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Retention and transport of mercury and nickel in soils

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RETENTION AND TRANSPORT OF MERCURY AND NICKEL IN SOILS

A Dissertation

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ABSTRACT

Nickel (Ni) is one of many trace metals widely distributed in the environment. High concentrations of Ni in soils and aquifers have been observed worldwide, causing several potential human health impacts. Better understanding of Ni transport in soils and aquifers is necessary to assess and remediate insitu environmental contamination. The movement of Ni in soils and aquifers is highly dependent on adsorption-desorption reactions in the solid phase. In this study, kinetic batch, sequential extractions, and miscible displacement experiments were conducted to investigate the effect of several of environmental factors including soil type, reaction time and competing ions, on the fate of Ni in soils. In addition, forward and inverse modeling efforts were made to mathematically predict the reactivity of Ni transport in soils.

Based on batch study results, adsorption of Ni was highly nonlinear and strongly kinetic. The comparison of Ni sorption on soil followed the sequences: Windsor < Olivier < Webster, which was related to soil propertities (CEC, clay content, pH and organic matter). Desorption of Ni from all soils were hysteretic in nature which is an indication of lack of equilibrium retention and/or irreversible or slowly reversible processes. A sequential extraction procedure provided evidence that a significant amount of Ni was irreversibly adsorbed on all soils. Moreover, a multi-reaction model (MRM) with equilibrium, kinetic and irreversible sorption successfully described the adsorption kinetics of Ni in Windsor, Olivier and Webster soils and was capable of predicting the desorption of Ni from these soils. Column transport experiments indicated strong Ni retardation followed by slow release or extensive tailing of the breakthrough curves (BTCs). We evaluated several MRM formulations for prediction capability of Ni retention and transport in soils and concluded that nonlinear reversible, along with a consecutive or concurrent irreversible reactions were the dominant mechanisms. The use of batch rate coefficients as model

parameters for the predictions of Ni BTCs underestimated the extent of retention and overestimated the extent of Ni mobility for all soils. When utilized in an inverse mode, the MRM model provided good predictions of Ni BTCs and the distribution of Ni with soil depth in soil columns.

In natural soil and water environments the competition between Ni and Cadmium (Cd) has the potential of increasing Ni mobility and bioavailability. Our results from batch experiments demonstrated that rates and amounts of Ni adsorption by these soils were significantly reduced by increasing Cd additions. The presence of Cd in soils increased mobility of Ni in columns as well as forced Ni sorption at higher affinity (or specific sorption) sites. The simultaneous presence of Ni and Cd also changed the distribution of Ni and Cd from an accumulation pattern to a leaching pattern in Olivier soil column, which has the potential risk of contamination of ground water.

CHAPTER 1: INTRODUCTION: LITERATURE REVIEW

1.1 General Description

Nickel (Ni) is the 24th most abundant element in the Earth's crust, comprising about 3% of the composition of the earth. It is the 5th most abundant element by weight after iron, oxygen, magnesium and silicon (Cempel and Nikel, 2005). Nickel is a common environmental pollutant which is considered as toxic at concentration greater than 15 mg/l. Its presence is detrimental to microorganism and plants (Srivastava et al., 2006). Nickel is not an essential element in human nutrition. All nickel compounds except for metallic nickel are classified as carcinogenic to humans. Metallic nickel and its compounds are widely used in industry. Nickel-containing products at all stages of production, comsumption, recycling and disposal inevitably lead to environmental pollution. Contamination of ground and surface water by nickel poses a significant threat to human health (Denkhaus and Salnikow, 2002).

Tremendous research effort in the last several decades, reflected by a huge volume of literature published in this area, has been devoted to unravel complex geochemical reactions of Ni in the natural environment, As a result, the scientific knowledge governing the fate and behavior of Ni in heterogeneous soil systems has been greatly expanded in recent years.

1.2 Nickel in Soil and Its Source

Nickel enters the environment from both natural and anthropogenic sources (Cempel and Nikel, 2005). The average concentration of nickel in soils worldwide is 40mg kg^{-1}. Atmospheric sources of nickel include wind-blown dust, derived from the weathering of rocks and soils, volcanic emissions, forest fires and vegetation (Cempel and Nikel, 2005). A large number of mineral and chemical compounds containing nickel are formed in soils (McIlveen and Negusanti, 1994). The availability of these forms to plant roots and to other organisms is biologically and ecologically important. Soil derived from some ultra-basic igneous rocks, especially serpentine, have been reported to contain extremely high concentrations of nickel (up to 1000 mg kg^{-1}); (He et al., 2005). Ni-containing minerals in soils include pentlandite ($(Fe, Ni)_9S_8$), awaruite (Ni_3), cohenite ($(Fe,Ni)_3C$), and haxonite ($(Fe,Ni)_{23}C_6$) (He et al., 2005). The +2 oxidation state is the most prevalent form of nickel in bio-systems. Solubilized Ni^{2+} ions in soil solution at neutral pH are hydrated as greenish hexahydrate $[Ni(H_2O)_6]^{2+}$ ions whose activity decreases with increasing pH (Mellis et al., 2004). There are other Ni^{2+} coordination complexes. The most favorable geometry is the square planar configuration, but octahedral, trigonal bipyramidal, square pyramidal and tetrahedral Ni^{2+} complexes may occur. Furthermore, several polynuclear coordination complexes of nickel are known, whereby nickel atoms are connected by either metal–metal bonds or bridging ligands (Denkhaus and Salnikow, 2002).

Fertilizer, sewage sludge, lime, and industrial waste materials introduce nickel into the natural environment (McIlveen and Negusanti, 1994). Nickel can be an environmental problem in land near towns, in industrial areas, or even in agricultural land receiving sewage sludge wastes. Nickel content in soil ranges from 3 to 1000 mg/kg (Cempel and Nikel, 2005; Bencko, 1983; Bak J, 1997). Nickel can exist in soils in several forms: inorganic crystalline minerals or precipitates, complexed or adsorbed on organic cation surfaces or on inorganic cation exchange surfaces, water soluble, free-ion or chelated metal complexes in soil solution. Nickel is apparently not an environmental concern outside urban areas at this time but could eventually become a problem resulting from decreased soil pH caused by reduced use of soil liming in agriculture and mobilization due to increased acid rain (Cempel and Nikel, 2005; Bencko, 1983). Mielke et al. (2000) investigated the effect of anthropogenic metals on the geochemical quality of urban soils. The median nickel content was 3.9 µg/g for fresh alluvium samples and 9.8 µg/g for urban alluvial soils (New Orleans from stratified by census tracts). Overall, significantly higher metal values occur in the inner city and lower values occur in outlying areas. (Cempel and Nikel, 2005)

Of the above sources, sewage sludge application cause the major concern due to the heavy metal uptake by plants in agricultural soils. Based on EU Directive 86/278/EEC which regulates the use of sewage sludge on agricultural soils, the permitted trace metal loads per year, calculated as a 10-year average is 3 kg/ha for Ni, and 30 kg/ha Zn. In Sweden, the allowed annual application rates to agricultural soils are set at 0.025 kg Ni/ha and 0.6 kg Zn/ha. In contrasted, permitted trace metal loads to soils in Canada and the USA are still much higher (Landner et al., 2000; Landner et al., 2004).

In field experiments in Germany where sludge was applied for almost 10 years to an old arable and ex-woodland soil, Ni concentration in soil reached 15-30 mg per kilogram and resulted in a 50% decrease in nitrification (Landner and Reuther, 2004). Moreover, some studies suggesting that there is risk of heavy metal movement down the soil profile posing potential contamination to surface water. The risk is greater in cases of heavy loading rates of Cd, Ni, and Zn, and where metals have been applied to low sorptive capacity soils. Antoniadis and Alloway (2003) reported that excessive metal movement to 80 cm depth in soil profile due to the heavy application of sewage sludge with metal levels of 40mg Cd, 335.6 mg Ni and 667.9 mg Pb per sewage sludge.

1.3 Environmental Toxicity of Nickel

Nickel is a nutritionally essential trace metal for at least several animal species, micro-organisms and plants, and therefore either deficiency or toxicity symptoms can occur when, respectively, too little or too much Ni is taken up. However, nickel has not been recognized as an essential element in humans and a deficiency state in humans has not been described (Cempel and Nikel, 2005; Bencko, 1983; Scott-Fordsmand, 1997). It is known that exposure to nickel compounds can have adverse effects on human health. Nickel allergy in the form of contact dermatitis is the most common and well-known reaction. The accumulation of nickel in the body through chronic exposure can lead to lung fibrosis, cardiovascular and kidney diseases, the most serious concerns relate to the carcinogenic activity of nickel (Denkhaus and Salnikow, 2002).

Human exposure to nickel occurs primarily via inhalation, ingestion and dermal absorption. Human exposure to nickel-polluted environments has the potential to produce a variety of pathological effects. Among them are skin allergies, lung fibrosis, cancer of the respiratory tract and iatrogenic nickel poisoning (Clarkson, 1988). In the general population, contributions to the body burden from inhalation of nickel in the air and from drinking water are generally less important than dietary intake and ingestion is considered to be the most important route of exposure (Cempel and Nikel, 2005). The absorption of nickel is dependent on its physicochemical form, with water-soluble forms (chloride, nitrate, sulphate) being more readily absorbed. In humans, the absorbed nickel average is $27 \pm 17\%$ of the dose ingested in water and $0.7 \pm 0.4\%$ of the dose ingested in food (40-fold difference) (Cempel and Nikel, 2005; Sunderman et al., 1989). In general, due to its slow uptake from the gastrointestinal tract, ingested nickel compounds are considered to be relatively non-toxic, with the primary reaction being irritation. However, when taken orally in large doses (>0.5 g), some forms of nickel may be acutely toxic to humans (Cempel and Nikel, 2005). The primary target organs for nickel-induced systemic toxicity are the lungs and the upper respiratory tract for inhalation exposure and the kidney for oral exposure. Other target organs include the cardiovascular system, the immune system and blood (Clarkson, 1988). The toxic functions of nickel probably result primarily from its ability to replace other metal ions in enzymes and proteins or to bind to cellular compounds (Cempel and Nikel, 2005).

Furthermore, since the most important route of nickel exposure is dietary intake and ingestion through food chain, the accumulation of nickel in crops, vegetables, and fruits grown on contaminated soil has received concern. The scientific literature reports that certain plant species that are called “hyper-accumulators” because of their ability to absorb extremely high concentration of nickel with no adverse effects (Severne and Brooks, 1972; McIlveen and Negusanti, 1994). The role of nickel in plant metabolism has been extensively investigated. Treatments with nickel can influence the enzyme activity and pigment content of some plants. Increased respiration and uptake rates of oxygen have been found in wheat and corn (McIlveen and Negusanti, 1994). Maranville (1970) found that nickel added either as sulphate, chloride or acetate enhanced nitrification in sorghum leaf tissue by up to six times. Besides overall reduction in size or yield of plants, excessive nickel can cause fairly specific injury symptoms in plants. Generally, the injury has similarities with iron deficiency. The most noticeable or prevalent injuries are those on graminaceous species in which white or bleached stripes develop between the leaf veins, which is the classic form associated with nickel toxicity to oat.(McIlveen and Negusanti, 1994)

1.4 Sorption

1.4.1 Sorption Isotherms

Sorption of Ni on minerals, clay fractions and whole soils had been conducted using traditional batch equilibration methods. The relationship between the equilibrium concentration in the aquatic solution and the amount adsorbed on the solid surface, that is, the partition distribution coefficient is commonly described with adsorption isotherms. Linear and nonlinear forms are usually employed to describe the Ni adsorption on mineral and soil surfaces. The linear equation can be expressed as

$$K_d = \frac{S}{C}$$ [1.1]

where S is the metal sorbed on soil at equilibrium given in mg kg^{-1} and C represented the metal concentration in solution at equilibrium given in mg L^{-1}; hence, the units for K_d values are in L kg^{-1}. Although somewhat simplistic, the K_d approach is easy to integrate into various chemical models and allows estimations of metal dissolved in soil solution and perdictions of mobility as well as potential leaching losses (Mellis et al., 2004; Sauve et al., 2000)**.** Covelo et al. (2004) employed the linear form to estimate the competitive sorption and desorption of heavy metals in mine soil and correlated K_d value to principle soil components such as organic matter, Fe oxides, CEC, etc. Modeling metal sorption using a single-valued K_d approach presumes that the sorption capacity of a material is relatively independent of soil physicochemical properties. However, due to the heterogeneity of the soil matrix, model of Freundlich (Antoniadis and Tsadilas, 2007; Echeverría et al., 1998) and Langmiur (Srivastava et al., 2006; Papini et al., 2004) equations are more commonly used to model equilibrium batch data.

Both types are nonlinear and indicative of high affinity chemical adsorption. Langmuir equation is defined as:

$$S = \omega \frac{K_L C}{1 + K_L C}$$ [1.2]

where C is the equilibrium concentration of Ni in the solution; S is the amount of Ni adsorbed on the solid surface; K_L is the Langmuir constant related to the binding strength; and ω is the maximum available adsorption sites on the solid surface. Srivastava et al. (2006) emplyed

Langmuir curve to fit data of Ni adsorption on bagasse fly ash. Their K_L and ω equal 0.153 L mg^{-1} and 6.488 mg g^{-1}, respectively.

The Freundlich equation is defined as:

$$S = K_f C^n \qquad [1.3]$$

where K_f is the Freundlich distribution constant; and n is a nonlinear reaction constant between 0 and 1. Buchter et al. (1989) have measured Freundlich parameters (K_f and n) for 11 different soils and 15 trace elements. They explored the correlation of the Freundlich parameter with selected soil properties and found that pH, cation-exchange capacity, and iron/aluminum oxide contents were the most important factors for correlation with the partitioning coefficients. A combined Langmuir and Freundlich equation was used by Papini et al. (2004) to describe Pb, Cu, Cd and Ni sorption onto an Italian red soil and can be express as:

$$S = \frac{MKC^n}{1 + KC^n} \qquad [1.4]$$

where M, K and n are the maximum adsorption capacity, the affinity constant and the heterogeneity index, respectively. All parameters derived from above equations were related to soil properties such as pH, organic matter, iron/aluminum oxide and cation-exchange capacity and corresponding reaction mechanisms with different adsorption sites in soils.

1.4.2 Sorption Mechanisms

Because of the intrinsic chemical and physical heterogeneity of soils, it is more difficult to describe and predict the kinetics of nickel adsorption on soil material with their heterogeneity of the sorption sites, differing in affinities for solute retention (Jeon et al., 2003). Correctly determining the mechanism of metal sorption to soils is therefore of great importance for understanding the fate of Ni in contaminated soils. Studies suggest that several phenomena occur at the solid/liquid interface: 1) cation exchange at the permanently negative sites on the clay fraction (outer-sphere complexes) and/or 2) inner-sphere complexes at specific functional group due an Fe, Mn and Al hydrous oxide and organic matter. In recent years X-ray absorption spectroscopy and its derivatives have made a large contributions to understanding of the structure and composition of Ni sorption complexes and surface binding sites, that is, nucleation of a mixed Ni/Al phase (Ni-Al Layered double hydroxide) precipitate formation)(Scheidegger et al., 1998).

It has been well established that Ni has lower affinities for soil colloids and is generally considered as weakly bonded and rather mobile metal under acidic conditions (Atanassova, 1999) compared to Cu, Pb and Hg. Papini et al. (2004) reported that Pb and Cu exhibit high affinity for the solid phase, whereas Cd and Ni are sorbed at a significantly lower extent. Tiller et al. (1984) defined the procedure for the adsorption separation between cation exchange sites and specific adsorption sites, representing non-specific bound forms and specifically bound forms, respectively. Sample of retained metal was washed with $Ca(NO_3)_2$ for 2 weeks (details can be found at Tiller et al. 2004). The amount of metal replaced by $Ca(NO_3)_2$ was defined as non-specifically adsorbed. The amount of metal remaining on the clay following washing was defined as specifically adsorbed. Their results indicated that the proportion of Cd , Zn and Ni bound at those two sites were strongly dependent on soil of pH and surface saturation.

Studies reported that cation exchange was the major sorption mechanism for Ni often related the adsorption of Ni to a few factors, including charge to radius ratio, electronegativity, softness parameter, and first hydrolysis constant (Tsang and LO Irene, 2006; Sposito, 1984; Echeverría et al., 1998; Antoniadis and Tsadilas 2007), whereas, the reaction of heavy metal cations with soil minerals was related to metal-ion hydrolysis in studies of specific sorption. If hydrolysis of metal ions, either in solution or at the soil surface, is a primary adsorption mechanism for metal ions, higher affinity for Ni is expected. Using Ni reaction with illite as example, the different sites available for Ni sorption by illite may lead to different Ni retention mechanisms. The planar sites constitute a permanent negative charge. Metal interactions with these sites are electrostatic in nature and lead to the formation of outer-sphere metal complexes; that is, the metal ions do not lose their primary hydration spheres upon interaction with the clay mineral surface. At the illite edge sites, both the formation of outer-sphere complexes and chemisorption may occur. Chemisorption leads to the formation of inner sphere metal complexes through a ligand exchange process, where the metal ions form chemical bonds with the clay mineral surface by coordination to surface hydroxy ligands (Elzinga and Sparks, 2001).

Iron and Al oxides are important tropical soil secondary mineral, responsible for the low mobility and bioavailability of heavy metals. The metal ions can be eletrostatically adsorbed such materials, or specifically, through covalent or partly covalent bindings to oxygen atoms from the mineral structure. Organic matter may negatively or positively affect the metal availability as a result of the formation of metal complexes. Mellis et al. (2004) compared the Ni adsorption of organic matter (OM) and iron oxide (IO) free soils with that of original soils. Their results indicated that for OM-free soil samples, the average adsorption values were 28% lower than those obtained for the original soil samples at pH lower than 6.0. For pH above 6.0-6.5, the effect of organic matter on Ni adsorption was not significant due to great part of the negative, pH dependent charge. The organic matter provides sites for cation exchange, but its strong affinity for metals is due to the presence of specific binders or groups that form metal complexes. The removal of Fe oxide can drastically reduce positive charges, which could favor the soil-metal adsorption reactions (Yu, 1997; Mellis et al., 2004). Under low pH conditions, the oxides may contribute to metal retention by specific mechanisms involving covalent binding. The removal of Fe-oxide by the sodium citrate-bicarbonate method, can also remove part of the active aluminum, thus altering the balance of superficial charges. Hence, when soil pH is lower than the zero point saline effect (ZPSE), iron oxide removal may contribute to the Ni adsorption. Ni adsorption was higher in the 3.5 to 4.0 pH range as compared to the adsorption for the same pH range in soil samples without organic matter. This was due to reduction in the metal repulsion by the positively charged surface, in consequence of oxide removal (Silveira et al., 2002). For pH close to 7.0, Ni adsorption capacity did not change after removal of organic matter and iron oxides. Here, Mellis et al. (2004) and several other scientists point out that Ni adsorption increased drastically when soil pH were raised above 7.0 (Harter, 1983; Barrow et al., 1989; Schulthess & Huang, 1990; Scheidegger et al., 1998). Ni adsorption is affected not only by soil pH, but also by CEC, clay content, organic matter and Fe oxides present in the soil and other factors (Mellis et al., 2004).

As mentioned above, with increased soil pH, the adsorption of Ni dramatically increased. Some scientists proposed that Ni may form poly-nuclear surface complexes on mineral phases at alkali conditions or neutral pH (Scheidegger et al., 1998). The importance of the formation of induced nucleate surface precipitates has recently been demonstrated in spectroscopic studies of Ni sorption to Al-bearing clay minerals and oxides. Since illite is an Al-containing clay mineral, the formation of Ni-Al layered double hydroxide (LDH) phases may also be expected. Ni-Al LDH formation may be considered as a separate sorption mechanism that occurs simultaneously with, and therefore competes with, adsorption processes at illite planar and edge sites(Elzinga and Sparks, 2001). The Ni speciation in illite suspensions will therefore be determined by how effective each of the different sorption mechanisms competes for Ni uptake, which may be affected by a range of experimental parameters, including pH, reaction time, and ionic strength.

Recent XAFS studies with Ni(II) and Co(II) have further proved that metal sorption on clays and aluminum oxides can result in the formation of mixed-cation hydroxide phases(Scheidegger et al., 1998). The formation of Ni-Al layered double hydroxide (LDH) phase was observed at pH values $>$ 6.25 with formation rate increasing with increasing pH (Elzinga and Sparks, 2001). Voegelin et al. (2005) found Ni-LDH (layered double hydroxide) precipitates by using EXAFS spectroscopy to analysis the soil from a column experiment. The high resistance of Ni-LDH against dissolution at low pH could also be shown in dissolution studies(Voegelin and Kretzschmar, 2005). Using FeFF simulations and experimental XAFS data of model compounds to Ni surface precipitates, Scheinost and Sparks (2000) found that LDH preferentially forms in the presence of containing sorbents: pyrophyllite, illite, kaolinite, gibbsite, and alumina above pH 7.0. α –type metal hydroxides, instead of LDH, form in the presence of the Al-free sorbents talc, silica, and rutile, and in the presence of the Al-containing clay minerals montmorillonite and vermiculite. They reported that the high permanent charge of the latter minerals prevents or retards the release of Al. When Al is available, the formation of LDH seems to be thermodynamically and/or kinetically favored over the formation of α –type metal hydroxides. The formation of surface-induced precipitates may play an important role in the immobilization of Ni in non-acidic soils(Yamaguchi et al., 2001).

1.4.3 Competing Ion

The simultaneous presence of several heavy metals is common in contaminated soils due to application of fertilizers, sewage sludge, liming materials, and other industrial and waste materials into natural environment (McIlveen and Negusanti, 1994). This situation can create considerable difficulty in assessing the impact of heavy metal contamination if only considering a single element in the contaminated environment. With an understanding that there are far more than two-ions out of many possible co-contaminants (Pb, Cu, Zn), this study will focus on Ni and Cd competion, especially the case of comparatively weakly sorbing metals of Ni and Cd which are rather mobile in soil and water environments (Tsang and LO Irene, 2006; Atanassova, 1999).

Both Ni and Cd are specifically and/or nonspecifically sorbed on the mineral phase, clay and whole soils, by forming inner-sphere or outer-sphere complexes. Whereas, only Ni was found to form induced Al-Ni LDH in the presence of Al bearing minerals at pH higher than 7.0. Being somewhat similar in prosperities between Ni and Cd, these two ions may compete with each other for same adsorption sites. The competitive sorption of Ni and Cd were extensively investigated on Oxisols (Bibak, 1997), humic umbrisols (Covelo et al., 2004), soil clays (Atanassova, 1999) and whole soils (Antoniadis and Tsadilas, 2007; Echeverría et al., 1998). However, there is no agreement on the selectivity sequence of heavy-metal adsorption. Several studies indicated that for several soils Cd is of higher affinity than Ni (Gomes et al., 2001; Echeverría et al., 1998; Papini et al., 2004). Moreover, cation exchange was considered as the major sorption mechanism for both ions. Echeverría et al. (1998) and Antoniadis and Tsadilas (2007) reported that Ni adsorption was stronger than Cd and was related to hydrolysis of divalent ions capable of forming inner-sphere complexes with clay lattice edges. Other studies with minerals, e.g., kaonilite, montmorillonite, and goethite, indicated stronger affinity for Cd than Ni (Barrow et al., 1989; Puls and Bohn, 1988). For hematite, kinetic sorption results indicated that Ni is of stronger affinity than Cd (Jeon et al., 2003). Schulthess and Huang (1990) showed that Ni adsorption by clays is strongly influenced by pH as well as silicon and aluminum oxide surface ratios. Generally, the selectivity sequence of heavy metal sorption was found to be related to a few factors, including charge to radius ratio, electronegativity, softness parameter, and first hydrolysis constant (Tsang and LO Irene, 2006; Sposito, 1984; Echeverría et al., 1998; Antoniadis and Tsadilas 2007). Many authors observed that the selectivity sequence should theoretically depend on the characteristics of the metal ion. For example, Sposito (1989) defined the tendency of the metals to form covalent bonds according to the ionic radius and ionization potential and considering Cd prefered over Ni. Metal ions with low electronegativity, high polarizability and large ionic size are called “soft” ions (Sparks, 1995). Acidic soils seem to show preference for the “softer” Cd^{2+} compared to the “less soft” Ni^{2+}. This sorption order is in line with that observed by Puls and Bohn (1988) and their explanation of metal sorption capacity based on the concept of conventional hard-soft acid-base (HSAB) principle. If specific metal sorption (inner sphere complexion) for Ni was considered as the dominant adsorption reaction, the reactions of heavy metal cations with soil minerals were related to metal-ion hydrolysis. The *pK* values for metal hydrolysis: $Me^{2+} + H_2O = MeOH^+ + H^+$, are 10.08 and 9.86 for Cd^{2+} and Ni^{2+}, respectively (Gomes et al., 2001). The lower *pK* value for Ni is indicative of stronger specific sorption (Antoniadis and Tsadilas, 2007). If hydrolysis of metal ions, either in solution or at the soil surface, is a primary adsorption mechanism for metal ions on adsorbent, higher affinity for Ni is expected.

