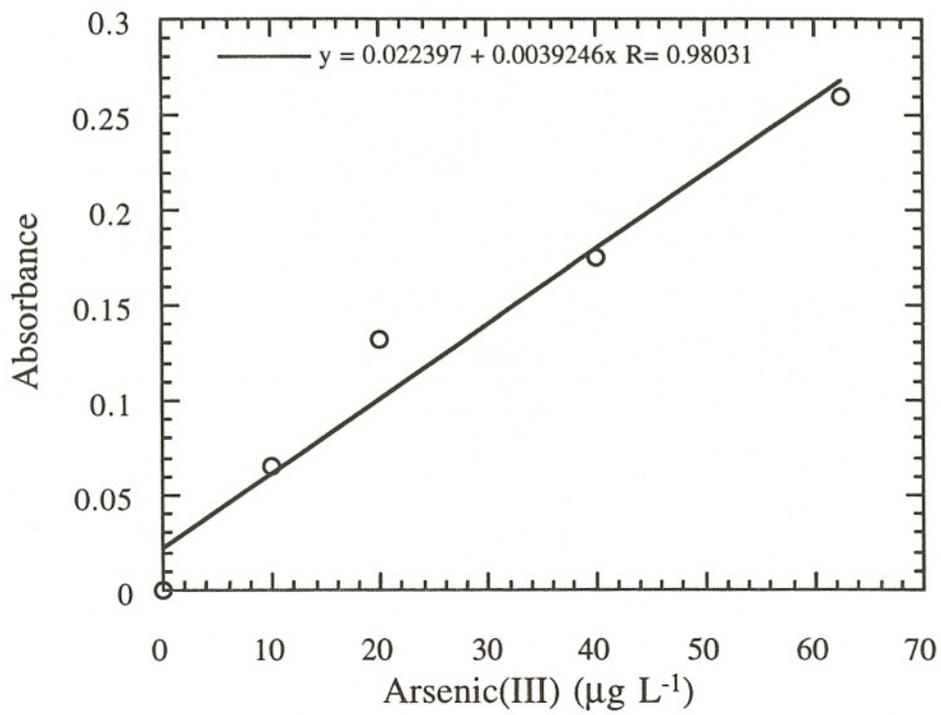


Figure 6.4. Calibration curve for arsenic(V) using hydride generation atomic absorption

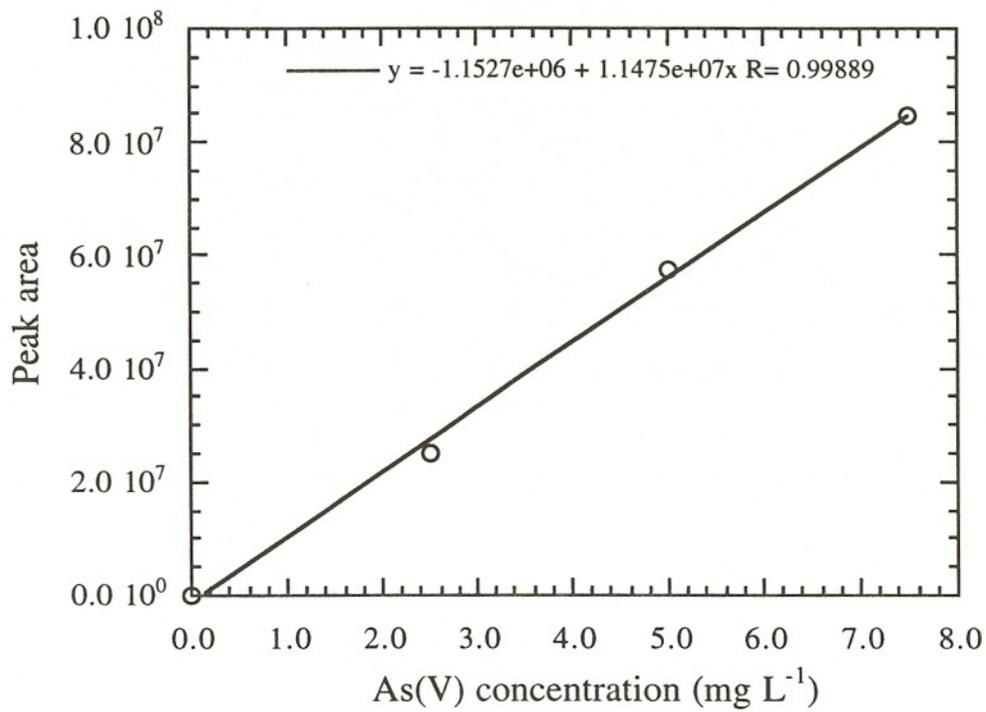


Figure 6.3. Calibration curve for arsenic(V) by ion chromatography

this paper, a sharp drop in effluent Hg concentration was observed after stopping flow for 30 min. This indicated that the reaction of Hg with soil was time dependent, rather than instantaneous.

Kinetics of Hg sorption on four soils at an influent concentration of 8 mg L^{-1} are shown in Figure 5.1. Sorption was initially very fast. At the end of the first 2 min, the adsorbed Hg was $96 \mu\text{g g}^{-1}$ on Freehold sandy loam (A horizon), $153 \mu\text{g g}^{-1}$ on Sassafras sandy loam, $180 \mu\text{g g}^{-1}$ on Dunellen sandy loam, and $176 \mu\text{g g}^{-1}$ on Rockaway stony loam, which respectively accounted for 38%, 12%, 5%, and 4% of the total Hg adsorbed by these soils within 5 h. The time required to reach equilibrium depended on soil properties. Generally, the higher the soil organic matter content, the longer the time needed for a reaction to reach equilibrium. For example, the sorption of Hg on Freehold sandy loam (A horizon), which contained a very small amount of organic C, did not significantly increase after 60 min, while sorption on Dunellen sandy loam kept increasing until equilibrium was achieved at about 5 h. For Rockaway stony loam, which had a similar particle size distribution as Dunellen sandy loam did, sorption equilibrium was not achieved even within 5 h. This probably resulted from the higher organic C content of Rockaway stony loam. Higher organic matter content also resulted in higher sorption. This was also observed in a previous study (Yin et al., 1995b). Based on the equilibrium Hg concentrations in both soil and solution phases, the partition coefficient ($K_p = \text{Hg concentration in soil} / \text{Hg concentration in the solution}$) was calculated. The K_p value for an influent concentration of 8 mg L^{-1} was 0.032 L g^{-1} for Freehold sandy loam (A horizon), 0.152 L g^{-1} for Sassafras sandy loam, and 0.451 L g^{-1} for Dunellen sandy loam.