The competitive effect may slow down the nuclear process or facilitate the release Ni during sorption. However, this topic has not been extensively investigated. Voegelin and Kretzschmar (2005) investigated the formation and dissolution of single and mixed Zn and Ni precipitates in soil by using column and XAFS techniques. They found that only 23% of the retained Ni was leached in experiments with Ni alone, whereas 87% of the retained Ni were released upon acidification in the presence of Zn. EXAFS analysis revealed that the Zn-Ni LDH phases formed in the Ni-Zn mixed condition had been completely dissolved, while the LDH phase formed in the Ni only condition was still present. This finding indicated that competitive effect facilitates the release of nuclear complexes of Ni.

A consequence of heavy metal ion competition maybe mutually suppress Ni and Cd adsorption and enhanced mobility in the soil environment. Antoniadis and Tsadilas (2007) investigated the competitive effect of Ni Cd and Zn and concluded that metal competition resulted in decreased metal sorption. However, the suppressive effect of competition on metal sorption was evident only at the higher end of the range of added metal concentrations, while there were no observable differences between single-element and competitive sorption at low added metal concentrations. This shows that the competition effect only occurred when the available sorption sites tended to be saturated by the adsorbates. An excess of surface sites for metal cations negated competition, explaining why the competitive effect was not strong or even not necessarily observed at low heavy metal loading (Tsang and LO Irene, 2006; Voegelin and Kretzschmar, 2005). Tsang and LO Irene (2006) also suggested that the competitive effect of sorption depends on the number of available sorption sites and the extent of saturation of those sites by competing ions. As a result, when the competing concentration is lower, a weaker competitive effect is expected. The suppressive effect of competition was also exhibited by metal K_f values (derived from Freundlich equation), which were lower in the binary systems compared to the monometal sorption. Metal K_f decrease was even more pronounced in the ternary systems. The parameters used to estimate the competitive effects are described in the following section.

When more than one competing ion is present in the solution and solid phase, several competitive models, and parameters derived from models, were utilized to estimate the competitive effect. The most commonly used model is the Sheindorf-Rebhun-Sheintuch (SRS) equation. It was assumed that the single-component sorption follows the Freundlich equation (Sheindorf et al., 1981). The derivation of SRS equation is based on the assumption of an exponential distribution of adsorption energies for each component. A general form of the SRS equation can be written as

$$S_i = K_i C_i \left(\sum_{j=1}^{l} \alpha_{i,j} \; C_j \right)^{n_i - 1} \qquad [1.5]$$

where the subscripts *i* and *j* denote metal component *i* and *j*, *l* is the total number of components, and $\alpha_{i,j}$ is a dimensionless competition coefficient for the adsorption of component *i* in the presence of component *j*. The parameters K_i and n_i are the Freundlich parameters representing a single component system *i* as described in Eq [l.3] above. By definition, $\alpha_{i,j}$ equals 1 when $i = j$. If there is no competition, i.e., $\alpha_{i,j} = 0$ for all $j \neq i$, Eq [1.5] yields a single species Freundlich equation for component *i* identical to Eq [1.3]. Freundlich *K* and *n*, where no competing ions were present, were utilized as input parameters in the SRS Eq [1.5]. Nonlinear least square optimization was used in the estimates for best-fit $\alpha_{i,j}$. The SRS equation may be regarded as a multi-component model and does not imply certain reaction mechanisms. Roy et al. (1986) suggested that the SRS parameters could be used to describe the degree of the competition under specific experimental conditions. Gutierrez and Fuentes (1993) concluded that the SRS approach was suitable in representing competitive adsorption of Sr, Cs, and Co in a system with Ca-montmorillonite suspensions. Recently, Antoniadis and Tsadilas (2007) used the SRS successfully to predict competitive sorption of Cd, Ni and Zn in a Greek vertic xerochrept soil. They found Zn was strongly retained and competition suppressed the sorption of the three metals.

Barrow et al. (1989) successfully utilized a variable charge surface model in an effort to describe Ni, Zn and Cd adsorption in a goethite-silicate system. A modified competitive surface complexation model developed by Papini et al. (2004) was adopted to describe competitive adsorption of Pb, Cu, Cd and Ni by an Italian red soil. Equilibrium and kinetic ion exchange type models were employed to describe sorption of heavy metals in soils by several investigators (Abd-Elfattah and Wada, 1981; Hinz and Selim, 1994). The affinity of heavy metals increases with decreasing concentration in heavy metal fraction on the exchanger surfaces. Using an empirical selectivity coefficient it was shown that Zn affinity increased up two orders of magnitude for low Zn surface coverage in a Ca-background solution (Abd-Elfattah and Wada, 1981). The Rothmund-Kornefeld approach incorporates variable selectivity based on the amount of metal sorbed. Based on the Rothmund-Kornefeld approach, Hinz and Selim (1994) results showed strong Zn and Cd affinities at low concentrations.

1.4.4 Kinetic Adsorption and Desorption

Traditionally, Ni sorption has been studied using equilibrium batch experiments conducted within a short period of reaction time. Few studies investigated the effect of long residence time on adsorption of Ni in soils. However, a long and slow but significant reaction phase may exist due to diffusion into interparticle spaces, sites of different reactivity, or surface precipitation. The kinetics of Ni adsorption-desorption must be understood if accurate predictions are to be made about the fate of Ni in soil environment (Sparks, 1989). Several studies indicated that Ni sorption by natural solids is time dependent ranging from a few days to several months for quasi equilibrium to be attained (Scheidegger et al., 1998; Roberts et al., 1999; Eick et al., 2001). Such two-stage reaction is characteristic of the sorption of several heavy metal on clays, oxide surfaces and soils as suggested by Eric et al. (2001), Voegelin et al. (2001), Jeon et al. (2003), Bruemmer et al. (1988), Dzombak and Morel (1986) and Scheidegger et al. (1998). Although the sorption of divalent metal ions onto oxides has been reported to be completed within few seconds (Voegelin et al., 2001), slow kinetics have also been observed where sorption continued for several days or months (Eric et al., 2001). Barrow et al. (1989) studied kinetics of Ni, Cd and Zn by goethite. In their study, the diffusion process was measured over a wide range of periods (2 h to 42 days). A diffusion parameter D was used to estimate the time effect of nickel sorption.The estimated D value for nickel adsorbed by goethite was 10^{-14} cm^2 d^{-1}, lower than diffusion in water, indicating that Ni very slowly diffused into goethite. The low values for Ni sorption by goethite provided evidence that diffusion is indeed involved. This work has also shown that in order to describe the effects of concentration, it was necessary to postulate that the surface was heterogeneous (even it is pure mineral). Benjamin and Leckie (1981) included a range of concentrations in their studies of heavy metal sorption by amorphous iron oxyhroxide detecting heterogeneity and reaction between Ni and sorbents continued with time. Jeon et al. (2003) studied sorption kinetics of Fe(II), Zn(II), Co(II), Ni(II), Cd(II), and Fe(II)/Me(II) onto hematite. Their results showed that instantaneous sorption occurred within 1 min resulting in uptaking of 4.3% Ni of applied by hematite followed by 25% uptaken during 5 days. They suggested that surface diffusion was not a reasonable explanation for slow sorption in these systems because mixing was continuous and sorption at 1 min was substantial. Pore diffusion was eliminated because the hematite was not micro-porous. The slow uptake could have been due to multi-sorption sites with different sorption kinetics or due to slow conversion from outer- to inner-sphere surface complexes. The most favorable sorption sites for metal ions might be occupied first followed by continued sorption to less favorable sites. Scheidegger and Sparks (1998) studied the kinetics of formation of Ni surface precipitation on pyrophyllite and concluded that Ni sorption at pH=7.5 were initially fast. Twenty-five % of the initial Ni was removed within minutes. Thereafter, a gradual slow sorption was observed. They attribute the fast reaction stage to adsorption phenomena and the slow reaction stage to nucleation processes on the pyrophylliite surface. XAFS data revealed that further growth of a mixed Ni/Al phase with increasing reaction time (Scheidegger et al., 1998).

Generally, several mechanisms are suggested to contribute to the kinetics of Ni sorption on soils including (1) slow diffusion through intra-particle micropores; (2) heterogeneity of sorption sites having different affinities; (3) slow sorption due to the increase in surface charge upon the inner-sphere complexation of such ions (Jeon et al., 2003); (4) at neutral or basic pH, slow formation of new solid phases such as hydroxides or layered double hydroxides may cause kinetic effects and immobilization of nickel (Voegelin et al., 2001; Eric et al., 2001; Scheidegger et al., 1998; Businelli et al., 2004).

Sorption and desorption isotherms, together, show whether sorption is reversible or, on the contrary, wholly or partially irreversible (hysteresis) (Vega et al., 2009). In contrast to adsorption studies, relatively little work has been done to investigate desorption or release of Ni from the soil minerals or soils. Research has shown that sorption of Ni is highly hysteric and sorbed Ni is not easily removable from the soil matrix, especially at higher pH. In 2000, Scheckel et al. investigated the influence of residence time on the release of nickel from three sorbents and found Ni-LDH precipitate drastically increased in stability, as was known by decreasing amounts of Ni released by nitric acid (HNO_3) with increasing residence time(Scheckel et al., 2000). Data from adsorption-desorption kinetics experiment can be described by a series of kinetic equations, which will be extensively discussed in the later chapter. However, few researchers have investigated the kinetics of Ni adsorption-desorption in soils.

1.5 Transport of Nickel under Dynamic Flow

Batch experiment was commonly used to study the fate and behavior of nickel. However, only limited studies have investigated Ni transport under dynamic flow conditions. Miscible displacement techniques have been widely proposed to study the transport of heavy metal in natural porous media since the experiment conditions in column studies could more closely mimic the behavior of contaminants in heterogamous geological material.

The transport of heavy metal ions in heterogeneous natural soils is largely controlled by the adsorption-desorption on the surface of solid matrix. For example, rate-limited sorption tends to increases the residence time of release for heavy metal but has no effect on symmetry of transport. And nonlinear sorption produces a constant degree of asymmetry as the spreading forces balance the concentration-dependent retardation behavior (Srivastava and Brusseau, 1996). Antoniadis et al. (2007) demonstrated that breakthrough curves of Ni in single and competitive system of London clay were asymmetrical, displaying a relatively slow breakthrough front and prolonged tailing. This indicated that the transport of Ni was a non-equilibrium process. In their study, the Rd (retardation factor) values obtained from the CXTFIT model were 204 for Cu, 131 for Ni, and 168 for Zn indicating that the order of metal mobility was Ni > Zn > Cu. The mobility of Ni compared with several heavy metals was also investigated by Voegelin et al., (2001). An experiment was conducted by combining breakthrough of Cd, Zn and Ni in 10^{-2} M $CaCl_2$ background solution and the results showed that breakthrough of Cd and Zn occured simultaneously, while Ni was slightly more retarded with a longer tailing. Whereas, Liu et al. (2006) studied transport of Cd, Ni and Zn in one Chinese red soil and found the sequence of retardation factor was Cd > Zn > Ni. Granado-Castro et al. (2008) observed that the overall transport of Ni was slower than the overall transport of Cu and Cd when they studied the kinetics of the transport of Cu(II), Cd(II) and Ni(II) ions through a liquid membrane. The retarded transport of Ni was related to its kinetic sorption in soils where rate limited sorption was extensively observed.

Studies of Ni release using miscible displacement experiments are limited. Antoniadis et al. (2007) observed that after 475 hours leaching under acidic condition, 95% of applied was removed. Whereas at pH 7.4, only 23% of the retained Ni was leached from a 1.7 cm long uniform packed soil column (Voegelin and Kretzschmar, 2005). Nickel leaching in columns of an acidic soil was also conducted by (Voegelin and Kretzschmar, 2001) in an acidic soil; however, they did not report the amount of Ni recovered from soil column. The maxima concentration of Ni breakthrough curve reached 1.0 (relative concentration) and the right side (leaching) of BTC was tailed.

Seveval studies have focused on the leaching of heavy metal from contaminated soil. Soil and water pollution resulting from disposal of contaminated dredged materials on land is a problem in many industrialized countries. Runoff, erosion and movement of sediment from the soil surface are the major transport mechanisms for heavy metals (Singh et al., 2000). In the Netherlands and Germany, there are 30 – 50 million m^3 annually of dredged materials. Some fractions of the dredged material cannot be relocated to the river, the estuary or the sea, but have to be treated or deposited on land. Lager et al. (2005) sampled the dredged materials and separated the materials into fine and sandy fractions. Using a modification of the centrifugation technique the sandy fraction was studed in column experiments conducted under saturated and unsaturated conditions. The saturated column was 48 cm in length and 5 cm in diameter. The unsaturated column was 48 cm in length and 10 cm in diameter.5.88 kg of the wet material was incorporated and slightly compacted. The column was irrigated once a day for over an hour with 50 mL artificial rainwater applied through six precipitation cocks. Tap water was diluted with de-ionized water to yield a water hardness of 0.0895 mmol/L. Acid rain was simulated by application of an average pH of 4.1. Rresults from the column experiments showed that nickel concentration in effluent exceeded its threshold value in saturated column and nickel concentration exceeded the threshold value in the first flush of the unsaturated column. The breakthrough curves of all the column experiments conducted showed a high initial concentration followed by a decrease. The concentration of nickel in the unsaturated column was almost twice as high as the threshold value at the beginning of the leaching process. The observed strong and rapid increase of the concentrations in the breakthrough of the column experiments, the so-called ‘first flush’, a phenomenon that also occurs under natural conditions of deposition. This indicated that the risk of polluting the underlying groundwater is much higher from the deposition of the sandy fraction.

A number of saturated column studies have been conducted to evaluate the competitive effect on Ni transport and mobility in soils. At any given pH level, the competitive effect can enhanced the Ni mobility in soils. Voegelin and Kretzschmar (2001) observed that when Zn and Ni were present in same soil column, 87% of the retained Ni were released, which is much higher than that of Ni in single element system. Antoniadis et al. (2007) studied competitive filtration of Ni with Cd or Zn using column infiltration tests and observed that competitive infiltration increased metal mobility in all cases. The distribution factors (K_d) of Ni determined from column transport experiments decreased by a factor of 3.4 when in competition with Cu, and Zn by a factor of 3.2. Nickel and Zn when infiltrated as a pair, decreased their K_d compared with their mono-metal state 2.6 times in the case of Ni and 2.3 times in the case of Zn.

1.6 Movement of Ni in Field

The elevated concentrations of Ni in soils and aquifers have caused concern over the potential pollution of surface and ground water resulting from Ni release and leaching. The potential downward mobility of sludge-applied trace metals in soil via leaching has been investigated for several decades. Many researchers conclude that there is little potential for trace metal mobility via water percolating through the soil profile and resulting contamination of groundwater (Smith, 1996; Richard et al., 1998). However, an examination of recent and past work suggests that the case for determing potential metal mobility is not yet closed.

The distribution of heavy metals in soil profiles is continuously changing due to anthropogenic activities, the natural turnover, preferential flow in field, salinity condition, and reduction condition (flood condition in different seasons), in rock-soil-plant systems. Heavy metals are associated with the various components of the soil in different ways, and these associations indicate both their mobility in the soils as well as their bioavailability (Ahumada et al. 1999; Kashem et al., 2007). Water-soluble and exchangeable fractions are considered to be readily mobile and bioavailable, while metals incorporated into the crystal lattice of clays appear to be relatively inactive. Other forms of heavy metals in soils – precipitated as carbonate, occluded in Fe–Mn and Al oxides or complexed with organic matter – are considered to be relatively active fractions, depending upon the specific combination of physical and chemical properties of the soils (Shuman, 1985; Kashem et al., 2007). In the field, the occurrence of microbiologically catalysed Fe/Mn oxide and sulphate reduction and the oxidation of Fe/Mn and sulphides are related to the frequency and duration of flooding and the water table level (Laing et al., 2009).

Preferential flow can accelerate the movement of water and solutes through soil profiles. Water and solutes traveling in preferential flow pathways in soils (i.e. soil fractures, shrink-swell cracks, root and worm holes, or, in coarse soils, fingering phenomena) often bypass the bulk of the soil matrix (Steenhuis et al., 1995; Richard et al., 1998). The fact that preferential flow paths typically occupy a small fraction of the subsoil volume may allow metals (particularly if complexed) to pass through the subsoil without leaving detectable 'tracks' (McBride et al., 1997). Richard et al. (1998) studied the distribution and mobility of sludge-applied metals at a heavily loaded field site long after application. Preferential flow phenomena were investigated through a dye tracer. Their results showed that the HNO_3-extractable Ni concentrations decreased from 95.5 to 25.4 mg kg^{-1} with the soil depth increased from 10-150 cm. There are no significant difference for Ni concentrations in dyed soil (representing the preferential flow path) and non-dyed soil.

Under reduced condition, significant changes in the abundance of the major iron – sulfur phases have been observed which may potentially influence metal mobility (Preda and Cox, 2004; Burton et al., 2008). In particular, reductive dissolution of Fe(III)-phases may release Fe as well as previously bound trace metals (Burton et al., 2008). Laing et al. (2009) reported heavy metal mobility in intertidal sediments of the Scheldt estuary through field monitoring. The level of the water table was monitored at several experimental sites through all seasons. The highest sulphide concentrations were found at the sites where the water table level never decreased considerably. These sulphides primarily suppress the availability of Cd, Cu, Ni and Zn. The metal concentration also changed with sampling depth in sediments. Total concentrations of Ni significantly increased with increasing sampling depth, 4 times higher than the metal contents at depth of 0-20 cm. The heavy metal concentration in pore water in this study was also investigated. Their results showed that, at 10 cm below the water surface, Ni concentrations in the porewater did not differ substantially between the sampling locations. At 90 cm below the surface, Ni concentrations were significantly lower at the sites which contained significant sulphide amounts. This can be attributed to the fact that Ni is also expected to be released upon reduction of Fe and Mn oxides. The oxidation rate is higher in the more sandy sediments, as oxygen can penetrate more easily. Thus, at the more sandy sampling sites, Ni had probably already migrated towards higher or lower sediment layers and subsequently co-precipitated with oxides or sulphides. This immobilization of Ni under reduced condition was also observed by Burton et al. (2008). In their study, they describe the mobility of Al, As, Fe, Mn, Ni and Zn during controlled re-flooding of a Fe- and organic-rich acid-sulfate soil material. Soil re-flooding caused the onset of microbial mediated Fe(III)-reduction, which raised the pH of the initially acidic (pH 3.4) soil to pH 6.0 to 6.5, thereby immobilizing Al. The process of Fe(III)-reduction released high concentrations of Fe(II). The mobility of Fe(II) was subsequently controlled by the precipitation of siderite ($FeCO_3$). The formation of acid-volatile sulfide (AVS), as a product of SO_4-reduction, further retarded the mobility of Fe(II). Interactions with AVS also strongly immobilized Mn, Ni and Zn. They considered that re-flooding of soils, via the re-establishment of more natural drainage regimes, is a potential remediation approach since more Ni was immobilized therefore less Ni dissolved in water.

Salt water irrigation is becoming an increasing important practice in the USA. (Wahla and Kirkham, 2008); however, this practice may increase the risk of ground water contamination by heavy metal ions. Wahla and Kirkham (2008) reported that the heavy metal mobility is one of the consequences of saline-water irrigation during sludge application into soil during phytoremediation. They found that irrigation with NaCl (10,000 mg L^{-1}) solution increased the concentration of heavy metal in drainage water above drinking-water standards where this did not happened when irrigation with tap-water, therefore they concluded that the saline water was not recommended for the irrigation of sludge farms, especially for sandy soil. Salinity effects on the partitioning of metal between the solid phase and solution phase was also reported by Hartnett et al. (2006). A numerical model based on partition coefficient and salinity condition in field was developed to predict Ni distribution and transformation in the Mersey Estuary watershed (UK). A relationship between partition coefficient and salinity was developed using field data, and the partition coefficient correlated well with the salinity in the watershed. Based on this relationship, this numerical model successfully predicted dissolved Ni throughout the Mersey Estuary.

Sewage sludge addition to agricultural lands requires judicious management to avoid environmental risks arising from heavy metal contamination of surface water and accumulation in edible plants. The US Environmental Protection Agency (USEPA) advocated recycling of sewage sludge back to land (Christen, 1998). A field study was conducted on a silty-loam soil of 10% slope at Kentucky State University Research Farm (Antonious et al., 2008). The concentrations of heavy metals in sewage sludge used in this study were below the allowable limits (issued by the USEPA). The transport of heavy metal (Cd, Cr, Ni, Pb, Zn, Cu, and Mo) into surface water was assessed as function of soil amendments. Soil amendments used in this investigation were typically enriched, relative to the native soil, in N, C, organic matter, P, and Ca. Nitrate (NO_3), NH_4, P, K, Ca, Cd, Cr, Ni, Pb, Zn, Cu, and Mo, common sewage sludge constituents, likely altered the chemical and physical properties of soil, which in turn affected soil nutrient balance. Addition of sludge to native soil also increased the soil pH from 7.0 to 7.9. Soil pH affects ion availability. Runoff water following natural rainfall or irrigation events may accumulate heavy metals down the land slope, which may therefore reach surface waters like rivers and streams. In this study, Ni concentration expressed mg L-1 in runoff water was under the TMDL (USEPA). This may be due to the low concentration of Ni in the sludge studied. Whereas the movement of heavy metal down to deeper soil layers has been reported by Giusquiani et al. (1992), soil column study was conducted to assess the vertical movement of certain heavy metals in soil amended with urban waste compost. They found the elevated levels of Cu, Zn, Ni and Cr eluted from 50 cm soil columns when compost is added into a clay loam and a sandy loam.

There are two main patterns for movement of Ni in soils: leaching pattern (downward movement) and accumulating pattern (retained in surface soils). In the accumulating pattern, Ni is strongly sorbed on the soil solid phase (Sukkariyah et al., 2005), with sorption irreversible or only partially reversible. This pattern was observed when Sukkariyah et al. (2005) who investigated the distribution and mobility of Ni in a clay loam. After 17 years, 85% of Ni applied was remained in the topsoil where biosolids from wastewater treatment plant were incorporated. On the other hand, Antoniadis and Alloway (2003) reported that there is a risk of heavy metal movement down the soil profile where heavy loading of mobile metals in soils such as Cd, Ni, and Zn have been applied to low sorptive capacity soils. The sludge was deposited for decades on a sandy soil, Ni moved down to 80cm of soil profiles. Ni mobility was related to adsorption and desorption parameters in 21 soils by Businelli et al. (2009), when 21 soils was investigated. They concluded that adsorption is strongly hysteresis (irreversible or partially reversible) and that leaching of heavy metals is not very likely to occur. In contrast, when the adsorption is not completely hysteresis, there is risk of groundwater pollution (leaching through with profile).

1.7 Statement of Problem

The transport and mobility of Ni in soils are highly depended on the adsorption desorption process and the competitive effect since simultaneous present of several heavy metals. Most studies have focused on the equilibrium partitioning in the soil and minerals (Atanassova, 1999; Bibak, 1997; Covelo et al., 2004; Echeverria et al., 1998; Harter, 1992), with less emphasis on the kinetic aspects of Ni(II) and the transport of Ni(II) (Eick et al., 2001; Jeon et al., 2003; Liu et al., 2006; Voegelin and Kretzschmar, 2005). Kinetic adsorption data have the advantage of accounting for the nonequilibrium sorption behavior which may arise from the heterogeneity of sorption sites on soil surface and slow diffusion process on the interface between the liquid phase and soil matrix.

Based on literature review, studies of Ni transport under dynamic flow conditions are limited. Moreover, the modeling attempts to simulate the transport of Ni in heterogeneous soil material have not been very successful due to the time-dependent, concentration dependent and multi-reaction sorption of Ni. In order to predict the fate of Ni in soil environment, it is necessary to incorporate the complex geochemical reactions into the solute transport model.

1.8 Objective

In this study, kinetic batch experiments and miscible displacement experiments will be conducted to quantify the retention and transport of Ni(II) in soils with different properties. The results from the experiment will be simulated using numerical models incoporating equilibrium and kinetic reactions with solute transport equation. The specific objectives of this study are: 1) study the competitive sorption of Ni and Cd under equilibrium condition; 2) study the adsorption-desorption kinetics of Ni in three soils using both kinetic batch experiments and numerical simulation with equilibrium-kinetic multireaction (MRM) model; 3) to study the nonequilibrium transport of Ni with saturated miscible displacement experiment and multireaction transport simulation; 4) to study the effect of Cd on the adsorption-desorption kinetics and transport of Ni in soils.

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CHAPTER 2: COMPETITIVE SORPTION OF NICKEL AND CADMIUM IN DIFFERENT SOILS

2.1 Introduction

Heavy metals are potential pollutants to the soil and groundwater environment mainly from different industrial and anthropogenic activities. Industrial waste and sewage sludge disposed on land often contain appreciable amounts of heavy metal such as Cu, Zn, Cd and Ni and thus create a risk for croplands, as well as animals and humans (Atanassova, 1999; McIlveen and Negusanti, 1994). In most cases, soil contamination involves several heavy metals, i.e. a multiple component system. Understanding the fate and transport of heavy metals in a multi-component systems is a prerequisite in identifying dominant mechanisms governing their competitive sorption behavior in the soil environment.

Several studies on Ni and Cd indicate that their sorption behavior on minerals and soils are somewhat similar. These two cations have lower affinities for soil colloids and are generally considered as weakly bonded metals (Atanassova, 1999). A consequence of weak bonding for heavy metals ions such as Cd and Ni is that ion competition may increase their mobility in the soil environment. Moreover, a number of studies reported varying Cd and Ni affinities in soils and minerals. Several studies indicated that for some soils Cd is of higher affinity than Ni (Gomes et al.,2001; Echeverría et al., 1998; Papini et al.,2004). Moreover, cation exchange was considered as the major sorption mechanism for both ions. Echeverría et al. (1998) and Antoniadis and Tsadilas (2007) reported that Ni adsorption was stronger than Cd and was related to hydrolysis of divalent ions capable of forming inner-sphere complexes with clay lattice edges. Other studies with minerals, e.g., kaonilite, montmorillonite, and goethite, indicated stronger affinity for Cd than Ni (Barrow et al., 1989; Puls and Bohn, 1988). For hematite, kinetic sorption results indicated that Ni is of stronger affinity than Cd (Jeon et al., 2003). Schulthess and Huang (1990) showed that Ni adsorption by clays is strongly influenced by pH as well as silicon and aluminum oxide surface ratios.

Recent studies using XAFS and HRTEM techniques, Ni-Al layered double hydroxide (LDH) was considered responsible for the sorption behavior for pH above 6.5 on pyrophyllite and kaolinite surfaces (Scheidegger et al., 1996; Eick et al., 2001). They suggested that Al dissolved at high pH values could be responsible for Ni precipitate on clay surfaces. The formation of surface-induced precipitates may play an important role in the immobilization of Ni in non-acidic soils. However, surface-induced precipitates were not found for Cd in non-acid soils. This suggests that competitive behavior of Cd/Ni in neutral and alkaline soils may be different from that in acidic soils.

Several attempts were made to model competitive adsorption between Ni and Cd in soils. Examples of such attempts include variable charge surface models and surface complexation models. Barrow et al. (1989) successfully utilized variable charge surface model in an effort to describe Ni, Zn and Cd adsorption in a goethite-silicate system. A modified competitive surface complexation model developed by Papini et al. (2004) was adopted to describe competitive adsorption of Pb, Cu, Cd and Ni by an Italian red soil. Equilibrium and kinetic ion exchange type models were employed to describe sorption of heavy metals in soils by several investigators (Abd-Elfattah and Wada, 1981; Hinz and Selim, 1994). The affinity of heavy metals increases with decreasing heavy metal fraction on exchanger surfaces. Using an empirical selectivity coefficient it was shown that Zn affinity increased up two orders of magnitude for low Zn surface coverage in a Ca-background solution (Abd-Elfattah and Wada, 1981). The Rothmund-Kornefeld approach incorporate variable selectivity based on the amount of metal sorbed. Based on the Rothmund-Kornefeld approach, Hinz and Selim (1994) showed strong Zn and Cd affinities at low concentrations.

Another type of competitive adsorption modeling is that based on the Freunelich approach. The Shenindrof-Rebhun-Sheituch (SRS) was developed to describe competitive or multicomponent sorption where it was assumed that the single-component sorption follows the Freundlich equation (Sheindorf et al., 1981). The derivation of SRS equation was based on the assumption of an exponential distribution of adsorption energies for each component. Gutierrez and Fuentes (1993) concluded that the SRS approach was suitable in representing competitive adsorption of Sr, Cs, and Co in a system with Ca-montmorillonite suspensions. Recently, Antoniadis and Tsadilas (2007) used the SRS successfully to predict competitive sorption of Cd, Ni and Zn in a Greek vertic xerochrept soil. They found Zn was strongly retained and competition suppressed the sorption of the three metals.

A literature search revealed that in most competitive adsorption studies the affinity of one heavy metal was measured where only one or two concentration levels of a competing ion were maintained. A wide range of concentrations of the competing ions is necessary to delineate the adsorption characteristics for different heavy metals and for modeling of single and multi-component (competitive) systems. The main objectives of this study were to quantify the sorption of Ni and Cd in single and binary Ni-Cd systems for soils having different properties; two acidic soils (Olivier loam, Windsor sand) and one non-acidic soil (Webster Loam). Different molar ratios of Ni/Cd for a wide concentration range were used to investigate competitive Cd and Ni in all soils. Sorption isotherms for single ions as well as binary systems were modeled using the Freundlich and competitive approaches. Moreover, the predictive capability of the SRS model for describing the simultaneous adsorption of Cd and Ni was examined.

2.2 Materials and Methods

Surface sample of Olivier loam, Webster loam, and Windsor sand were used in this study (Table 2.1). Olivier loam is a common alluvial soil occurring in the lower Mississippi River basin in Louisiana and southern Mississippi. Webster loam was sampled in Story County, Iowa and is characterized as very deep, poorly drained, moderately permeable soil formed in glacial till or local alluvium derived from till on uplands. Windsor sand was sampled Near Hanover, New Hampshire and is a fine sandy soil formed on glacial outwash plains, deltas of the U.S northeast region. The soil samples were air dried and passed through 2 mm sieves for analysis. Soil properties such as soil pH, cation exchange capacity (CEC), and particle size analysis were determined earlier in our laboratory by Buchter et al. (1989) and are given in Table 1.

A batch equilibration technique was used to investigate Ni and Cd adsorption for the selected soils. Six initial Cd(II) or Ni(II) concentrations (C_o) of 0.025, 0.50, 0.100, 0.250, 0.500, and 0.800 *mM* were applied in single metal sorption studies. All solutions were prepared in 0.005 *M* $Ca(NO_3)_2$ background solution at pH=6.5. For adsorption, 30 *mL* of the various $Cd(NO_3)_2$ or $Ni(NO_3)_2$ concentration solutions was added to 3 g of soil in 40 *mL* teflon centrifuge tubes in triplicate. The tubes were sealed with teflon screw caps and placed on a reciprocal shaker. The mixtures were continuously shaken for 24 h and then centrifuged at 5000 ×g for 10 minutes. A 6-*mL* aliquot was sampled and total heavy metal concentration in the supernatant solution was analyzed using ICP-AES (Spectro Citros CCD, Kleve, Germany). Amounts of Cd and Ni sorbed by the soil matrix were determined as the difference between the concentrations of the supernatant and that of the initial solutions.

In another set of experiments, competitive Cd-Ni sorption was carried out over a wide range of Cd and Ni concentrations. The batch technique described above was used to investigate

Ni sorption in the presence of several initial concentrations of Cd as the competing counter ion. Similarly, Cd sorption experiments in the presence of several initial concentrations Ni as the competing ion was carried out for all soils. Solutions of $Cd(NO_3)_2$ and $Ni(NO_3)_2$ were used to prepare solutions with different Cd/Ni molar ratios in the 0.005 *M* $Ca(NO_3)_2$ background solution as described above. Specifically, for both Ni and Cd sorption, the concentrations of the competing ions were 0.047, 0.235, and 0.766 *mM*. As an example, for one set of Ni sorption isotherms, the amounts of Ni and Cd added, expressed as (*mM* Ni/*mM* Cd) were 0.025/0.047, 0.050/0.047, 0.100/0.047, 0.250/0.047, 0.500/0.047, and 0.800/0.047. As a result, for all soils, sorption isotherms for both Ni as well as Cd were obtained for four different initial concentrations of the competing ions.

Table 2.1. Selected physical and chemical properties of the soils used in this study.

Soil		Olivier	Windsor	Webster
pH		5.80	6.11	6.92
TOC ‡	%	0.83	2.03	4.02
CEC §	cmol kg^{-1}	8.6	2.0	27.0
Sand	%	5	77	39
Silt	%	89	20	39
Clay	%	6	3	22

‡ TOC, total organic carbon. § CEC = cation exchange capacity.

2.3 Results and Discussion

2.3.1 Sorption Isotherms

Ni and Cd sorption isotherms, after 24 h of reaction, are shown in Figs. 2.1 and 2.2 for Olivier, Windsor and Webster soils. These isotherms are highly nonlinear and depict strong affinities at low heavy metal concentrations. For all three soils, the overall shape of the isotherms suggests some similarities in sorption mechanisms of the two cations. The Freundlich approach was used to describe both Ni and Cd isotherms

$$S_i = K_i C_i^{n_i} \qquad [2.1]$$

where S_i represents the (total) amount sorbed (*mmol* per kg soil) of the metal species *i*, and C_i is the concentration in solution (*mM)* of *i*. The parameter K_i is the Freundlich distribution or partition coefficient ($L\ kg^{-1}$) and n_i is a dimensionless reaction order for *i* in a single component system (Ni or Cd). Omitting the subscript *i*, the estimated Freundlich parameters *n* and *K* for Ni and Cd for all soils are given in Table 2.2. These parameters were subsequently used in the SRS model in order to assess competitive adsorption between Ni(II) and Cd(II) as will be discussed in later sections.

Isotherms for Ni and Cd were well described by the Freundlich Eq [1] with coefficients of correlation (r^2) ranging from 0.982 to 0.999 (Table 2.2). The dimensionless parameter *n* may be regarded as a representation of energy distribution of heterogeneous adsorption sites for solute retention by matrix surfaces (Sheindorf et al., 1981). Nonlinearity and competition are often regarded as characteristics of site-specific adsorption processes. Adsorption occurs preferentially at the sites with highest adsorption affinities and available sites with lower adsorption become occupied with increasing concentration. The *n v*alues for Windsor, Olivier and Webster soil are 0.64, 0.57 and 0.55 for Cd and 0.50, 0.56 and 0.52 for Ni, respectively. These *n* values were within a narrow range (0.50-0.64) for all three soils and reflect the observed similarities of the overall shape of both Ni and Cd sorption isotherms as shown in Fig 2. 1 and 2.2. Moreover, the shape of these isotherms depicts an L-type curve as described by Sposito (1984). These *n* values are within the range of values of those reported earlier by Buchter et al. (1989); 0.57-0.78 for Cd and 0.65-0.74 for Ni.

A comparison of the adsorption isotherms indicates that for both Ni and Cd sorption affinities follows the sequence; Windsor < Olivier < Webster soil (Fig.1). This is also illustrated by the respective *K* values for Cd; 5.62, 24.59 and 26.78 L kg^{-1} and for Ni; 2.55, 13.30 and 37.57 L kg^{-1}, respectively (Table 2.2). This sequence correlates well with the CEC values

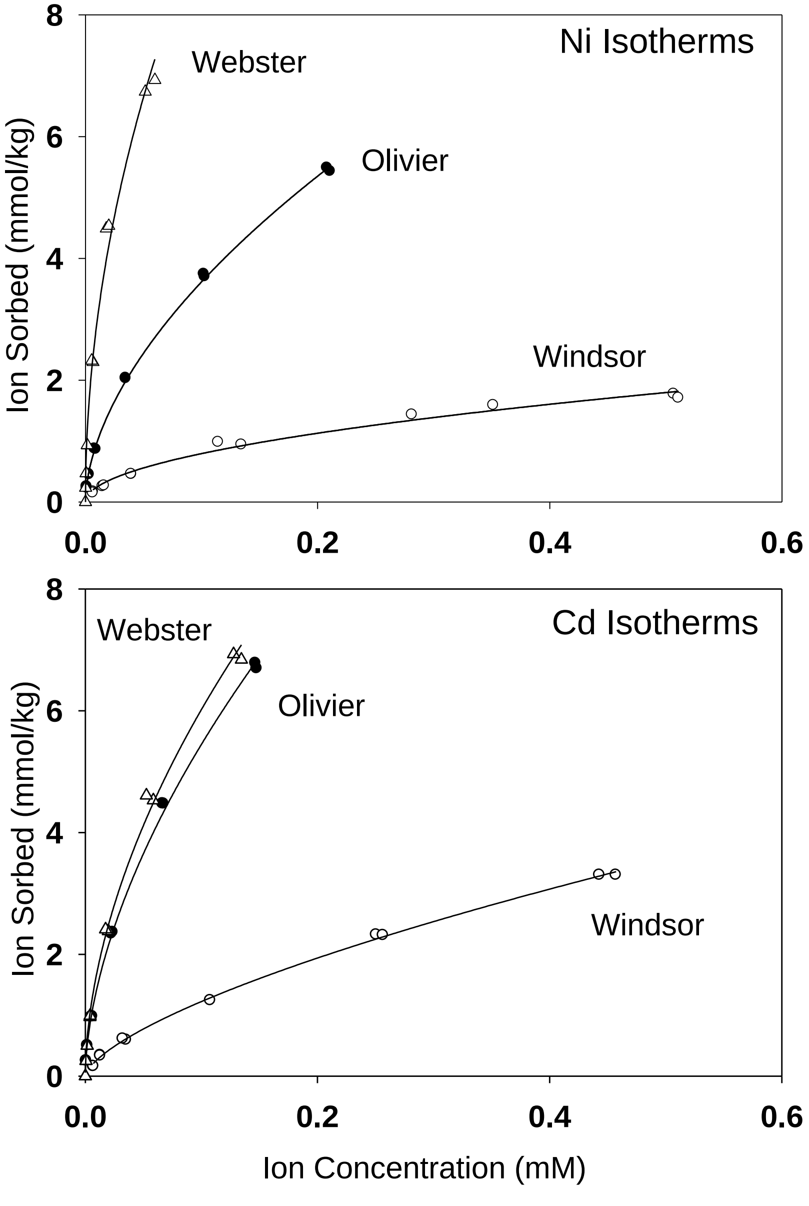

Figure 2.1. Adsorption isotherms for Ni (top) and Cd (bottom) for Windsor, Olivier and Webster soil. Solid curves are Freundlich model calculations

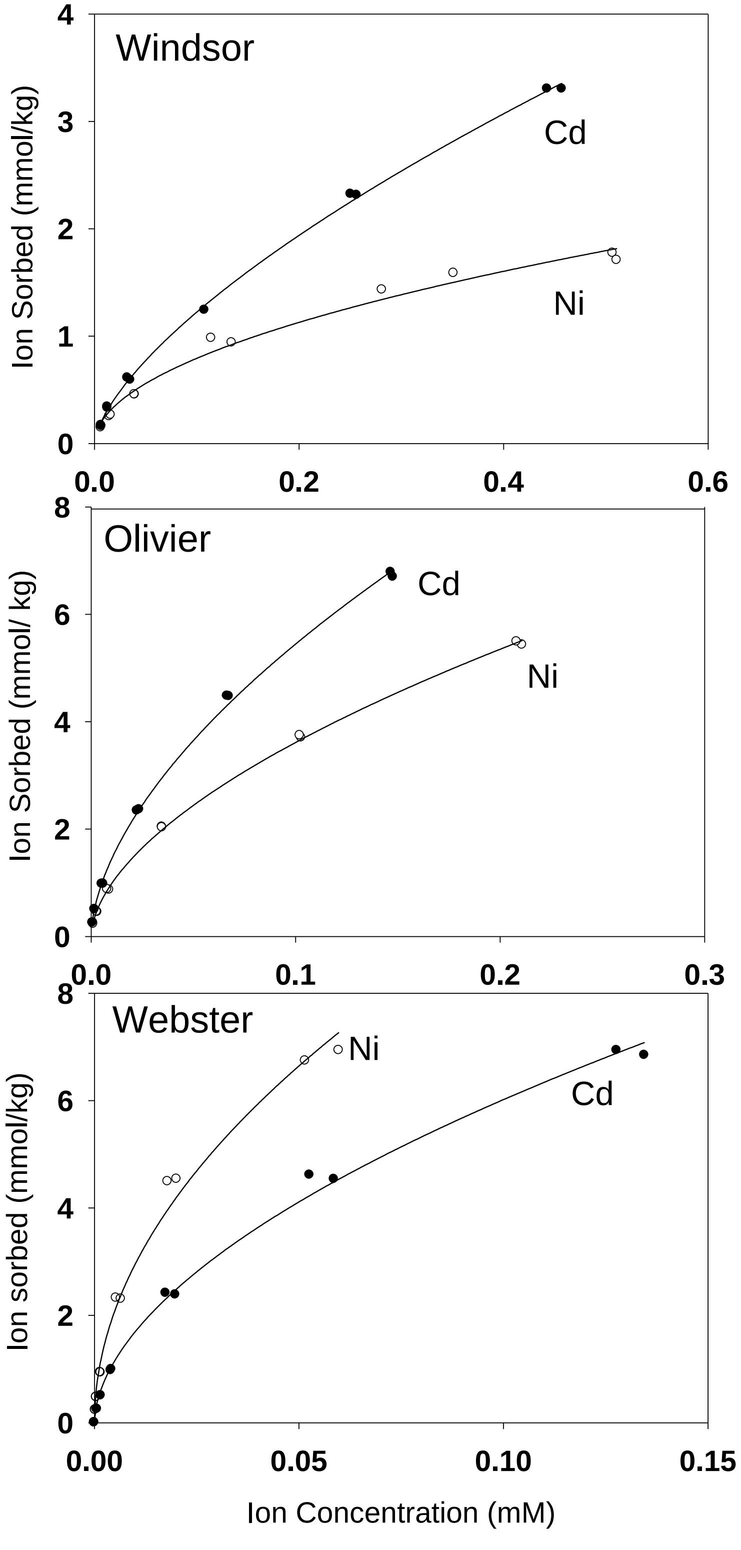

Figure 2.2. Adsorption isotherms for Ni and Cd for Windsor (top), Olivier (middle) and Webster (bottom) soil. Solid curves are Freundlich model calculations

Table 2.2. Estimated Freundlich and SRS parameters for competitive adsorption of Nil and Cd for the different soils.

Soil	Competing ion concentration (*mM*)	Ni Isotherms			Cd Isotherms			SRS parameters §			
		K (L kg^{-1})	*n*	r^2	*K* (L kg^{-1})	*n*	r^2	α_{Ni-Cd}	α_{Cd-Ni}	r^2	RMSE §§
Windsor	0	2.55±0.09	0.50±0.02	0.987	5.62±0.19	0.64±0.02	0.993	1.50	0.61	0.999	0.016
	0.048	2.45±0.04	0.54±0.01	0.997	5.63±0.09	0.66±0.01	0.999				
	0.240	2.01±0.04	0.53±0.01	0.996	4.66±0.07	0.66±0.01	0.998				
	0.766	1.41±0.05	0.53±0.03	0.984	4.20±0.09	0.67±0.01	0.997				
Olivier	0	13.30±0.23	0.56±0.08	0.999	24.59±0.57	0.57±0.01	0.999	1.50	0.82	0.994	0.014
	0.048	11.44±0.32	0.54±0.01	0.999	24.96±0.99	0.64±0.01	0.999				
	0.240	10.45±0.33	0.56±0.01	0.999	23.32±0.50	0.66±0.00	0.999				
	0.766	10.19±0.33	0.62±0.01	0.999	20.17±1.20	0.68±0.02	0.997				
Webster	0	37.57±5.87	0.52±0.05	0.982	26.78±1.23	0.55±0.02	0.997	0.20	4.00	0.975	0.020
	0.048	37.09±4.42	0.57±0.03	0.994	23.51±1.30	0.64±0.02	0.998				
	0.240	37.54±5.21	0.59±0.04	0.992	15.17±1.77	0.54±0.05	0.984				
	0.766	32.13±4.55	0.59±0.04	0.989	13.85±1.11	0.57±0.03	0.992				

§ SRS = Shenindrof-Rebhun-Sheituch parameters.

§§ RMSE = Root mean square error.

for the three soils given in Table 2.1. The work of Gomes et al. (2001), among others, indicated that Cd and Ni adsorption by a number of soils were correlated with CEC. Papini et al. (2004) reported that Cd and Ni adsorption was largely due to cation-exchange reaction on an Italian red soil.

Figure 2.2 is a representation of the results given in Figure 1 except that the isotherms for Ni and Cd are now being compared for each soil. The isotherms indicate that Cd adsorption for the two acidic soils (Windsor and Olivier) was larger than Ni. This result may be related to their ionic radii and chemical properties. The electronegativity (X) values are 1.46 and 1.75 for Cd and Ni, respectively, and their respective radii of 0.098 and 0.069 nm. The average electric dipole polarizabilities of Cd and Ni atoms are 7.2 and 6.8×10^{-24} cm^3, respectively (Liu et al., 2006). Metal ions with low electronegativity, high polarizability and large ionic size are called "soft" ions (Sparks, 1995). These two acidic soils seem to show preference for the "softer" Cd^{2+} compared to the "less soft" Ni^{2+}. This sorption order is in line with that observed by Puls and Bohn (1988) and their explanation of metal sorption capacity based on the concept of conventional hard-soft acid-base (HSAB) principle.

In contrast to the observed affinities for the acidic soils discussed above, Webster soil with a neutral pH, exhibited higher affinity for Ni than Cd (see Fig. 2.2). Gomes et al. (2001) reported an adsorption sequence of Ni > Cd for two soils with pH higher than 6.0. They also reported that for acidic soils the adsorption of Cd was larger than Ni which is in agreement with our results illustrated in Fig 2. Increased metal sorption with increasing pH is attributed to changes in the hydrolysis state of ions in solution (Harter, 1983; Echeverría et al., 1998). Adsorption preference of Ni over Cd on a soil having pH of 6.89 was reported by Antoniadis and Tsadilas (2007). In their study, specific metal sorption (inner sphere complexion) for Ni was considered as the dominant adsorption reaction. The reaction of heavy metal cations with soil minerals were related to metal-ion hydrolysis. The *pK* values for metal hydrolysis: $Me^{2+} + H_2O = MeOH^+ + H^+$, are 10.08 and 9.86 for Cd^{2+} and Ni^{2+}, respectively (Gomes et al., 2001). The lower *pK* value for Ni is indicative of stronger specific sorption (Antoniadis and Tsadilas, 2007). If hydrolysis of metal ions, either in solution or at the soil surface, is a primary adsorption mechanism for metal ions on adsorbent, higher affinity for Ni is expected.

Sorption mechanisms of Ni reactions on minerals, at the molecular structure level, were investigated using XAFS and HRTEM techniques. Ni-Al layered double hydroxide (LDH) on pyrophyllite and kaolinite surfaces was considered as immobile form and responsible for Ni sorption for pH > 6.5 (Scheidegger et al., 1996, Eick et al., 2001). Based on soil column experiments where the pH was maintained at 7.5, Voegelin and Kretzschmarl (2005) reported that Ni LDH-type precipitates is a possible mechanism for Ni sorption. Such results are supportive of our findings of the observed strong affinity of Ni on Webster soil.

2.3.2 Competitive Adsorption

Results of competitive Ni sorption in the presence of a range of Cd concentrations are given in Fig. 2.3 for all three soils. Here the amount of Ni sorbed (*mmol* per kg soil) is presented versus input concentration of the competing Cd ion for two initial Ni concentration, 0.025 *mM* (Fig. 2.3 top) and 0.766 *mM* (Fig. 2.3 bottom). These results indicate that Ni sorption decreased as the competing Cd concentration increased. In Fig. 2.4, results are shown for Cd sorption in the presence of a range of Ni concentrations for all three soils. Here Cd adsorption decreased with increasing Ni concentrations. Moreover, the extent of the decrease in Ni or Cd sorption in our competitive systems was dissimilar among the three soils. For the two acidic soils (Windsor and Olivier), Ni adsorption decreased substantially with increasing Cd concentration in comparison to Webster, the neutral soil. This finding was consistent for both initial Ni concentrations (0.025 *mM* and 0.766 *mM*) (see Fig. 2.3). The amount of Ni sorbed in the presence of 0.766 *mM* Cd was reduced by 45%, 18% and 0.5% for Windsor, Olivier and Webster soil, respectively. When 0.766 *mM* Ni was present, sorbed Cd was reduced by 20%, 7.6% and 15% for Windsor, Olivier and Webster soil, respectively. These results illustrate the strong affinity of Ni in the neutral Webster soil where the effect of the competing Cd was least manifested compared to the two acid soils.

Metal ion competition is presented in the traditional manner as isotherms and is given in Figs. 2.5 and 2.6. These isotherms were described using the Freundlich model (Eq. [2.1]) in a similar manner to those for a single ion. The extent of nonlinearity of Ni and Cd isotherms are depicted by the dimensionless parameter n and was not influenced by input concentration of the competing ion. This was the case for Ni isotherms at different Cd concentrations (Fig. 2.5) and vise versa (Fig. 2.6). Specifically, in a competitive system, the parameter n did not exhibit appreciable changes for both metal ions investigated. In contrast, K values exhibited a decrease of sorption as the concentration of the competing ion increased (see Table 2.2). However, the extent of such a decrease was dissimilar for the three soils. For Windsor and Olivier, Ni adsorption decreased significantly over the entire range of concentrations of the competing ion (Cd). However, Cd adsorption was less affected by the competing Ni ions for both soils. For the neutral Webster soil, Ni was not appreciably affected by the presence of Cd, especially at low Ni concentrations. This may be due to the fact that, for a single component system, Ni adsorption was much stronger than Cd for Webster soil as discussed above. Another explanation of the competitive Ni sorption behavior is perhaps due to Ni-LDH precipitates which may be considered an irreversible form on soils and minerals (Voegelin and Kretzschmar, 2005). This process may lead to significant long-term stabilization of the metal within the soil profile (Ford et al., 1999). In acidic soils, Ni and Cd are both weakly bonded to soil particle surfaces and mainly forms out-sphere complexes, which are available for cation exchange. However, for the neutral Webster soil, Ni sorption may include a fraction of inner-sphere complexation or Ni-LDH precipitates, both of which are perhaps not available for competition via cation exchange.

2.3.3 The SRS Sorption Model

The Sheindorf-Rebhun-Sheintuch (SRS) equation was developed to describe competitive sorption where it was assumed that the single-component sorption follows the Freundlich equation (Sheindorf et al., 1981). The derivation of SRS equation is based on the assumption of an exponential distribution of adsorption energies for each component. A general form of the SRS equation can be written as

$$S_i = K_i C_i \left(\sum_{j=1}^{l} \alpha_{i,j} \ C_j \right)^{n_i - 1} \qquad [2.2]$$

where the subscripts *i* and *j* denote metal component *i* and *j*, *l* is the total number of components, and $\alpha_{i,j}$ is a dimensionless competition coefficient for the adsorption of component *i* in the presence of component *j*. The parameters K_i and n_i are the Freundlich parameters representing a single component system *i* as described in Eq [2.1] above. By definition, $\alpha_{i,j}$ equals 1 when $i = j$. If there is no competition, i.e., $\alpha_{i,j} = 0$ for all $j \neq i$, Eq [2.2] yields a single species Freundlich equation for component *i* identical to Eq [2.1]. Freundlich *K* and *n* given in Table 2.2 for Cd and Ni isotherms, where no competing ions were present, were utilized as input parameters in the SRS Eq [2.2]. Estimates for best-fit $\alpha_{i,j}$ using nonlinear least square optimization are given in Table 2.2.

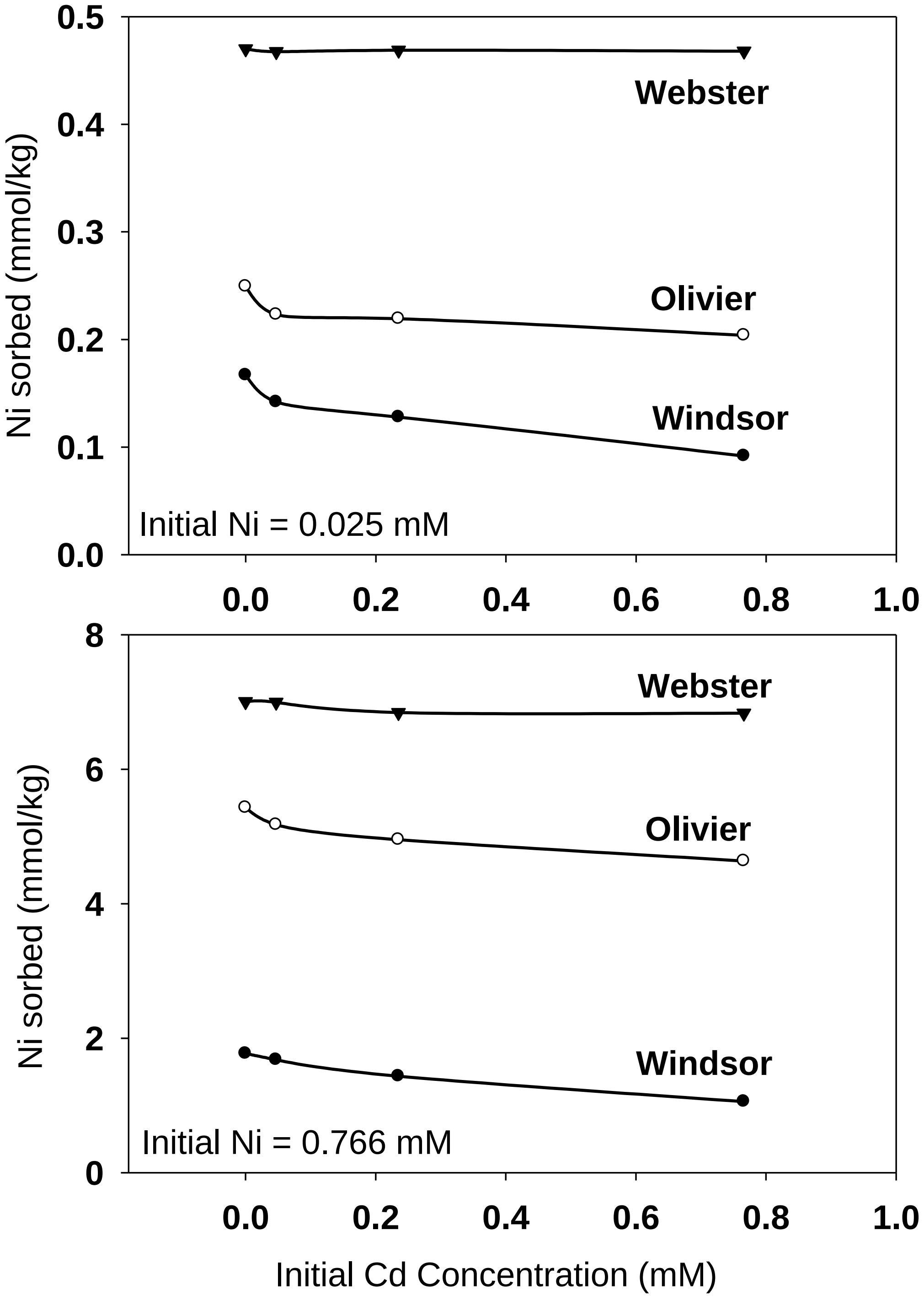

Figure 2.3. Competitive sorption of Ni in the presence of Cd for Windsor, Olivier and Webster soil. Initial Ni concentrations were 0.025 *mM* (top) and 0.766 *mM* (bottom).

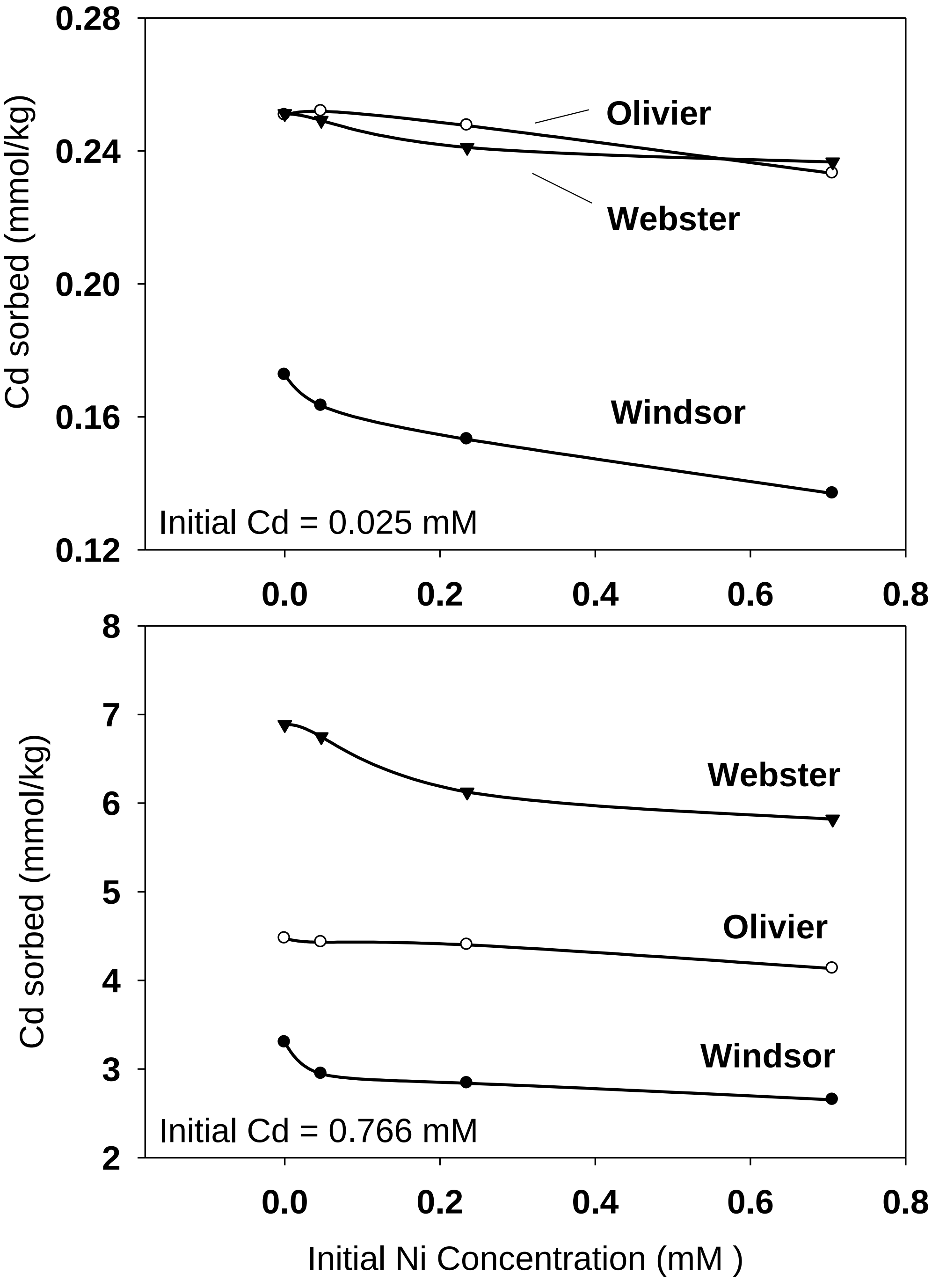

Figure 2.4. Competitive sorption of Cd in the presence of Ni for Windsor, Olivier and Webster soil. Initial Cd concentrations were 0.025 *mM* (top) and 0.766 *mM* (bottom).

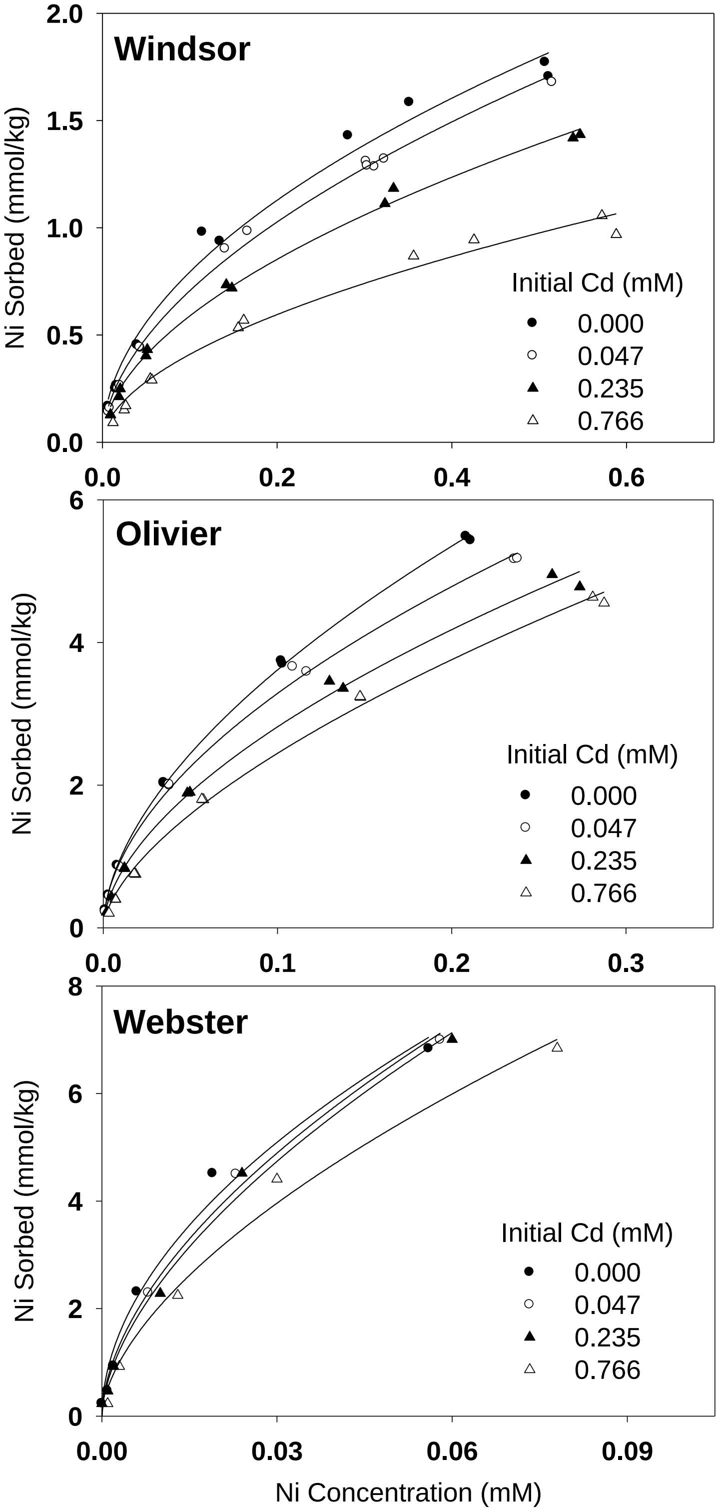

Figure 2.5. Competitive adsorption isotherms for Ni in the presence of different concentrations of Cd. Solid curves are Freundlich model calculations.

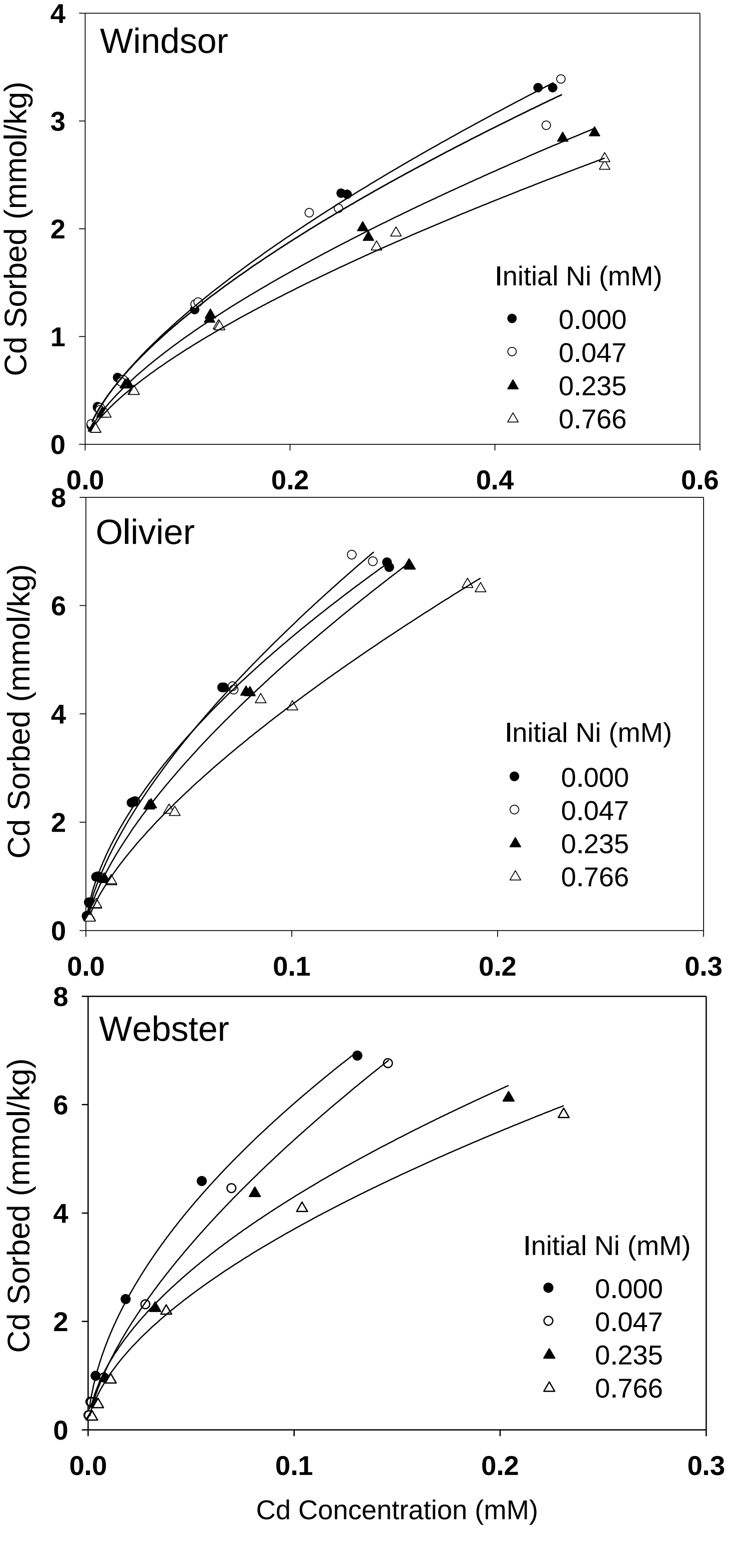

Figure 2.6. Competitive adsorption isotherms for Cd in the presence of different concentrations of Ni. Solid curves are Freundlich model calculations.

The estimated α_{Ni-Cd} for Ni adsorption, in the presence of Cd, were larger than 1 for Windsor and Olivier soils, indicating noticeable decrease of Ni in the presence of Cd. In contrast, α_{Ni-Cd} for Ni adsorption on Webster soil was less than 1, which is indicative of small influence of competing Cd ions (Table 2.2). These results are in agreement with the competitive sorption reported by Antoniadis and Tsadilas (2007). Such small α_{Ni-Cd} implies that Ni adsorption in Webster soil was least affected in a competitive Ni-Cd system in comparison to the other two soils. Moreover, the estimated α_{Cd-Ni} for Cd adsorption was 0.61 for Windsor and 0.82 for Olivier, whereas the competitive coefficient of Cd/Ni was 4.00 for Webster Soil. Although the SRS equation may be regarded as a multi-component model and does not imply certain reaction mechanisms, differences of competitive sorption between the neutral and the two acidic soils were illustrated based on the SRS models' competitive selectivity parameters. In fact, Roy et al. (1986) suggested that the SRS parameters could be used to describe the degree of the competition under specific experimental conditions. Calculated results using the estimated α_{Ni-Cd} are given in Figs. 2.7 and 2.8 and illustrate the capability of the SRS model in describing experimental data for competitive adsorption of Ni and Cd.

An F-test indicated that there was no statistical difference between our experimental results and SRS model calculations (at the 95% confidence level). Based on these calculations, the SRS model was capable of quantifying competitive adsorption for Ni and Cd. However, for both Ni and Cd, the SRS model deviated considerably from experimental data for high concentrations of the competing ions. This finding is consistent with the application of SRS made earlier by Gutierrez and Fuentes (1993) and illustrates the need for model improvement to better describe competitive adsorption of heavy metals over the entire range of concentrations.

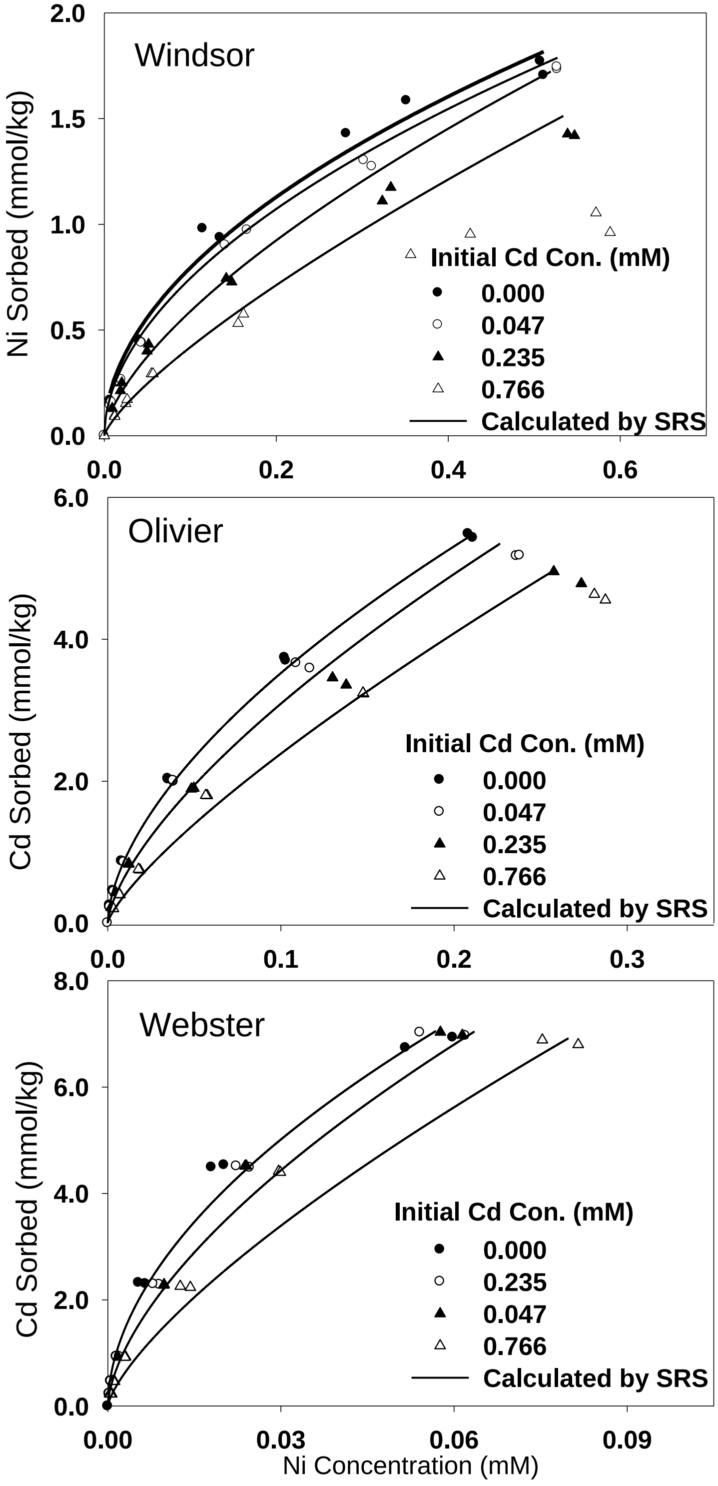

Figure 2.7. Competitive adsorption isotherms for Ni in the presence of different concentrations of Cd. Solid curves are SRS model calculations.

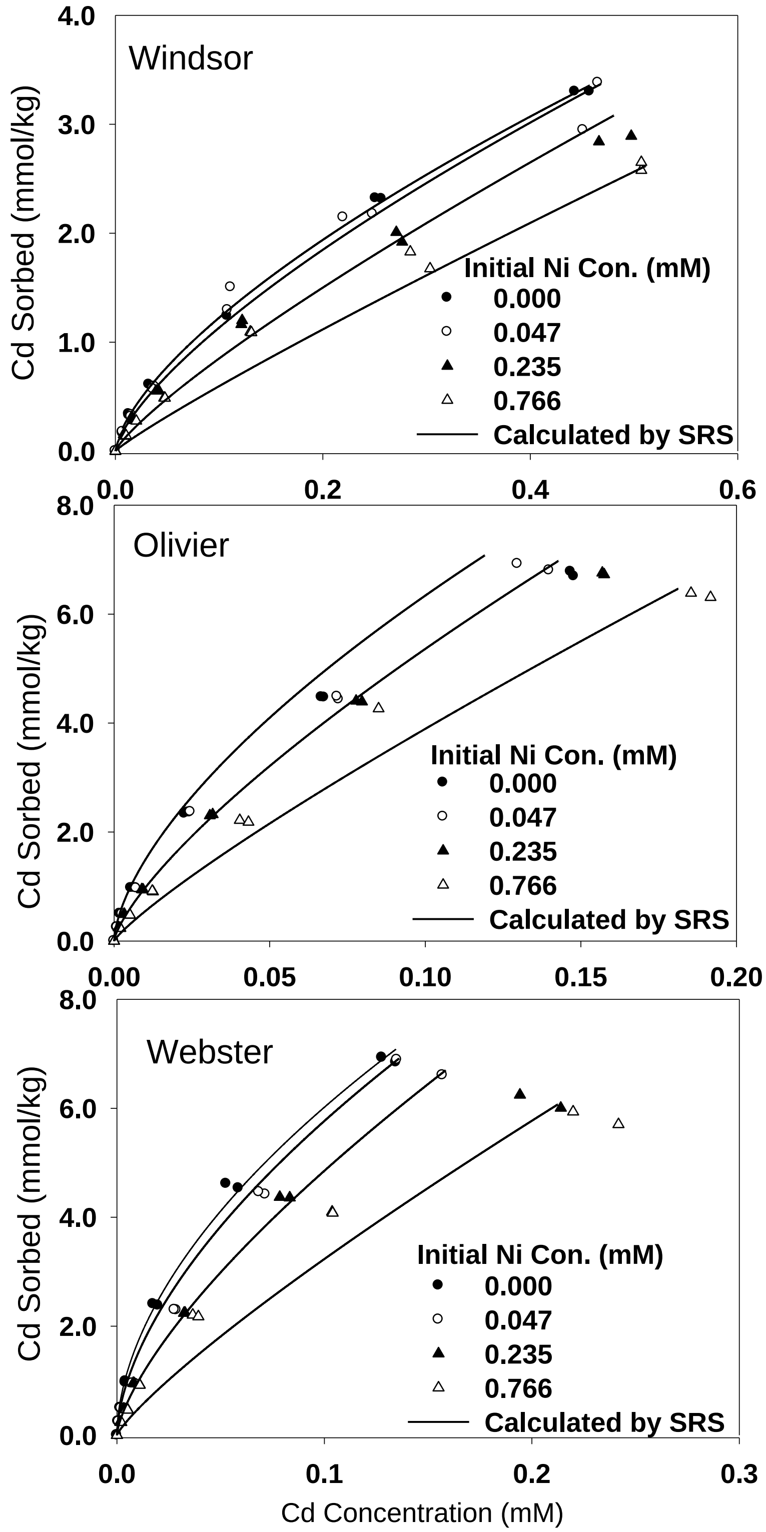

Figure 2.8. Competitive adsorption isotherms for Cd in the presence of different concentrations of Ni. Solid curves are SRS model calculations.

2.4 Conclusions

Isotherms measured by batch equilibriation methods for Ni and Cd sorption exhibited strong nonlinear behavior for all soils. Cd adsorption by the two acidic soils was greater than Ni, whereas for the neutral soil, Ni sorption was greater than Cd. The Freundlich parameter *K* decreased with increasing concentration of the competing ion whereas the parameter *n* was not affected by the presence of competing ions. The multi-component SRS model predicted competitive Ni-Cd sorption for Webster, Olivier and Windsor soils where parameters obtained from Freundlich modeling of single component for each heavy metal were used. This competitive SRS model provided less than adequate predictions for the highest competing concentrations. A major implication of this study is that changes in chemical composition of solutions in aquifer and vadose zones resulting in competition of heavy metal ions results in decreased sorption of individual metals. Decreased sorption enhances heavy metal mobility and potential contamination of surface and groundwater.

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CHAPTER 3: REACTIVITY OF NICKEL IN SOILS: EVIDENCE OF RETENTION KINETICS

3.1 Introduction

Nickel (Ni) is a nutritionally essential trace metal for at least several animal species, micro-organisms and plants, however toxicity symptoms can occur when too much Ni is taken up (McIlveen and Negusanti, 1994; Voegelin and Kretzschmar, 2005; Cempel and Nikel, 2006). Due to metal processing operations, combustion of coal and oil, application of sludge and certain phosphate fertilizers (Kabata-pendias and Pendias, 1992), Ni total concentration accumulated to > 50 mmol (McIlveen and Negusanti, 1994) in soils, which causes significant threats to soil and water environment and ecosystem system. The accumulation of nickel in the human body through chronic exposure can lead to lung fibrosis, cardiovascular and kidney diseases (Denkhaus and Salnikow, 2002). The +2 oxidation state is the most prevalent form of Ni in bio-systems, the availability of which is highly dependent on the mechanisms associated with Ni retention reaction and its kinetics in soils (McIlveen and Negusanti, 1994). Such information on reaction mechanisms is needed for the prediction of Ni mobility, potential bioavailability as well as environmental risk in the soils.

A few studies have suggested that Ni be considered as weakly sorbed heavy metal when compared to others such as Pb, Cu and Mg (Tiller et. al, 1984; Atanassova, 1999). Specifically, Ni was observed to have low affinity in acidic soils and was thus considered mobile and susceptible to transport in soils. Under neutral to alkaline conditions, Ni was found to form multinuclear complexes on several mineral phases including pyrophyllite (Scheidegger et al., 1996), montomorillite and gibbsite (Scheidegger et al, 1998), illite (Elzinga and Sparks, 2001, and kaonilite (Eric et al., 2001) using extended X-ray fine structure (EXAFS) spectroscopy.

However, due to the heterogeneous sorbents possess a broad array of sorption sites, each processing a unique spectroscopic signature (Roberts et al., 1999), fewer studies were carried out on clay size isolates (Businelli et al., 2004; Roberts et al., 1999) and soil (Voegelin and Kretzschmar, 2005). Ni-Al layered double hydroxide (LDH) was considered responsible for Ni sorption at pH above 6.5 (Scheidegger et al., 1996; Eick et al., 2001). The formation of surface-induced precipitates may play an important role in the immobilization of Ni in non-acidic soils due to the high stability of Ni-Al LDH.

Several studies indicated that Ni sorption by natural solids is time dependent ranging from a few days to several months for quasi equilibrium to be attained (Scheidegger et al., 1998; Roberts et al., 1999; Eick et al., 2001). A number of sorption mechanisms have been advanced to account for Ni kinetic behavior including heterogeneity of sorption sites. Elzinga and Sparks (1999) suggested that, for montmorillonite, adsorption was the likely mechanism responsible for the initial rapid Ni sorption. Whereas the mechanism controlling slow Ni sorption was likely surface precipitation on pyrophyllite as evidenced from EXAFS results. Over longer reaction times (time scales of days), surface precipitation is expected to occur on both phyrophyllite and montmorillonite. Other researchers also found kinetic behavior of Ni sorption with minerals such as kaolinite and goethite (Scheidegger et al., 1998; Barrow et al., 1989; Eick et al., 2001).

Information on the sorption rate of Ni on soils is limited and most of the studies focused on equilibrium conditions (Atanassova, 1999; Antoniadis and Tsadilas, 2007; Barrow et al., 1989; Papini et al., 2004; Mellis et al., 2004; Echeverría et al., 1998). However, the utility of results from short duration studies for predictions of the fate and transport of Ni is often limited because equilibrium conditions are rarely achieved in 24 h. Fewer studies have investigated release or desorption of Ni from minerals and soils (Atanassova, 1999, Scheckel and Sparks, 2001, Barrow et al., 1989, Vega et al., 2006). Antnassova (1999) reported that most of the Ni sorbed by a Netherland's soil in 24 equilibrium batch experiments could be released by excess of calcium and only a small proportion of Ni was specifically sorbed. Whereas Vega et al. (2006) reported that no significant amount of the heavy metal (Pb, Zn, Cu and Ni) was desorbed from mine soils. The results from the correlation of soil components with retention of heavy metal indicated that mine soils with higher organic matter and Fe/Al oxides have less Ni desorbed. They reported that desorption or release of heavy metal are highly dependent on sorption capacities of the soils used. Scheckel and Sparks (2001) found that Ni precipitated as Ni/Al layered double hydroxide (LDH) or α-$Ni(OH)_2$ on a mineral phase, and that the stability of Ni/Al LDH or α-$Ni(OH)_2$ increased with as residence time increased form 1 h to 2 yr; the amount of Ni released by EDTA or HNO_3 from the Ni precipitates decreased from 98% to 0%.

In this present study, two acidic soils (Olivier loam, Windsor sand) and one non-acidic soil (Webster loam) were used. The objective was to quantify Ni kinetic retention and release for soils having different properties. Moreover, the predictive capability of the MRM model for describing the kinetic sorption of Ni was examined.

3.2 Materials and Methods

3.2.1 Soils

Three surface soils having different properties were used in this study (Table 3.1). Olivier loam is a common alluvium soil in Louisiana; Webster loam formed in glacial till or local alluvium derived from till on uplands and was sampled from Story County, Iowa. Windsor loam is a fine sandy loam soil formed on glacial outwash plains collected near Lebanon, New Hampshire. All soil samples were air dried and passed through 2 mm sieves for analysis. Soil physical and chemical properties of Windsor and Olivier were determined earlier in our laboratory (Liao and Selim, 2009) and listed in Table 3.1.

3.2.2 Adsorption and Desorption:

Kinetic retention using the batch method described by Amacher et al. (1988) was used to quantify adsorption and desorption isotherms for nickel by the three soils at constant room temperature of 25 °C. Triplicate 3-g samples of each soil were place in Teflon centrifuge tubes and mixed with 30-mL solution of 5 initial Ni concentrations, which were 0.023, 0.093, 0.234, 0.465 and 0.746 m*M* $Ni(NO_3)_2$ prepared in 0.005 M $Ca(NO_3)_2$ background solution. The mixtures were continuously shaken on a reciprocal shaker and then centrifuged at 5000 ×g for 10 minutes prior to sampling. After 2, 6, 12, 24, 72, 168, 336 and 504 hours of reaction time (for Windsor and Olivier and extended to 672 h for Webster), a 1-mL aliquot was taken and analyzed using ICP-AES (Spectro Citros CCD). Amounts of Ni sorbed by the soil matrix were determined by the difference between the concentrations of the supernatant and that of the initial solutions.

The mixtures were reweighed, vortex mixed, and returned to the shaker. Desorption or release experiments were conducted to assess the release of nickel as well as the extent of hysteresis behavior by the different soils. Sequential or successive dilutions were initiated immediately after the last adsorption step for all initial concentrations. Each desorption step was carried out by replacing the supernatant, followed by adding 30 mL of 0.005 *M* $Ca(NO_3)_2$ background solution and shaking for 48 h. Six desorption steps were carried out. The fraction of nickel desorbed from each soil was calculated based on the change in concentration in solution (before and after desorption). The pH of the mixed solutions was measured after each reaction time using a standard Multi-pH/millivolt meter. The amount of nickel released/desorbed was calculated from the difference between concentrations of the supernatant and that of the amount initially sorbed at each desorption step.

Table 3.1 Selected physical and chemical properties of the soils studied.

Soil		Olivier Loam	Webster Loam	Windsor Sand
Taxonomic classification		fine-silty, mixed, thermic Aquic Fragiudalf	Fine-loamy, missed, mesic Typic Haplaquoll	Mixed, mesic Typic Udipsamment
pH		5.80	6.92	6.11
TOC[a]	%	0.83	4.02	2.03
CEC[b]	cmol kg^{-1}	8.6	27.0	2.0
Sand[c]	%	5	39	77
Silt	%	89	39	20
Clay	%	6	22	3
Selective extraction by				
Ammonium oxalate (pH 3.0)				
Fe	g kg^{-1}	0.32	0.98	0.36
Al	g kg^{-1}	0.08	0.89	0.69
Citrate-bicarbonate-dithionite (CBD)				
Fe	g kg^{-1}	4.09	4.42	3.68
Al	g kg^{-1}	1.29	0.77	3.65

[a] TOC = total organic carbon. [b] CEC = cation exchange capacity. [c] Grain size distribution: sand (2.00-0.05 mm), silt (0.05-0.002 mm), and clay (<0.002 mm).

3.2.3 Sequential Extraction

The biological and physicochemical availability, mobilization and transport of nickel in soil depend on its complexation and/or bonding strength when reacting with soils, which can be extracted selectively by using an appropriate sequential extraction method. A sequential extraction procedure (Tessler et al., 1979) was conducted here to investigate the amount of nickel retained at various binding phases on different soils following the last desorption step. Five fractions were quantified: exchangeable, bound to carbonates, bound to Fe-Mn oxide, bound to organic matter, and residual. Those fractions were extracted by $CaCl_2$ (pH 7.0), NaOAc/HOAc (pH 5.0), $NH_2OH \cdot HCl$ in 25% HOAc (pH~2), H_2O_2/HNO_3 (pH~2) and subsequently NH_4OAc, and HNO_3 in hot water bath respectively. Following each extraction, the samples were centrifuged at 5000 g for 10 min and the Ni concentrations in supernatant were analyzed using ICP-AES (Spectro Citros CCD). The samples were then washed with deionized water prior to the next extraction step.

3.3 Multi-reaction Model (MRM)

For heavy metal sorption, retention-release reactions in solid phases have been observed to be strongly time-dependent (Businelli et al., 2004; Scheidegger et al., 1996; Eick et al., 2001). The model approaches based on soil heterogeneity and kinetics of adsorption-desorption have been proposed for the purpose of describing the time-dependent sorption of heavy metals in soil environment (Zhang and Selim, 2007). This multipurpose model assumes that heavy metals in the soil environment are retained by different sites having different affinities for trace elements. It assumes that a heavy metal such as Ni is present in soil solution (C) and in several phases representing heavy metal retained by the soil as depicted in the schematics of Figure 3.1. Retention-release processes are governed by concurrent and consecutive type reactions. The governing equilibrium reaction mechanism is that of the Freundlich equation,

$$S_e = k_e\left(\frac{\theta}{\rho}\right)C^n \qquad (3.1)$$

where S_e is the amount retained on equilibrium-type sites (mM/kg) and has a low binding energy. The coefficient K_e is an equilibrium constant (dimensionless) associated with instantaneous reactions. θ is the soil water content (cm^3/cm^3), and ρ is the soil bulk density (g/cm^3).

The heavy metal present in the soil solution phase is assumed to react kinetically (time dependent) and reversibly and consecutively irreversibly. The kinetic reaction between C and S_k may be represented by

$$\frac{\partial S_k}{\partial t} = k_1\left(\frac{\theta}{\rho}\right)C^n - [k_2 + k_3]S_k \qquad (3.2)$$

$$\frac{\partial S_s}{\partial t} = k_3 S_k \qquad (3.3)$$

where k_1 and k_2 (h^{-1}) are the forward and backward reaction rate coefficients associated with the kinetic-type sites, respectively. The parameter k_3 (h^{-1}) is the irreversible rate coefficient associated with the kinetic sites. S_k is the amount retained on kinetic-type sites (m*M*/kg) through strong interactions with the soil matrix, and S_s represents the amount retained by the consecutive irreversible sites (m*M*/kg).

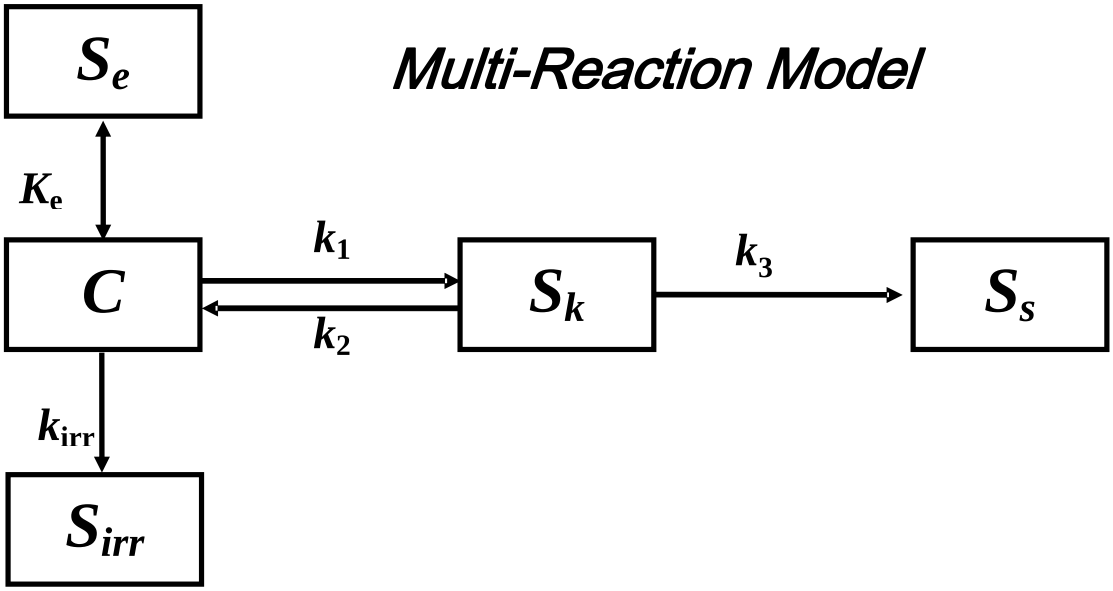

Figure 3.1. A schematic diagram of the multireaction model (MRTM). Here *C* is concentration in solution, S_e, S_k, S_s and S_{irr} are the amounts sorbed on equilibrium, kinetic, consecutive and concurrent irreversible sites, respectively, where K_e, k_1, k_2, k_3 and k_{irr} are the respective rates of reactions.

The parameter n is the reaction order (dimensionless) associated with S_e and S_k. The irreversible reaction between C and S_{irr} is represented by

$$\rho \frac{\partial S_{irr}}{\partial t} = k_{irr} \theta C \qquad (3.4)$$

where K_{irr} is the rate coefficient for the irreversible retention reaction. Thus, S_{irr} represents an irreversible sink term. And the total amount retained S is now defined as:

$$S = S_e + S_k + S_s + S_{irr} \qquad (3.5)$$

Kinetic batch data were fitted to the MRM described above using nonlinear least square optimization method.

3.4 Results and Discussion

3.4.1 Adsorption Isotherms

Adsorption isotherms which depict the distribution between aqueous and sorbed phases for Ni are presented in Fig. 3.2 for three soils. The effect of time of reaction on the extent is clearly depicted in all figures and indicates an increased Ni retention vs time for all three soils. The set of sorption isotherms shown exhibited strong nonlinear Ni retention behavior for all soils and also indicate that nonlinear in nature. This nonlinear sorption behavior for Ni was described using the Freundlich equation,

$$S = K_f C^N \qquad (3.6)$$

where *S* represents the (total) amount sorbed on solid phase (*m*mol kg^{-1}), C is the concentration in the liquid phase (*m*M), K_f is the partitioning coefficient (L kg^{-1}), and *N* is a dimensionless reaction order commonly less than one (Buchter et al. 1989). The exponent N in the Freundlich model represents the energy distribution of the heterogeneity of sorption-site, where the highest energy sites are preferentially sorbed at low concentrations, and as the concentration increases, successively lower energy sites become occupied (Sheindorf et al., 1981). Estimates for the Freundlich parameters *N* and K_f are presented in Table 3.2 for selected reaction times.

The family of isotherms of Figure 3.2 clearly exhibit that Ni sorption increased with increasing reaction time for all soils. As a result the K_f parameters increased with reaction time for each soil as (see Table 3.2).

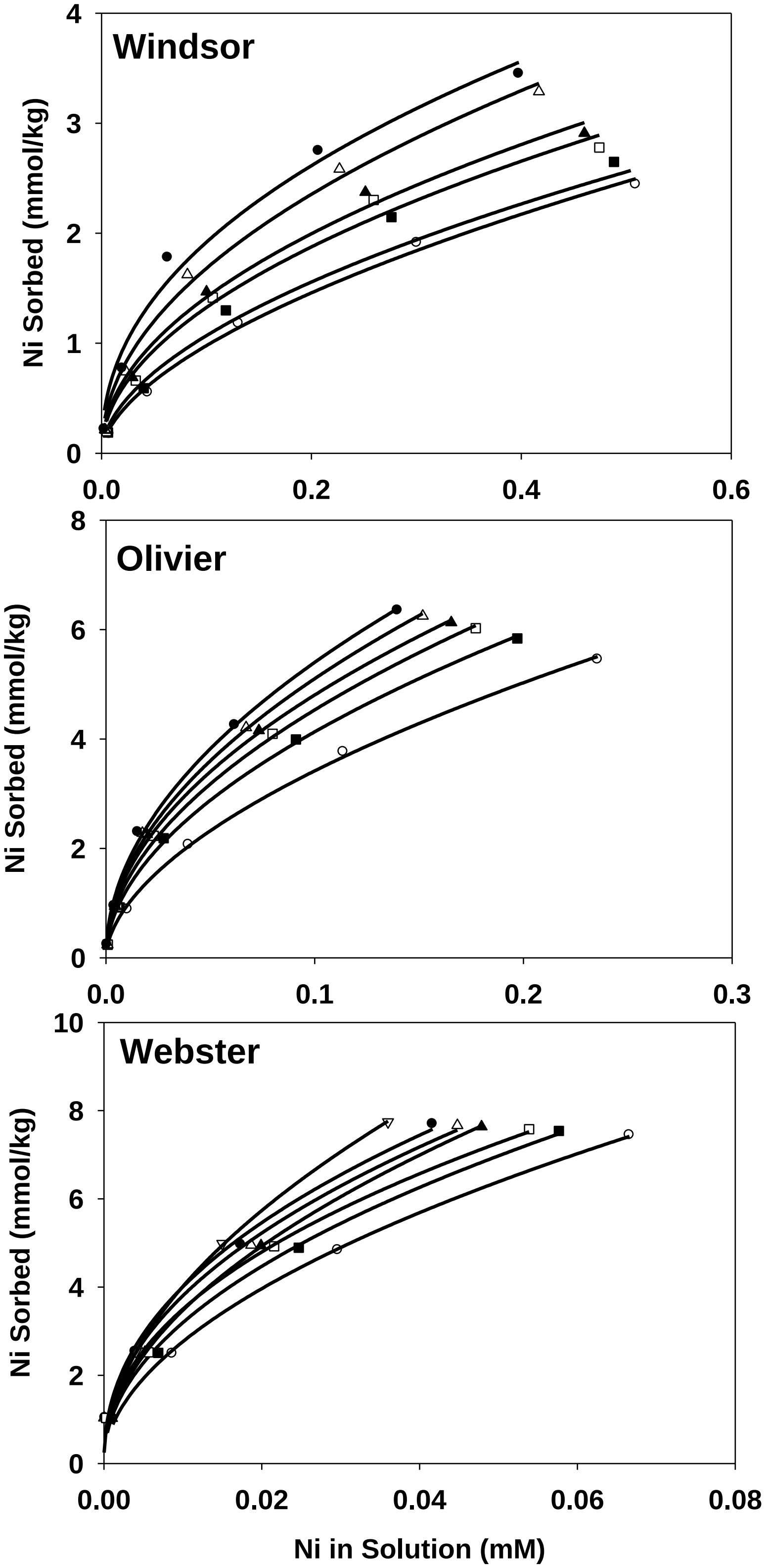

Figure 3.2. Adsorption isotherms of Ni by three soils at different reaction time. Symbols are for different reaction time of 2, 24, 72, 168, 336 and 504 h for Windsor and Olivier, of 2, 24, 72, 168, 336, 504 and 672 h for Webster.

Table 3.2. Estimated Freundlich parameters with stand errors for Nickel adsorption and desorption at different reaction times for three soils.

	Windsor			Olivier			Webster		
Time (h)	K_f (L kg^{-1})	N	R^2	K_f (L kg^{-1})	N	R^2	K_f (L kg^{-1})	N	R^2
2	3.680±0.153	0.575±0.033	0.998	12.332±0.458	0.558±0.019	0.999	28.338±3.897	0.454±0.039	0.999
8	3.654±0.126	0.556±0.027	0.998	12.740±0.347	0.542±0.013	0.999	29.879±4.036	0.486±0.040	0.997
12	3.724±0.204	0.542±0.042	0.996	13.301±0.489	0.540±0.018	0.999	30.083±3.684	0.462±0.063	0.997
24	4.068±0.271	0.556±0.027	0.994	13.716±0.532	0.521±0.018	0.999	30.404±1.761	0.501±0.018	0.999
72	4.203±0.299	0.501±0.050	0.996	14.753±0.738	0.513±0.022	0.999	31.385±3.513	0.447±0.047	0.986
168	4.405±0.263	0.492±0.041	0.996	15.131±0.757	0.498±0.021	0.998	31.388±3.212	0.458±0.088	0.995
336	5.146±0.273	0.486±0.034	0.997	16.246±1.036	0.503±0.026	0.998	35.509±1.021	0.505±0.008	0.999
504	5.363±0.452	0.477±0.050	0.992	17.053±1.114	0.499±0.026	0.997	42.998±1.100	0.515±0.007	0.993

For example, for Webster soil, the K_f value increased from 28.34 Kg L^{-1} for 2 h of reaction time to 43.00 Kg L^{-1} for 504 h. In contrast, the parameters N varied in a narrow range with time of reaction. Specifically, little change in N values was observed for times greater than 24 h, for all three soils (see Table 3.2). Lack of time dependency of the Freundlich parameter N has been observed for other heavy metals such as As (Zhang and Selim, 2006) and Cu (Selim and Ma, 2001). Average N values were 0.522, 0.521 and 0.479 for Windsor, Olivier and Webster, respectively. N is an indicative of the extent of heterogeneity of sorption sites impliying that Ni mobility tends to increase as Ni concentration increases. These estimated N values were subsequently utilized with the multireaction model to assess Ni adsorption kinetic for all three soils.

3.4.2 Sorption Kinetics

The time dependence of Ni sorption and release for all concentration is illustrated in Fig 3.3. For any soil, the rate of Ni sorbed compared to that applied decreased with the input concentration increase. This result is in line with the N value concept of the Freundlich equation (mentioned above), indicating the nature of Ni sorption by soils. Initial sorption was rapid for any input concentration. However, the rate of sorption varied for different soils. At the highest input concentration, 31% of initial Ni was sorbed in 2 hours, and this value increased to 46%

after reaction of 504 h for Windsor soil. Although this is a large relative increase, the total amount sorbed is small as compared to sorption for Olivier. For Olivier, the Ni sorption proceeded quite rapidly initially with 67% of the initial Ni sorbed in 2 h, followed by a more gradual sorption period in which 80% of the initial Ni was sorbed within 504 h. The kinetics for Webster were characterized by an extremely rapid initial step with nearly 91% of Ni sorbed in 2 hours, followed by a much slower sorption region where about 95% of the Ni was sorbed from the solution after reaction of 672 h. Such two-stage reaction is characteristic of sorption of several heavy metals on clays, oxide surfaces and soils as suggested by Eric et al. (2001), Voegelin et al. (2001), Jeon et al. (2003), Bruemmer et al. (1988) and Scheidegger et al. (1998). Although the sorption of divalent metal ions onto oxides has been reported to be completed within few seconds (Voegelin et al., 2001), slow kinetics have also been observed where sorption continued for several days or months (Strawn and Sparks, 1999; Eric et al., 2001; Jeon et al., 2003). Several mechanisms are suggested to contribute to the kinetics of heavy metal sorption on soils including (1) slow diffusion through intra-particle micropores (Strawn and Sparks, 1999); (2) heterogeneity of sorption sites ; sites having different affinities; (3) slow sorption due to the increase in surface charge upon the inner-sphere complexation of such ions (Jeon et al., 2003); (4) at neutral or basic condition, slow formation of new solid phases such as hydroxides or layered double hydroxides may cause kinetic effects and immobilization of nickel (Voegelin et al., 2001; Eric et al., 2001; Scheidegger et al., 1998; Businelli et al., 2004).

Among the various sorption mechanisms mentioned above, the formation of surface-induced precipitates perhaps plays a significant role in the Ni sorption in neutral non-acidic soils. For acidic soils, cation exchange seems to be the major mechanism for Ni sorption (Gomes et al., 2001; Echeverría, 1998; Papini et al., 2004).

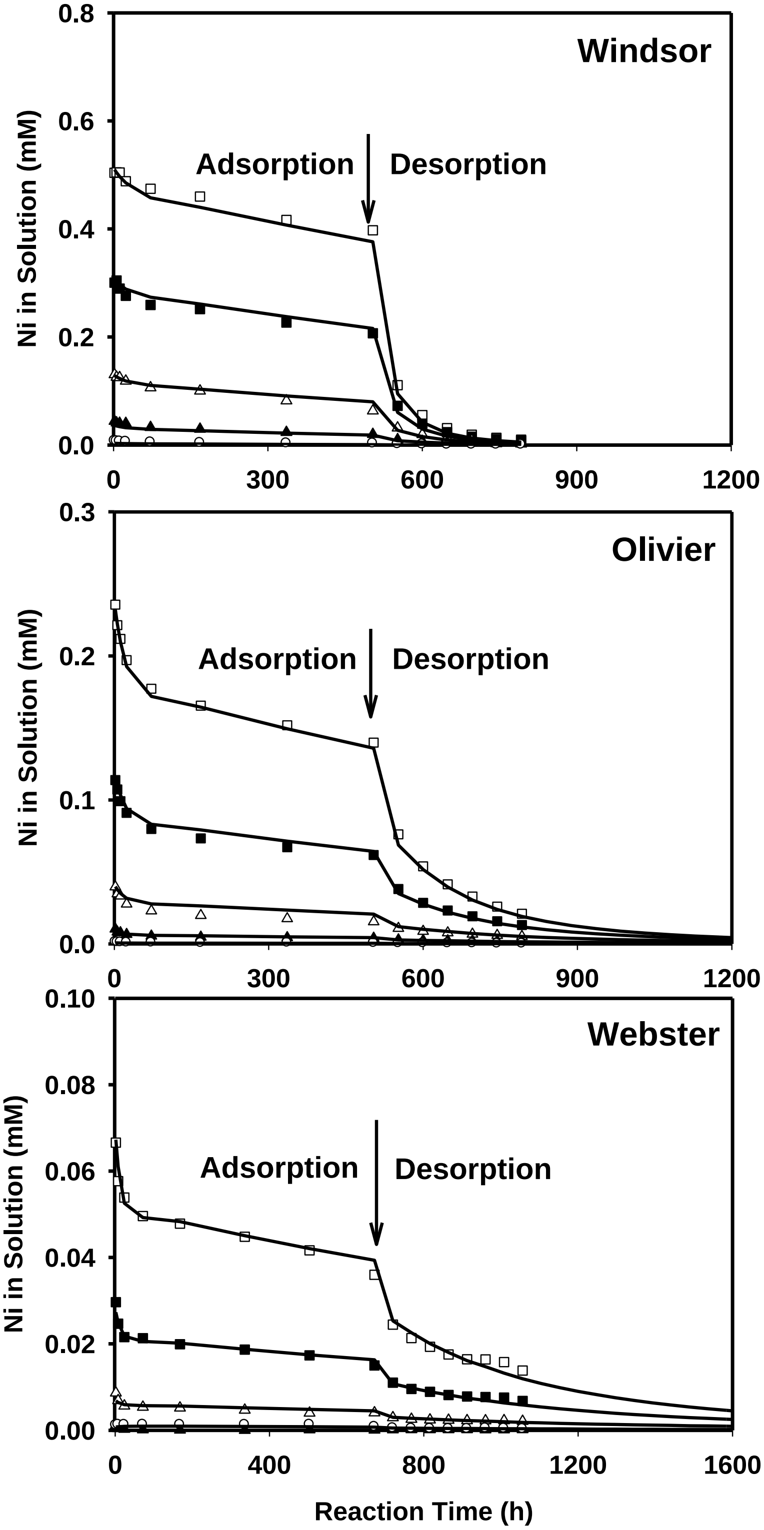

Figure 3.3. Nickel concentration in solution versus reaction time for three soils. Symbols are for different initial concentrations from bottom to top of 0.023, 0.093, 0.234, 0.465 and 0.746 m*M* respectively. Solid lines are MRM simulations by utilizing parameters optimized from experimental adsorption data sets listed in Table 3.3.

As the pH increases, Ni sorption was related to hydrolysis of divalent ions capable of forming inner-sphere complexes with clay lattice edges (Antoniadis and Tsadilas, 2007). Schulthess and Huang (1990) showed that Ni adsorption by clays was strongly influenced by pH as well as silicon and aluminum oxide surface ratios. Moreover, based on XAFS and HRTEM techniques, Ni-Al layered double hydroxide (LDH) was considered responsible for Ni sorption at pH above 6.5 on pyrophyllite and kaolinite surfaces (Scheidegger et al., 1996; Eick et al., 2001). This is also the evidence for such LDH in soils at pH 7.5 (Businelli et al., 2004; Voegelin et al., 2005; Roberts et al., 1999). These investigators suggested that at high pH increased Ni sorption was due to precipitates on mineral surfaces which were characterized as a time-dependent mechanism. Our results (Figs. 3.3 and 3.4) show that Ni sorption in the neutral Webster soil was significantly higher than the other two (acidic) soils.

3.4.3 Desorption Hysteresis and Release

Results of Ni concentration versus time during desorption, following adsorption, are shown in Fig. 3.3. Desorption results are also presented as isotherms in the traditional manner in Fig. 3.4. The family of desorption isotherms shown in Fig. 3.4 represent the amount of Ni sorbed during desorption for various initial (input) Ni concentrations and clearly indicated extensive hysteresis. Such hysteretic effect as depicted by the deviation of the adsorption isotherm from the desorption isotherms was highest for Webster soil and lowest for Windsor. Lack of equilibrium as well as irreversible sorption are perhaps responsible for the observed hysteresis of the desorption isotherms (Strawn and Sparks, 1999). This was not surprising in view of the kinetic retention behavior of Ni sorption on soils and various minerals (Scheidegger et al., 1998; Eric et al., 2001; Voegelin et al., 2005). Observed Ni release behavior at early stages of desorption was likely due to desorption of chemisorbed Ni from three soils. The slow release of Ni was probably due to dissolution of inner-sphere complexes. For Webster soil with neutral pH, nuclear precipitation on the mineral phase may be another mechanism responsible for the limited desorption or partially reversible as described by Scheidegger et al. (1998) and Eric et al., (2001). We should also emphasize that the amount of Ni desorbed as a percentage of the amount total sorbed varied among our soils, which were 24-63%, 7-38% and 1-16% for Windsor, Olivier and Webster soil, respectively (see Fig. 3.3). Such low desorption rates, especially for Webster soil, was perhaps due to the reasons just mentioned. Moreover, release curves (Fig. 3.3 and 3.4) demonstrate that at low Ni surface coverage, only small portion of Ni was desorbed, indicating high sorption affinity of Ni by the soil matrix. In contrast, at high Ni input concentrations, the percentage of desorption for all soils increased, indicating lower Ni affinity.

After the last step of the desorption process, the soils with the highest three initial concentrations were then sequentially extracted, for the five fractions: exchangeable, carbonate, Fe/Al, organic matter and residual, as illustrated in Fig. 3.5. The exchangeable fraction were the sum from the amount of six step desorption and that extracted by $Mg(NO_3)_2$. The amount of each Ni fraction is shown as the percentages of the sum of Ni from the five extractions, compared with the total Ni sorbed on soil. Ni recovery was 93%-102%, which was an acceptable accuracy of this sequential extraction. Generally, sequential extraction methods can provide an insight into the understanding of the chemical binding of Ni in soil (Tessier et al., 1979).

The exchangeable fraction was considered as weakly sorbed and nonspecific, which sorption on the latter four fractions is of high binding strength and considered as specific. Metal cations were spontaneously sorbed on exchangeable were completed in 1 min and equilibrium was obtained within 30 min, but the sorption on specific fraction required a much longer to reach equilibrium (Tsang and Lo, 2006).

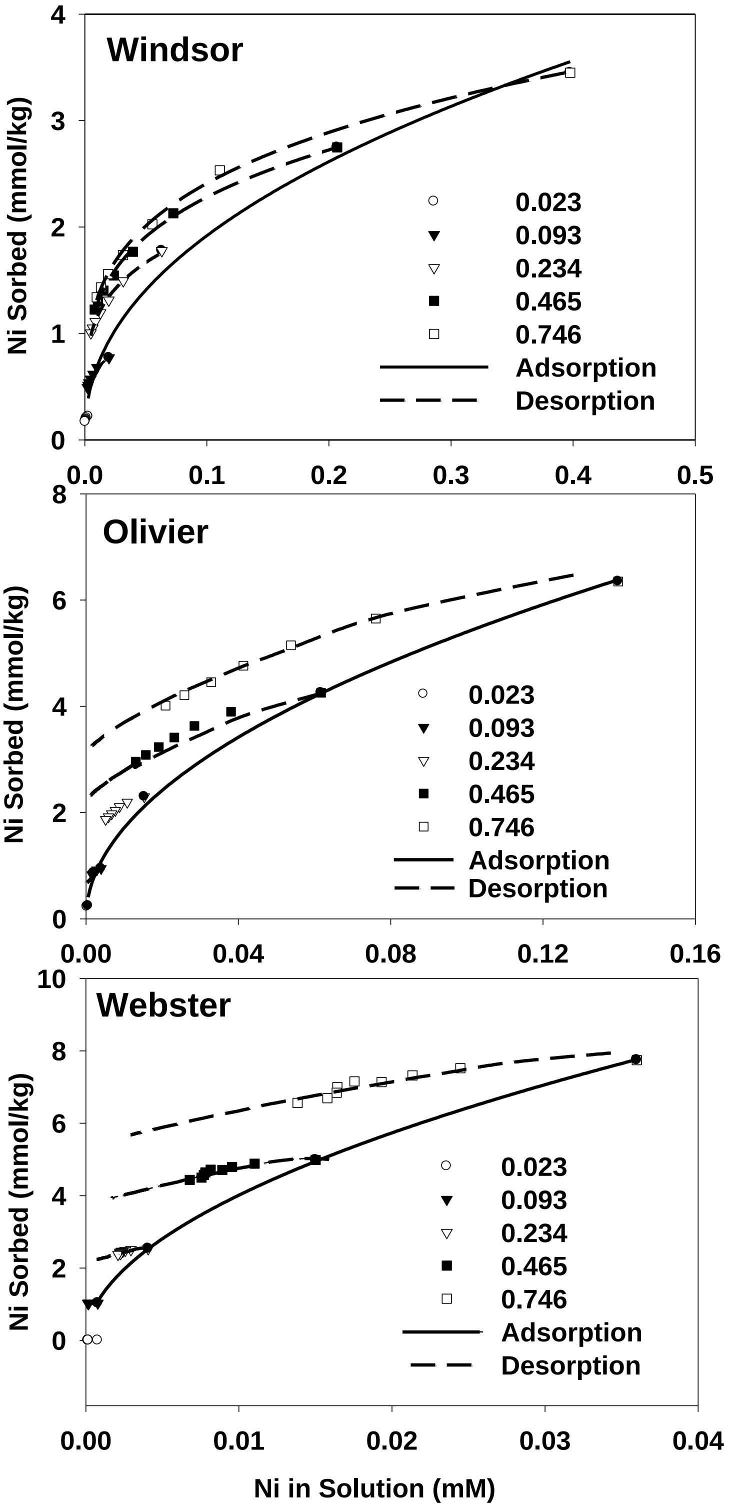

Figure 3.4. Traditional desorption isotherms of nickel by three soils. The solid curve is the adsorption isotherms of 504 h. Symbols are for different initial concentrations from bottom to top of 0.023, 0.093, 0.234, 0.465 and 0.746 m*M* respectively. The dash lines are MRM simulations by utilizing parameters optimized from experimental adsorption data sets listed in Table 3.3.

For all three soils, Ni bounded with Fe/Al and organic matter fractions were from 19 to 60%, explaining the observed kinetics of Ni on all soils. Singh et al. (1992) found that major proportions of the Ni in the soils were concentrated with the iron oxides, and the dissolution kinetics of these elements indicate that some may be present in the structure of the iron oxides, which is partially irreversible or slow reversible. This provided evidence that iron oxides may be responsible for the observed hysteretic or partially reversible Ni for all soils.

For Webster soil, there were highly irreversible fractions (carbonate and Fe/Al) for all initial concentrations, which were expected since Webster soil is a fine loamy Haplaquoll with 3.7% $CaCO_3$. Businelli et al. (2004) found that calcium carbonate contributes to Ni retention through the formation of a strong complex via co-precipitation that involves Ni/Ca carbonate double salt or mixed Ni/Al hydroxides and carbonates formation. Ni/Al layered double hydroxide was observed at pH 6.5 or higher (Scheidegger et al., 1998) and increased with time. Moroever, Ni/Al layered double hydroxides are highly stable and irreversible; even resistant to dissolution in dilute HNO_3 (Scheckel and Sparks, 2001).

3.4.4 Multireaction Model

The estimated parameters K_f and N listed in Table 3.2 indicated that Ni sorption and desorption on three soils are strongly time-dependent and heterogeneous in nature. Such behavior was described by the multireaction model (MRM) in this study. Estimated parameters and their goodness-of-fit for different MRM model formulations are given in Table 3.3 and Table 3.4. Generally, the time dependent behavior and heterogeneity of Ni sorption and desorption by soils were well described by our MRM as illustrated by low RMSE and high r^2 close to 1. In most models (e. g., simple linear, Freundlich, Langmuir, dual domain reactivity models, and treble domain reactivity models), two distinct sets of parameter are obtained, one for adsorption and one for desorption. On the other hand, the MRM accounts for the kinetic sorption as well as desorption of heavy metals or other chemicals by soils in one model (Selim and Zhu, 2005). We choose a three-phase model variation with reversible and irreversible phase to test the model's capability to predict desorption results on the basis of model parameters obtained from adsorption data (Table 3.3) on the three soils. There was no significant difference between the kinetic parameters calculated from ADS and BOTH data sets (Table 3.3), indicating that the adsorption and desorption processes can be described on the basis of parameters from either data set. Specifically, we used the MRM in a descriptive or simulation mode where the necessary parameters were based on adsorption data only. In other words, we utilized adsorption parameters (ADS) to predict desorption or release data, the model calculations shown in Figures 3.3 and 3.4. The desorption or release of Ni from the three soils was well described by the adsorption data simulation using the MRM. Since adsorption rather than desorption data sets are commonly available, it is significant to point out that simulations on release or desorption can be obtained relying on parameters based on adsorption data alone.

We further tested several variations of MRM for each soil. Based on RMSE and r^2, the three-phase model, that is, equilibrium, kinetic and irreversible sorption phases, provided best overall predictions with lowest RMSE to describe the time dependent Ni sorption by all soils.

Table 3.3 Fitted three-phase reversible and irreversible MRM parameters (with standard error) for adsorption and desorption kinetics of Ni on soils.

Soil	Data set[a]	r^2	RMSE	Ke	K1 (h^{-1})	K2 (h^{-1})	K3 (h^{-1})
Windsor	ADS	0.996	0.5881	2.08±0.10	0.0346±0.0178	0.0505±0.0244	0.0000±0.0005
	BOTH	0.996	0.6856	2.12±0.08	0.0304±0.0129	0.0477±0.0188	0.0000±0.0004
Olivier	ADS	0.999	0.1870	7.36±0.07	0.1607±0.0131	0.0439±0.0038	0.0013±0.0001
	BOTH	0.998	0.1739	7.38±0.06	0.1542±0.0099	0.0406±0.0027	0.0011±0.0001
Webster	ADS	0.996	0.1030	18.77±0.40	0.4455±0.0810	0.0645±0.0101	0.0017±0.0002
	BOTH	0.995	0.0867	19.08±0.29	0.3712±0.0495	0.0510±0.0060	0.0013±0.0001

[a] ADS: only adsorption data were used for parameter optimization; ADS-DES: both adsorption and desorption data were used for parameter optimization.

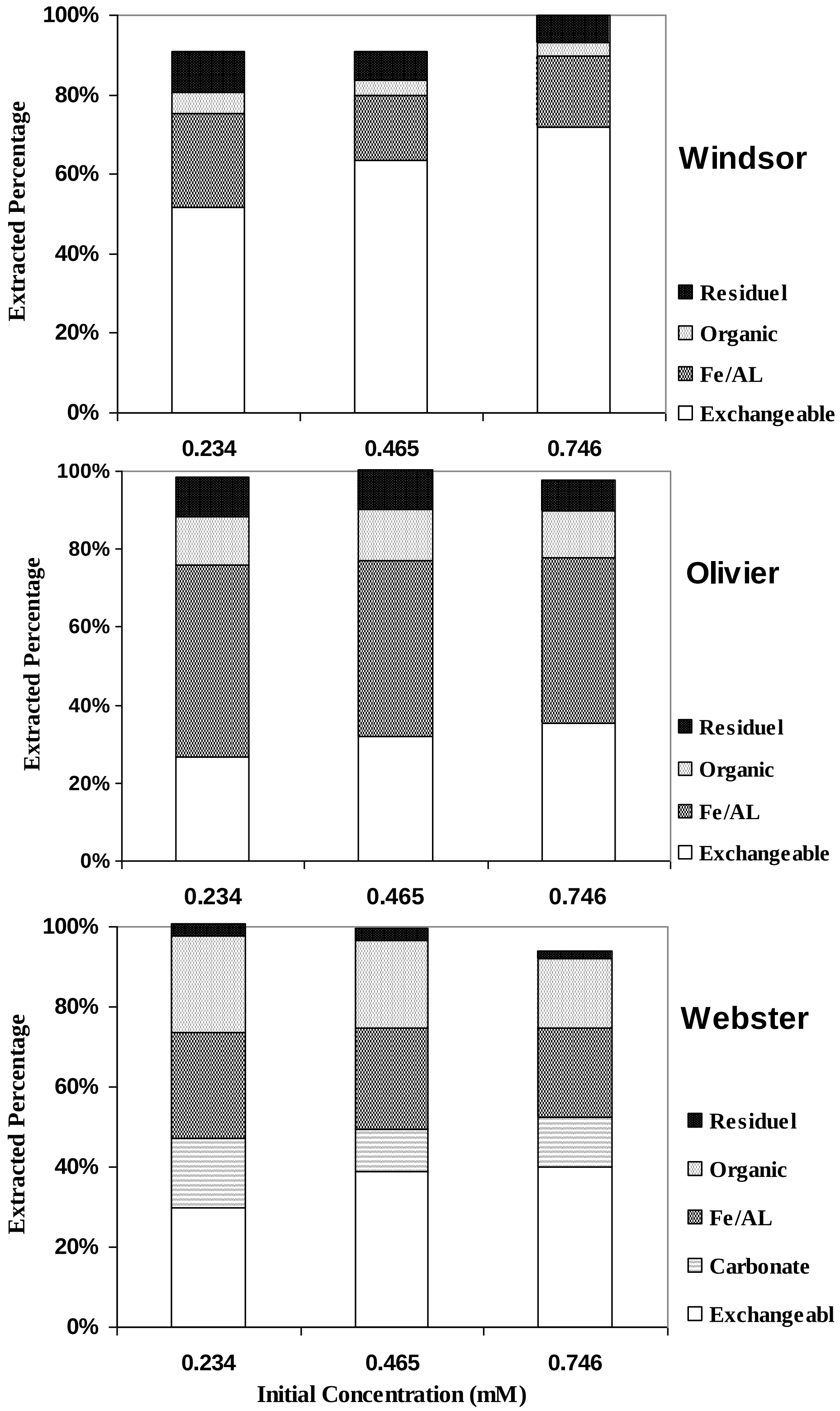

Figure 3.5. Recoveries of Ni from desorption and sequential extractions as percentages of total adsorption amounts for different soils. Different groups indicate different initial concentrations of 0.234, 0.465 and 0.746 m*M*.

Table 3.4. Comparison of parameters and goodness-of-fit determined from fitting different MRM model variations to kinetic adsorption and desorption data for all soils.

Soil	r^2	RMSE	Ke	K1 (h^{-1})	K2 (h^{-1})	K3 (h^{-1})	Kirr (h^{-1})
Windsor	0.980	1.5588	2.39±0.09	-	-	-	0.0000±0.0001
	0.996	0.7206	2.18±0.09	0.0267±0.0203	0.068±0.0447	-	-
	0.996	0.6856	2.12±0.08	0.0304±0.0129	0.0477±0.0188	0.0000±0.0004	-
	0.998	0.5306	2.27±0.04	0.0110±0.0011	0.0051±0.0008	-	0.0000±0.0001
	0.998	0.5623	2.12±0.06	0.0306±0.0075	0.0288±0.0088	0.0040±0.0006	0.0000±0.0001
Olivier	0.984	0.5407	8.99±0.01	-	-	-	0.1035±0.0002
	0.998	0.1736	7.39±0.06	0.1527±0.0096	0.0396±0.0023	-	-
	0.998	0.1739	7.38±0.06	0.1542±0.0099	0.0406±0.0027	0.0011±0.0001	-
	0.998	0.1733	7.39±0.06	0.1500±0.0092	0.0378±0.0025		0.0009±0.0001
	0.999	0.1798	7.40±0.15	0.0583±0.0088	0.0382±0.0024	0.0017±0.0001	0.0000±0.0003
Webster	0.981	0.1681	23.23±0.21	-	-	-	0.0045±0.0004
	0.994	0.0918	18.86±0.27	0.3799±0.0455	0.0461±0.0049	-	-
	0.995	0.0867	19.08±0.29	0.3712±0.0495	0.0510±0.0060	0.0013±0.0001	-
	0.995	0.0850	19.06±0.29	0.3767±0.0507	0.0532±0.0062	-	0.0027±0.0004
	0.995	0.0850	19.04±0.38	0.2980±0.0513	0.0534±0.0063	0.0009±0.0002	0.0030±0.0009

Moreover, based on model predictions of Ni sorption with time for all soils, there was little distinguishable differences among several model variations.

In fact, for all three soils, it was not possible to determine whether the dominant irreversible reactions are concurrent (S_{irr}) or consecutive (S_s) when observed versus prediction results are compared. For all soils, variation that accounted for kinetics reactions (S_k) is essential parameter to provide better model predictions of measured Ni retention compared that model variation with S_e and S_{irr} (significant higher RMSE). This agreed with the observed highly kinetic adsorption and desorption of Ni by soil discussed above. On the other hand, in model variations, equilibrium retention (S_e) was necessary to describe the initial rapid retention for Webster soil. A poor fit of the model to measured results was obtained when S_e was not incorporated in the model (results not shown). This is consistent with measured results where some 90% of retention was observed in the first 2 h of reactions. For Webster soil, the full model formulation was the best to describe the highly irreversible and low desorption behavior of Ni.

A major implication of this study is that contamination of soils with Ni could result in slow release extended from weeks to months. The types of bonding and the characteristics of surface sites are crucial for Ni release or availability in soil environment. The kinetic sorption and desorption or release of Ni were successfully related to soil Fe/Al oxides and organic matter and with carbonate for Webster soil. The desorption or release of Ni is highly dependent on sorption capacities of the soils used. Secondly, the nonlinear multireaction model (MRM) with equilibrium-kinetic-irreversible reaction sites successfully described the retention (adsorption) and subsequent release of Ni on the different soils.

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CHAPTER 4: TRANSPORT OF NICKEL IN DIFFERENT SOILS: COLUMN EXPETIMENTS AND KINETIC MODELING

4.1 Introduction

Heavy metals in soils pose serious threats to the ecosystem through groundwater contamination, plant uptake and accumulation in the food chain. The mobility, bioavailability and toxicity of nickel (Ni) in soils is highly dependent on its affinity to bind with different reactive surfaces in the soil matrix and pore water such as particulate and dissolved organic matter, clays or oxide surfaces (Dijkstra et al., 2004; Sauve et al, 2000). Thus, understanding of the complex interactions of Ni in the environment is a prerequisite in the effort to predict their behavior in the vadose zone.

Several soil properties influence Ni adsorption, desorption and equilibrium between the solid and solution phases. These factors include soil pH, clay content, organic matter (OM), cation exchange capacity (CEC) and Fe/Al oxides. Specifically, chemical and physical processes occurring at different reaction sites in the soil-solution phase control the level of heavy metal in solution and its transport, therefore influence the release of heavy metal ions to water phases (McIlveen and Negusanti, 1994; Sposito, 1989). Several studies investigated Ni affinity for different reaction sites in soils based on batch equilibration techniques. Mellis et al. (2004) found that Ni adsorption decreased with the elimination of organic matter in three Brazilian soils and amorphous iron oxides and hydroxides in these soils are not responsible for the high Ni adsorption capacity. Tiller et al. (1984) found that the soil clay fraction has highest affinity for Ni which is strongly dependent on pH. According to Atanassova (1999) and Voegelin et al. (2001) heterogeneity of soil surfaces was responsible for the observed highly nonlinear Ni sorption reactions.

Models of the Freundlich and Langmuir type are commonly used to describe equilibrium sorption of Ni by soils (Tiller et al., 1984; Atanassova, 1999; Voegelin et al., 2001). However, the occurrence of kinetic (non-equilibrium) reaction of Ni with mineral (Eick et al., 2001), clay (Scheidegger et al., 1998) and natural soils (Businelli et al., 2004) was commonly observed. The utility of results from short duration (equilibrium) studies to accurately describe non-equilibrium behavior of heavy metals in the soil environment were questioned (Srivastava and Brusseau. 1996; Selim et al., 1992). Non-equilibrium retention and transport conditions of heavy metals were due to physical non-equilibrium processes (media heterogeneity of the soil matrix and multi-porosity or preferential flow) and/or chemical rate-limited processes (precipitation at mineral surfaces, that is for Ni, induced layered double hydroxide growth with time) (Scheidegger et al., 1998), hysteretic desorption and slow diffusion to sites within the soil matrix (Pang and Close, 1999; Zhang and Selim, 2006).

Several mathematical models were developed to describe heavy metals transport in soils. Earlier scientists proposed linear analytical model to predict solute transport. They assumed that solute transports were due to dispersion alone and local equilibrium occurs instantaneously and reversibly in a homogenous porous medium. Liu et al. (2006) used linear adsorption with convection-dispersion equation to obtain the retardation factors and dispersion coefficient of Cd, Ni and Zn transport in an acidic soil in China. Their assumptions are acceptable for transport under equilibrium condition or in homogenous porous medium. A CXTFIT program, which incorporates two region/sites with non-equilibrium reaction, was applied for estimating transport parameters of Cd in alluvial gravel columns (Pang and Close, 1999). Their results showed that non-equilibrium models provided better description of measured data than an equilibrium model. Another model combining cation exchange/specific sorption (Voegelin et al., 2001) was used to describe Ni, Cd and Zn transport in an acidic soil. This model gave good prediction when heavy metal adsorption was reversible and kinetic effects were negligible under acidic condition. During later research of Voegelin et al. (2005), they found that only 23% of the retained Ni was leached during a Ni transport experiment under alkali condition. They also pointed out that greater sorption of Cd, Ni and Zn will be expected and that the kinetic effects during transport can not be ignored at higher pH level (Voegelin et al., 2001).

Barrow (1989) emphasized that the use of a single reaction and linear equation are not adequate since different reaction sites with different affinities exists for heavy metal and soils. Therefore, the validity of these models for accurately describing non-equilibrium transport phenomena has been questioned (Goltz and Roberts, 1986; Pang and Close, 1999; Hu and Brusseau, 1996; Selim et al., 2001). Michel et al. (2007) used a parameter optimization program in combination with PHREEQC2 to describe and predict Ni and Cd transport in acidic soils columns, in which Freundlich, Langmuir, cation exchange and competitive sorption approaches were attempted. They found that none of the models tested was universally applicable and suggested that the accuracy of model prediction appeared to be dependent on the mineral composition of the soil, for example, suggested that the cation exchange and competitive sorption model may be further improved by adding more binding sites and sorption coefficients. The above modeling did not incorporate the irreversible and kinetic reaction between heavy metal and soil surfaces, which is extensively observed and is an important process that can not be ignored when Ni reaction with soil matrix (Scheidegger et al., 1998; Voegelin and Kretzschmar, 2005). A multireaction transport model based on soil heterogeneity and sorption kinetics has been proposed for the purpose of describing time-dependent nonlinear sorption and irreversible or slowly reversible reactions of heavy metals in soil environment (Selim et al., 1992). This multipurpose model assumes that heavy metals in the soil environment are retained by different sites having different affinities, which incorporates both chemical and physical non-equilibrium in the transport model. The estimation procedure uses a nonlinear least-squares parameter optimization method. It successfully described the retention and transport of some heavy metal ions in soils (Selim et al., 1992; Zhang and Selim, 2006; Liao et al., 2009).

Transport under conditions where non-equilibrium is dominant is often characterized by retardant and asymmetrical breakthrough curves (BTCs) (van Den Brink and Zaadnoordijk, 1997; Pang and Close, 1999; Goltz and Roberts, 1986; Selim et al., 1989). Recently, asymmetrical Ni BTCs were observed by Antoniadis et al. (2007) in a clay soil using modified centrifuge infiltration columns. Such asymmetry of Ni BTC displays a relatively slow breakthrough front as well as prolonged tailing during leaching. The work of Voegelin et al., 2001, 2005) results indicated a sharp concentration decrease of BTCs of Ni during leaching. We should emphasize here that most Ni transport studies were often carried out using continuous application of Ni resulting in a plateau of concentration over time (Michel et al., 2007; Liu et al., 2006).

A literature search revealed little research on the kinetics of Ni retention and transport in soils. Such information is a prerequisite in quantifying Ni mobility in the soil environment. In this study, our focus was investigating the retention of Ni soils having different properties and subsequent influence on Ni mobility in soils. Specifically, we carried out several miscible displacement experiments designed to quantify Ni interaction and mobility in soil columns. In addition, we carried out batch studies to quantify the retention of Ni with time. Our hypothesis was that time-dependent rather than equilibrium-type reactions are the dominant mechanisms for the prolonged tailing of adsorbed Ni during transport in soils. To test this hypothesis, we examined whether the transport of applied Ni in different soil columns can be successfully described based on nonlinear multireaction models which account for kinetic as well as equilibrium retention mechanisms.

4.2 Multi-reaction and Transport Model

In this study, a conceptual-type model: multireaction transport model (MRM) was used to describe kinetic retention behavior and transport of heavy metals in soils. MRM assumes that the solute in the soil environment is present in the soil solution (*C*) and in several phases representing heavy metal retained by the soil (S_e, S_k, S_s and S_{irr}) depicted in the schematics of Figure 1. as well as expressed as (Zhang and Selim, 2006):

$$S_e = k_e\left(\frac{\theta}{\rho}\right)C^n \qquad [4.1]$$

$$\frac{\partial S_k}{\partial t} = k_1\left(\frac{\theta}{\rho}\right)C^m - [k_2 + k_3]S_k \qquad [4.2]$$

$$\frac{\partial S_s}{\partial t} = k_3 S_k \qquad [4.3]$$

$$\rho\frac{\partial S_{irr}}{\partial t} = k_{irr}\theta C \qquad [4.4]$$

Here t is the reaction time (h), ρ is the soil bulk density (g/cm^3), θ is the water content, (cm^3/cm^3), and C is solute concentration in solution (mg/L). In addition, S_e is the amount retained on equilibrium-type sites (mg/kg) and has a low binding energy, S_k is the amount retained on kinetic-type sites (mg/kg) through strong interactions with the soil matrix, and S_s and S_{irr} represent the amount retained irreversibly (mg/kg). The coefficient k_e is an equilibrium constant (dimensionless) associated with instantaneous reactions, whereas k_1 and k_2 (h^{-1}) are the forward and backward reaction rate coefficients associated with the kinetic-type sites, respectively. The parameter k_3 (h^{-1}) is the irreversible rate coefficient associated with the kinetic sites and k_{irr} (h^{-1}) is the irreversible rate coefficient for the concurrent irreversible reaction.

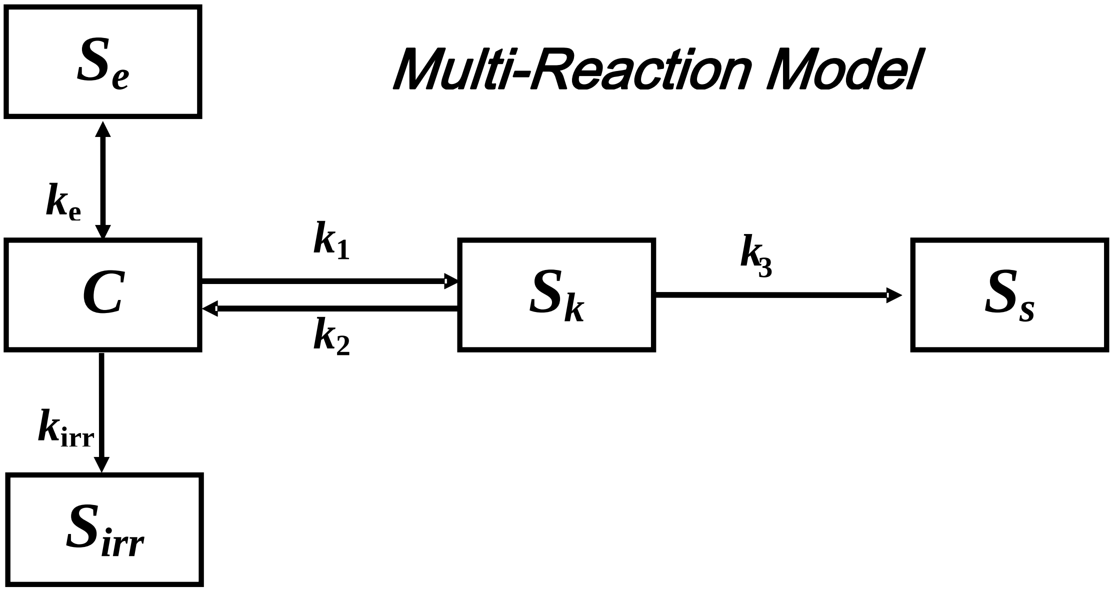

Figure 4.1. A schematic diagram of the multireaction model (MRM). Here C is concentration in solution, S_e, S_k, S_s and S_{irr} are the amounts sorbed on equilibrium, kinetic, consecutive and concurrent irreversible sites, respectively, where k_e, k_1, k_2, k_3 and k_{irr} are the respective rates of reactions.

The parameters n and m are the reaction orders (dimensionless) associated with S_e and S_k, respectively. Moreover, the total amount retained by the soil matrix S (mg kg^{-1}) is the total sum of all sorbed phases,

$$S = S_e + S_k + S_s + S_{irr} \qquad [4.5]$$

Incorporation of the above reaction mechanisms into the one-dimensional convection-dispersion transport equation (CDE) where steady-state water flow conditions are maintained yields,

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta}\frac{\partial S}{\partial t} = D\frac{\partial^2 C}{\partial z^2} + v\frac{\partial C}{\partial z} \qquad [4.6]$$

where D is hydrodynamic dispersion coefficient (cm^2 hr^{-1}), v (= q/θ) is the pore water velocity (cm hr^{-1}), q is Darcy's water velocity (cm hr^{-1}), and z is distance (cm).

Table 4.1 Selected physical and chemical properties of the soils studied.

Soil		Olivier Loam	Webster Loam	Windsor Sand
pH		5.80	6.92	6.11
TOC[a]	%	0.83	4.03	2.03
CEC[b]	cmol kg^{-1}	8.6	27.0	2.0
$CaCO_3$	%	-	3.7	-
Sand[c]	%	5	39	77
Silt	%	89	39	20
Clay	%	6	22	3
Clay mineralogical composition (fraction < 2um)[d]	%	Smectite (28%), Illite(30%), Kaolinit(31%), Quartz(11%)	Smectite (73%), Illite(7%), Kaolinit(9%), Quartz(11%)	Smectite (12%), Illite(33%), Chlorite(15%), Kaolinit(29%), Quartz(10%)
Selective extraction by				
Ammonium oxalate (pH 3.0)				
Fe	g kg^{-1}	0.32	0.98	0.36
Al	g kg^{-1}	0.08	0.89	0.69
Citrate-bicarbonate-dithionite (CBD)				
Fe	g kg^{-1}	4.09	4.42	3.68
Al	g kg^{-1}	1.29	0.77	3.65

[a] TOC = total organic carbon. [b] CEC = cation exchange capacity. [c] Grain size distribution: sand (2.00-0.05 mm), silt (0.05-0.002 mm), and clay (<0.002 mm). [d] percentage of mineral present.

4.3 Materials and Methods

4.3.1 Soils

Three surface soils having different properties were used in this study: Olivier loam is a common alluvial soil in Louisiana; Webster loam formed in glacial till or local alluvium derived from till on uplands and was sampled from Story County, Iowa. Windsor loam is a fine sandy loam soil formed on glacial outwash plains collected near Lebanon, New Hampshire. All soil samples were air dried and passed through 2 mm sieves for analysis. Soil physical and chemical properties of all soils were determined earlier in our lab and are given in Table 4.1 (Liao and Selim, 2009).

4.3.2 Adsorption

The kinetic batch method described by Zhang and Selim (2005) was used to quantify the adsorption and desorption isotherms for nickel by the different soils. Triplicate 3-g samples of each soil were place in Teflon centrifuge tubes and mixed with 30-mL solution of 5 initial Ni concentrations, which were 0.025, 0.050, 0.250, 0.500 and 0.800 *mM* $Ni(NO_3)_2$ prepared in 0.005 M $Ca(NO_3)_2$ background solution. The mixtures were continuously shaken on a reciprocal shaker and then centrifuged at 5000 × g for 10 minutes prior to sampling. After 2, 6, 12, 24, 72, 168, 336, 504, and 672 h of reaction time, a 1-mL aliquot was sampled and was analyzed using ICP-AES (Spectro Citros CCD). Amounts of Ni sorbed by the soil matrix were determined by the difference between the concentrations of the supernatant and that of the initial solutions. The pH of the supernatant was measured and the mixtures were reweighed, vortex mixed, and returned to the shaker.

4.3.3 Column Transport

The miscible displacement technique as described by Zhang and Selim (2006) was utilized to assess the transport of Ni in soils. Air-dry soil was uniformly packed into acrylic columns (10-cm in length and of 6.4-cm i.d.) and were saturated with a background solution of 0.005 M $Ca(NO_3)_2$ at low Darcy flux where upward flow was maintained. Between 10 and 20 pore volumes input solutions of 0.005 M $Ca(NO_3)_2$ were applied using a variable speed piston pump and the fluxes were adjusted to the desired flow rates. Two consecutive pulses of 0.8 mM Ni solution as $Ni(NO_3)_2$ in 0.005 M $Ca(NO_3)_2$ as background solution were introduced to each soil column. Each Ni pulse was approximately 10 to 12 pore volumes and was subsequently eluted by 0.005 M $Ca(NO_3)_2$ background solution. Column effluent was collected using a fraction collector (model Retriever II, Teledyne Isco, Inc., Lincoln, NE). The volume of each Ni pulse along with soil parameters associated with each column (ν, θ and ρ) are presented in Table 4.4. The pH of the effluent solution was monitored frequently during the miscible displacement experiments. To obtain independent estimates for the dispersion coefficient (D) of Eq. [4.8], separate pulses of a tracer solution were applied to each soil column before Ni pulse applications. The tracer used was tritium (^3H_2O) which is commonly utilized for miscible displacement experiments and the collected samples were analyzed using a Tri-Carb liquid scintillatio counter (Packard-2100 TR) by mixing 0.5-mL aliquot with 5 mL of cocktail (Packard Ultima Gold) for 10 min on the liquid scintillation counter. The radioactivity was recorded as counts per minute (CMP). Estimates for D values are given in Table 4.4.

4.3.4 Mass Balance and Nickel Distribution in the Soil Column

Each column was sectioned into 3 equal sections of 3.3 cm in length and the soil was air dried following the termination of miscible displacement transport experiments. The amount of Ni sorbed or retained by the soil matrix with depth was determined using DEENA, an automated sample digestion system, produced by Thomas Cain, Inc. The air dried soil samples were weighed and placed in 50ml disposable digestion vials. Due to the wide range of sample concentrations, several (500, 50 and 5mg) dilutions were prepared. The samples were placed in the rack on DEENA. A method was created in the software with all the steps corresponding to EPA Method 3050 (Edgell, 1988). The block temperature was preset to 120^0C. The reagents were DI water, nitric acid, hydrochloric acid, and hydrogen peroxide. The nitric acid and hydrogen peroxide were added incrementally to avoid excessive foaming. The block temperature was then set to high values in method so that the sample achieved the desired temperature (95^0C) in the allotted time. The final sample volume was 40 mL. All steps were carried out by DEENA including addition of reagents, agitation of samples, heating and cooling, and adjustments to the final volume. Samples were subsequently analyzed on a Thermo Intrepid inductively coupled plasma optical emission spectrometer (ICP-OES).

4.4 Results and Discussion

4.4.1 Sorption and Kinetics

Adsorption isotherms which depict the distribution between aqueous and sorbed phases for Ni are presented in Fig. 4.2 for our three soils. The set of Ni sorption isotherms exhibit strong nonlinear retention behavior for all soils. This nonlinear sorption behavior for Ni was described using the Freundlich equation,

$$S = K_f C^N \qquad [4.7]$$

where K_f is Freundlich partitioning coefficient (L kg^{-1}), and N is a dimensionless reaction order, commonly less than 1 (Buchter et al. 1989). Comparison of sorption isotherms among the three soils indicated that Webster soil has highest sorption for Ni, whereas Windsor exhibited lowest sorption as shown by the 24 h sorption isotherms of Fig. 4.2. The 24 h K_f values for Windsor, Olivier and Webster soils were 25.34, 96.35 and 268.53 L kg^{-1}, respectively. This adsorption sequence correlates well with the CEC values for the three soils given in Table 4.1. Consistent with observations by other researchers (Papini et al., 2004; Gomes et al., 2001), soils with higher CECs have higher sorption capacity with Ni. That Webster had the highest sorption of Ni was expected since it has higher organic matter and clay content dominated by smectite (resulted in high CEC), whereas, Olivier and Windsor soils have lower CECs due to their relative low organic matter and clay content dominated by kaolinite and illite and less smectite (Table 4.1)

Nickel sorption for all soils indicated highly time-dependent, as demonstrated by increasing values of the Freundlich parameter K_f with reaction time (Fig. 4.3 Top). Moreover, the nonlinearity of Ni isotherms is indicated by the small values of the Freundlich N (less than 1) for all reaction times as shown in Fig. 4.3 (bottom). The parameter N did not exhibit changes after reaction of 24 h for all three soils. Average N values were 0.52, 0.55 and 0.50 for Windsor, Olivier and Webster soil, respectively. This parameter N represents the energy distribution or the heterogeneity of sorption-sites, where the highest energy sites are preferentially sorbed at low concentrations, and as the concentration increases, successively lower energy sites become occupied (Sheindorf et al., 1981).

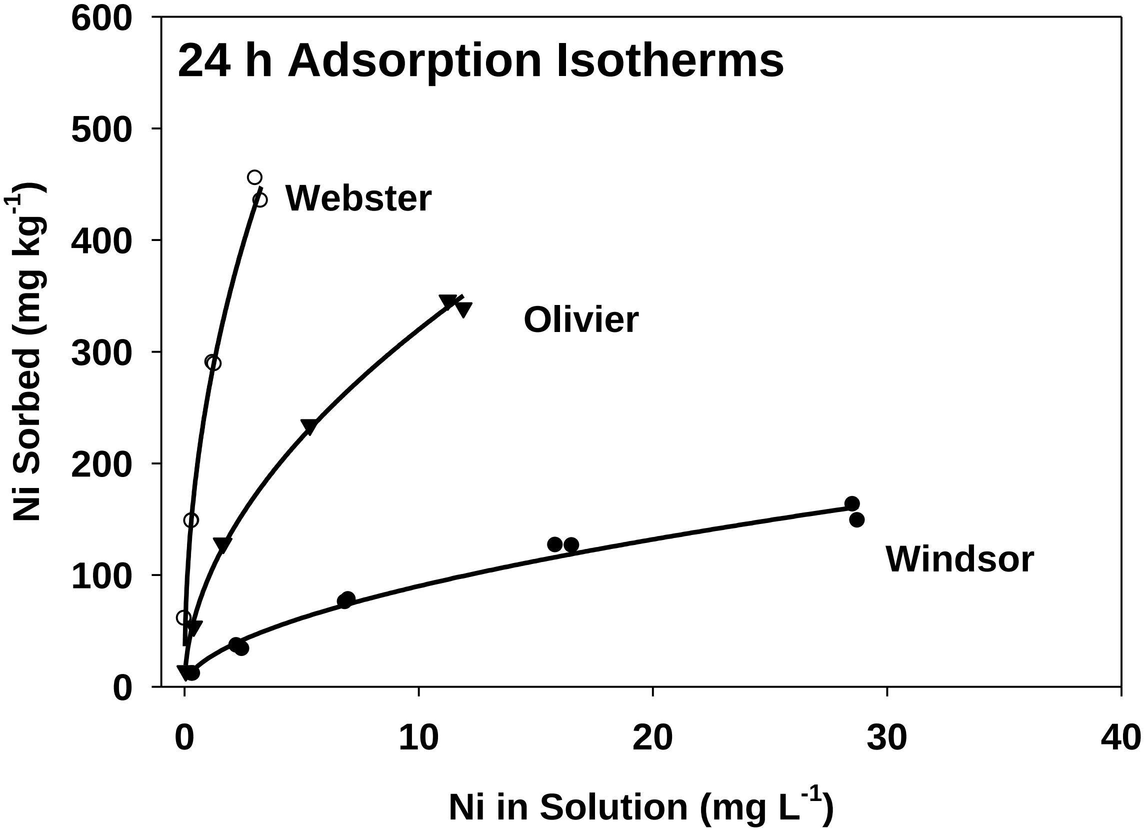

Figure 4.2. Nickel adsorption isotherms for Webster, Olivier and Windsor soils after 24 h of reaction time. Solid curves depict results of curve fitting using Freundlich Eq. [4.1].

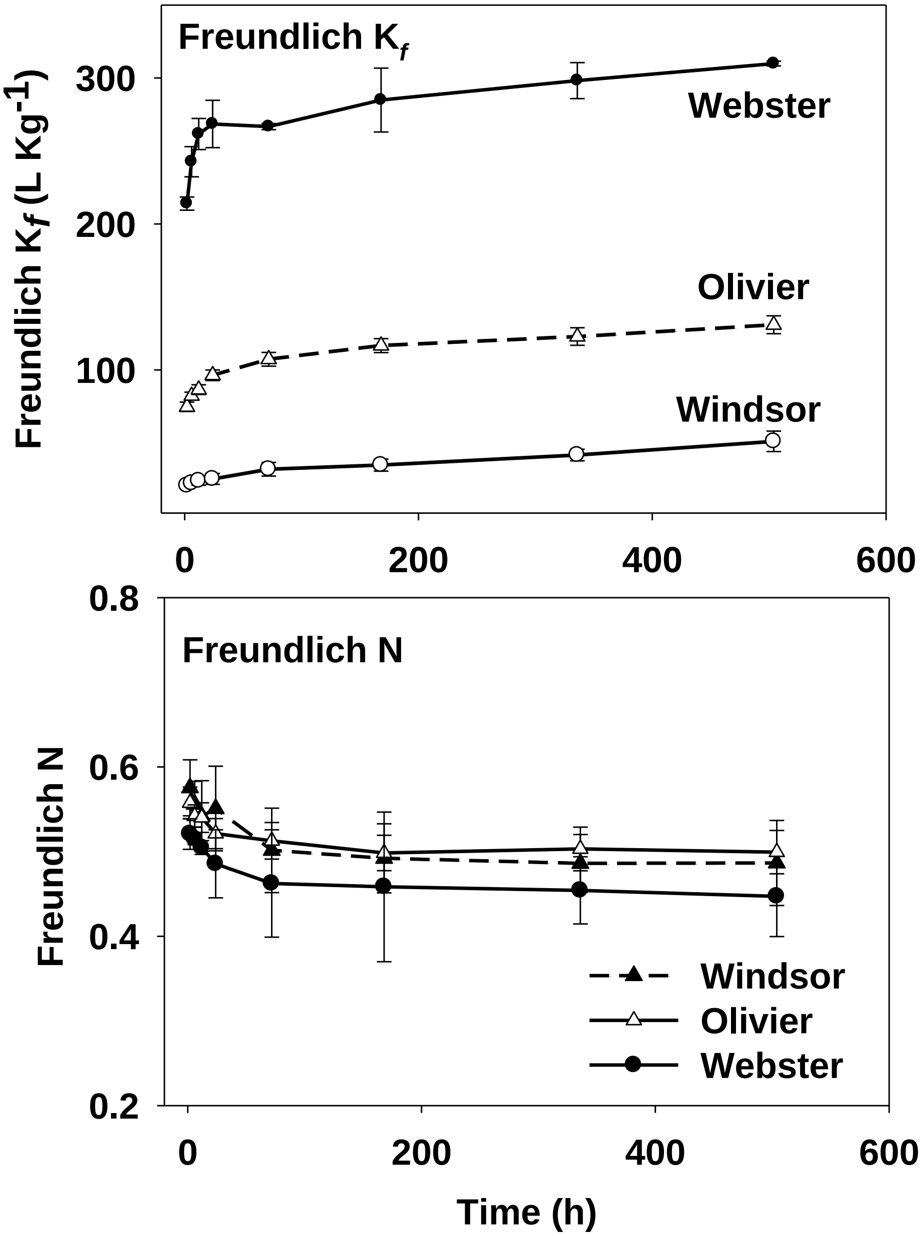

Figure 4.3. Freundlich Parameters K_f and N versus retention time for Ni sorption for Windsor, Olivier and Webster soils.

4.4.2 Model Evaluation

The Freundlich parameters shown in Fig. 4.3 indicate a time-dependent behavior of Ni adsorption for all soils. Therefore, the use of the multireaction model (MRM) to describe such time-dependent behavior is justified. Based on model simulation, the time-dependent behaviors of Ni retention in all soils were well described by the multireaction model (See Table 4.2 and Fig. 4.4). The adsorption pattern indicates an initial fast adsorption followed by slow reactions that seem to be the dominate process. This assessment is consistent with increased K_f during adsorption. Model parameter estimates given in Table 2 were obtained using nonlinear least-square optimization for each initial concentration (C_i) (2, 6, . . ,45 mg L^{-1}). Moreover, we obtained one set of model parameters where the entire data set for all C_is were used in the nonlinear least-square optimization procedure. As a result, a set of parameters corresponding, hereafter referred to the overall set of parameters, and parameters corresponding to each C_i were obtained (see Table 4.2). The kinetics of Ni adsorption were well described by the MRM model for the range of our experimental input concentrations and time of reaction. This is clearly shown by the solid curves that represent MRM predictions based on individual parameters for each C_i data set and the dashed curves that were obtained based on the overall set of model parameters (see Fig. 4.4).

The MRM model used to obtain the simulations shown in Fig 4.4 was a four parameters model formulation with k_e, k_1, k_2 and k_3. Such model formulation accounts for an equilibrium sorbed phase (S_e) and kinetic reversible and irreversible phased (S_k and S_{irr}) (see Fig.1). Since model parameters n and m are difficult to measure, their values were based on the Freundlich N at 24 h reaction for each soil (see Selim and Ma, 2001). In further attempts to describe Ni sorption kinetics with time, several other MRM model variations were tested (M1-M9).

Table 4.2 The goodness-of-fit of Ni adsorption data with time using a three-phase equilibrium, kinetic reversible and consecutive irreversible MRM model variation for Olivier, Windsor and Webster soil.

C_i	RMSE	r^2	k_e	k_1	k_2	k_3
mg L^{-1}				-------------------------h^{-1}	----------------------------	
			Olivier			
2	0.0053	0.993	4.22±0.27	0.1497±0.0439	0.0509±0.0145	0.0016±0.0004
6	0.0201	0.998	5.71±0.13	0.2069±0.0241	0.0446±0.0059	0.0015±0.0003
14	0.0556	0.999	6.96±0.11	0.1812±0.0166	0.0361±0.0040	0.0017±0.0002
28	0.1169	0.999	7.34±0.09	0.1668±0.0151	0.0421±0.0041	0.0014±0.0002
45	0.3755	0.999	7.39±0.14	0.1589±0.0278	0.0451±0.0083	0.0013±0.0003
Overall	0.2090	0.999	7.36±0.08	0.1607±0.0131	0.0439±0.0038	0.0013±0.0001
			Webster			
6	0.0280	0.968	13.07±1.66	0.0243±0.1776	0.0002±0.0456	0.0000±0.7523
14	0.0129	0.999	14.29±0.47	0.6820±0.0808	0.0613±0.0059	0.0011±0.0001
28	0.0481	0.999	16.36±0.62	0.7555±0.1447	0.0869±0.0126	0.0014±0.0001
45	0.1807	0.997	18.63±0.89	0.5351±0.2050	0.0769±0.0244	0.0017±0.0003
Overall	0.1025	0.996	18.78±0.41	0.4455±0.0810	0.0645±0.0101	0.0017±0.0002
			Windsor			
2	0.0160	0.998	1.50±0.03	0.0231±0.0040	0.0195±0.0048	0.0019±0.0005
6	0.1123	0.998	1.85±0.07	0.0245±0.0089	0.0243±0.0118	0.0028±0.0010
14	0.1338	0.999	2.12±0.05	0.0420±0.0096	0.0508±0.0126	0.0038±0.0005
28	0.2990	0.999	2.11±0.06	0.0466±0.0107	0.0485±0.0107	0.0001±0.0002
45	1.3782	0.998	2.07±0.21	0.0280±0.0390	0.0559±0.0683	0.0000±0.0015
Overall	0.8831	0.997	2.09±0.10	0.0346±0.0178	0.0505±0.0244	0.0000±0.0005

Table 4.3. Comparison the goodness-of-fit and parameters of nine MRM model variations from overall kinetic adsorption data set for Windsor, Olivier and Webster soils.

MRM[a]	RMSE	r^2	k_e	k_1	k_2	k_3	k_{irr}
			h^{-1}				
			Windsor				
M1	1.0586	0.995	-	1.1149±0.3209	1.1149±0.3209	-	-
M2	0.9479	0.996	-	1.2384±0.2265	0.8256±0.1621	0.0001±0.0002	-
M3	1.0894	0.995	-	0.3607±0.0534	0.2089±0.0367	0.0026±0.0008	0.0000±0.0004
M4	0.8498	0.997	-	1.1754±0.1795	0.7546±0.1241	-	0.0006±0.0001
M5	1.8707	0.984	2.22±0.10	-	-	-	0.0000±0.0001
M6	0.9024	0.996	2.16±0.12	0.0307±0.0288	1.0679±0.0266	-	-
M7	0.5881	0.996	2.08±0.10	0.0346±0.0178	0.0505±0.0244	0.0000±0.0005	-
M8	0.6650	0.998	2.28±0.05	0.0104±0.0014	0.0052±0.0011	-	0.0000±0.0001
M9	0.8831	0.999	2.08±0.07	0.0385±0.0117	0.0454±0.0155	0.0044±0.0007	0.0000±0.0000
			Olivier				
M1	0.6909	0.985	-	4.5196±0.0254	0.5358±0.0034	-	
M2	0.6867	0.985	-	4.4578±0.0351	0.5196±0.0040	0.0009±0.0000	-
M3	0.7307	0.983	-	4.3276±0.0260	0.5052±0.0032	0.0000±0.0001	0.0037±0.0000
M4	0.6701	0.986	-	4.2493±0.0084	0.4949±0.0066	-	0.0006±0.0000
M5	0.6679	0.987	8.89±0.12	-	-	-	0.0013±0.0002
M6	0.2151	0.999	7.38±0.07	0.1519±0.0117	0.0390±0.0028	-	-
M7	0.1870	0.999	7.36±0.07	0.1607±0.0131	0.0439±0.0038	0.0013±0.0001	-
M8	0.2163	0.999	7.38±0.07	0.1533±0.0122	0.0399±0.0034	-	0.0011±0.0002
M9	0.2090	0.999	7.37±0.07	0.1612±0.0115	0.0424±0.0033	0.0020±0.0001	0.0000±0.0000
			Webster				
M5	0.2171	0.982	22.94±0.28	-	-	-	0.0059±0.0007
M6	0.1235	0.994	18.74±0.39	0.4008±0.0660	0.0484±0.0070	-	-
M7	0.1030	0.996	18.77±0.40	0.4455±0.0810	0.0645±0.0101	0.0017±0.0002	-
M8	0.1034	0.996	18.72±0.41	0.4469±0.0819	0.0653±0.0101	-	0.0039±0.0006
M9	0.1025	0.996	18.77±0.41	0.4449±0.0819	0.0650±0.0103	0.0015±0.0004	0.0020±0.0017

[a] Required model parameters for different MRM formulations are as follows: M1= k_1 and k_2;; M2 = k_1, k_2, and k_3; M3 = k_1, k_2, k_3 and k_{irr}; M4 = k_1, k_2 and k_{irr} M5 = K_e and k_{irr}; M6 = K_e, k_1 and k_2;; M7 = K_e, k_1, k_2, and k_3;; M8 = K_e, k_1, k_2, and k_{irr}; M9 = k_e, k_1, k_2, k_3, and k_{irr} .

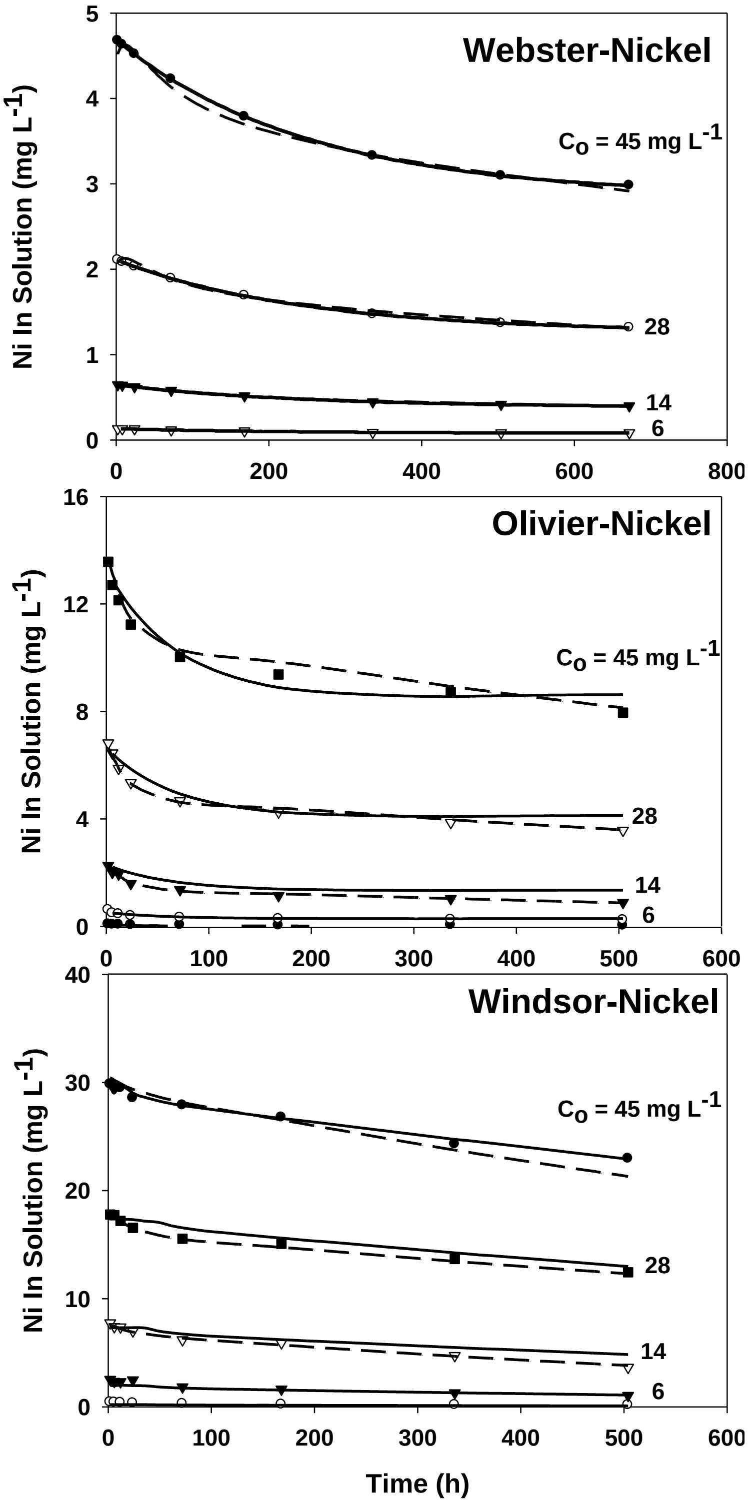

Figure 4.4. Ni concentrations in soil solution versus time during adsorption for Webster, Olivier, and Windsor soils. Symbols are for different initial Ni concentrations (C_o). Solid curves are multireaction model (MRM) simulations based on individual parameter for each C_o data set and the dashed curves are from overall set of model parameters.

Different MRM variations represent different reactions mechanisms for Ni retention (see Fig.4.1). The goodness-of-fit of nine variations of the model was tested using entire data set for each soil and the resulting best-fit parameter estimates along with their standard errors (SE) are presented in Table 3. Model variation M1 account for equilibrium and concurrent irreversible reactions (S_e and S_{irr}) where only two parameters were estimated (k_e and k_{irr}). In contrast M9 accounts for all sorbed phases (S_e and S_k, S_s and S_{irr}) where five parameters were estimated (k_e, k_1, k_2, k_3, and k_{irr}).

Based on r^2 and RMSE values, model variation that accounted for kinetic and concurrent irreversible reactions (S_k and S_{irr}) provided better model predictions of measured Ni retention with time than other model variations (without S_k) for Windsor and Olivier soils. For all three soils, M7 (with S_e, S_k and S_{irr}) provided best overall predictions with lowest RMSE. Moreover, based on model predictions of Ni sorption with time for all soils, there was little distinguishable differences among several model variations (results are not shown). In fact, for all three soils, it was not possible to determine whether the dominant irreversible reactions are concurrent (S_{irr}) or consecutive (S_s) when observed versus prediction results are compared. On the other hand, in all model variations, equilibrium retention (S_e) was necessary to describe the initial rapid retention for Webster soil. Specifically, for Webster soil (the neutral soil), a poor fit of the model to measured results was obtained when S_e was not incorporated in the model. This is consistent with measured results where some 90% of retention was observed in the first 2 h of reactions. This is well illustrated when one compares M4 (without S_e) with M5 (with S_e) for Webster soil (see Table 4.3). Improvements in model predictions were achieved when M5 was used (RMSE = 0.2171) when compare to M4 (RMSE = 1.9935). In both M4 and M5 irreversible retention was assumed (S_{irr}). Therefore, we concluded that equilibrium retention (S_e) as well as irreversible reactions: concurrent (S_{irr}) or consecutive (S_s) are necessary to describe observed initially fast reactions for Ni sorption which was followed by slow (kinetic) type reactions. Therefore, for Webster soil (neutral soil) the use of reversible (equilibrium and kinetic) and irreversible mechanisms is essential for describing Ni kinetic sorption.

4.4.3 Tritium Transport

BTCs for tritium pulses from the miscible displacement columns are shown in Fig. 4.5 for all three soils. Here tritium results from the column effluent is presented as relative concentration (C/Co) versus pore volume (V/V_o) where V_o is the volume of the entire pore space of each soil column (cm^3). Tri Tritium (^3H_2O) was considered a conservative tracer and was applied in order to assess flow characteristics by obtaining independent values for the hydrodynamic dispersion coefficient (D) of the classical CDE,

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + v\frac{\partial C}{\partial x} \qquad [4.8]$$

Where $R = 1 + \frac{\rho K_f}{\theta}$ is the retardation factor (dimensionless). Other experimental parameters such as the soil bulk density (ρ) and soil moisture content (θ) are given in Table 4. After pulse application of tritium and subsequent leaching by tritium free solution, the percent of recovery applied tritium in the column effluent were 98.7%, 99.2% and 98.2%, for Windsor, Olivier and Webster soil, respectively. For all tritium results, the BTCs appear symmetrical. Moreover, the BTCs conformed to the CDE (Eq 4.8) and were well described by convective-dispersive solute transport model. Such results are indicative that diffusional mass transfer of tritium was rapid, i.e., equilibrium conditions are dominant. However, for Webster soil column, some degree of tailing of tritium BTCs was observed. Such tailing is evidence of physical nonequilibrium and most likely due to intraparticle diffusion and the presence of immobile water regions (Brusseau

1992). These tritium BTCs were described using CXTFIT along with nonlinear least-square optimization as described in Toride et al. (1995) in order to obtain best-fit values for D and R parameters for each soil. The estimated values for all three soils are given in Table 4.4. Webster soil had the highest D value consistent with observed moderate slope of the influent front and the excessive tailing of the release side of the BTC. Values of D were subsequently used in the MRM model to predict Ni transport in the different soil columns.

Table 4.4. Column soil physical parameters for Ni miscible displacement experiments.

Soil Column	Bulk Denssty (ρ, Mg m^{-3})	Saturated Moisture Content (θ, %)	Pore Water Velocity (ν, cm h^{-1})	Disperse Coefficient (D, cm^2 h^{-1})	Effluent Recovery (%)	Recovery from Extracted (%)	Total Recovery That Applied (%)
Windsor	1.38	0.48	0.38	0.78 ± 0.04	68.3%	22.7%	90.98%
Olivier	1.30	0.49	0.37	0.78 ± 0.07	58.0%	32.2%	89.24%
Webster	1.31	0.50	0.37	1.93 ± 0.06	18.9%	67.2%	86.05%

4.4.4 Ni Transport

Breakthrough results (BTCs) for Ni in all three soils are shown Figs. 4.6-4.9. All BTCs appear retarded relative to the transport of the conservative tracer tritium. The peak position of the BTCs shows a significant shift to the right, and is indicated by the late arrival of Ni in the effluent solution. Such strong retardation is indicative of the extent of Ni retention during transport for all three soils. Such retardation feature strongly suggests kinetic (reversible and irreversible) retention in soils. The extent of retardation varied among the soils. BTCs for Windsor and Olivier soils indicate sharp rise of concentrations in the influent (left side of BTCs) where higher peak maxima was associated with the second pulse application of Ni in the miscible displacement columns. These peaks were accompanied by moderate tailing during desorption (right side of BTCs) (Fig. 4.7-4.8).

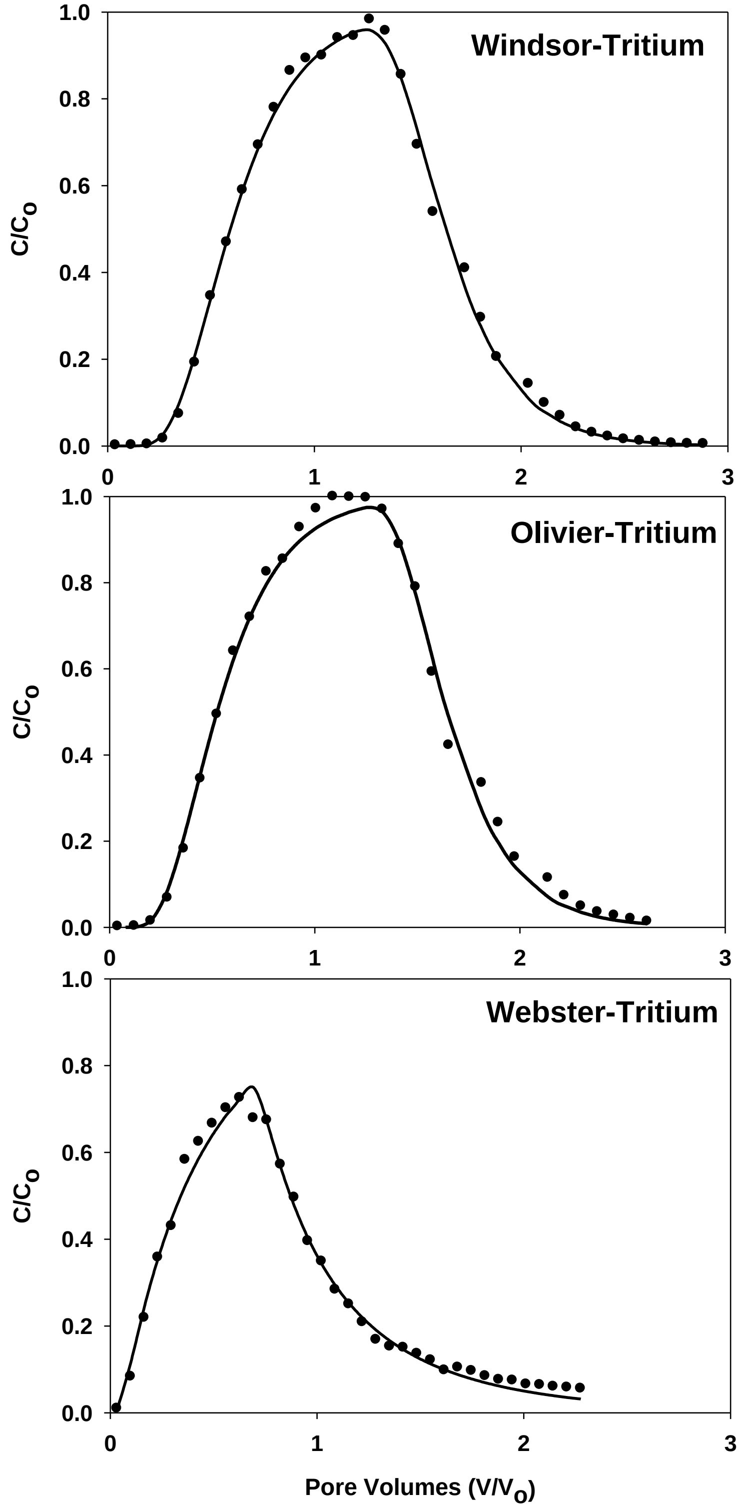

Figure 4.5. Tritium breakthrough curves from miscible displacement soil columns. Solid curves are simulation using the convection dispersion equation (CDE) for non-reactive solutes.

This is likely due to the highly nonlinear and kinetic adsorption behavior, which is consistent with our batch experimental results. Moreover, measured Ni BTC for Webster soil shown in Fig. 4.9, illustrates a gradual (or diffuse) front, followed by extensive tailing and a retardation of Ni in the effluent as well as a lowering of concentration maxima compared to Olivier and Windsor soil. Overall, highest retardation was observed for Webster soil, which exhibited strong affinity (with highest K_f value). In contrast lowest retardation for Ni was observed for Windsor soil, which is consistent with sorption affinities based on our kinetic batch experiments, where the affinity followed the sequence; Windsor < Olivier < Webster.

In our first attempt to describe BTCs of Ni in the soil columns, model simulations were obtained when the MRM model was utilized in a simulation mode. The simulated BTCs are presented by the family of solid and curves shown in Fig. 4.6. The simulations shown were obtained based on several model variations to demonstrate the capability of MRM in describing Ni BTCs for Olivier and Windsor soil. In these simulations, the necessary model parameters were derived earlier from the kinetic batch rate coefficient given in Table 4.3. In both Olivier and Windsor soil, significant discrepancies between predicted and experimental results are evident for all model variations used. There is a significant shift to the left of the entire BTC, suggesting that retardation (sorption-desorption) during the transport was underestimated by the MRM predictions. In addition, the predicted curves over-estimated maximum peak concentrations with sharp influent fronts accompanied by lack tailing of the desorption side of the BTCs. Overall, the use of batch model parameters resulted in underestimated Ni retention during transport in all soil columns. Such overestimates the potential mobility of Ni in all soils, and for all selected model variation. Model predictions shown in Fig. 4.6 clearly demonstrate the failure of the MRM model to describe the transport data when independently measured model parameters were used.

This failure result was also observed by Barnett et al. (2000) for Uranium(VI) transport through soils. They suggested that the likely explanation is due to fundamental differences between batch and column experiments that reduced the applicability of batch experiment data in simulating column transport experiments. Zhang and Selim (2006) argued that different retention capacities determined from batch and column experiments might result from the following reasons: difference between sorption time used for batch experiment and hydrologic retention time of column experiment; low solid/solution ratio of batch experiments; chemicals was added in one spike for batch study compare with continuous addition in column experiments. And more, the non-uniform of ion distribution with soil depth in soil columns may cause different reaction ratio of Ni with soil from that in batch experiments.

4.4.5 Inverse Multireaction Transport Model

In an attempt to describe Ni transport in the soil columns, the multireaction model (MRM) was utilized in an inverse mode to test its capability for predicting Ni BTCs without reliance on parameter estimates from the batch experiments. Nine Variations of MRM were tested for each soil column (as illustrated in Figs. 4.7-4.9). Overall excellent fit of the data were achieved for Ni BTCs of all soils as indicated by the low values of RMSE and high r^2 listed in Table 4.5. However, the goodness-of-fit of model prediction to experimental data varied among our soils. Specifically, for Windsor and Olivier soils model variations with kinetic reaction sites (S_k) was necessary to obtain such excellent predictions for all model variations (see Fig. 4.7 and 4.8). These results are consistent with previous batch experimental data, where Ni reaction in Olivier and Windsor soils exhibited highly time-dependent behavior (see Fig. 4.4). Also best predictions were obtained for model variations when the irreversible phase (S_{irr} or S_s) along with the reversible kinetic phase (S_k) were incorporated in the model.

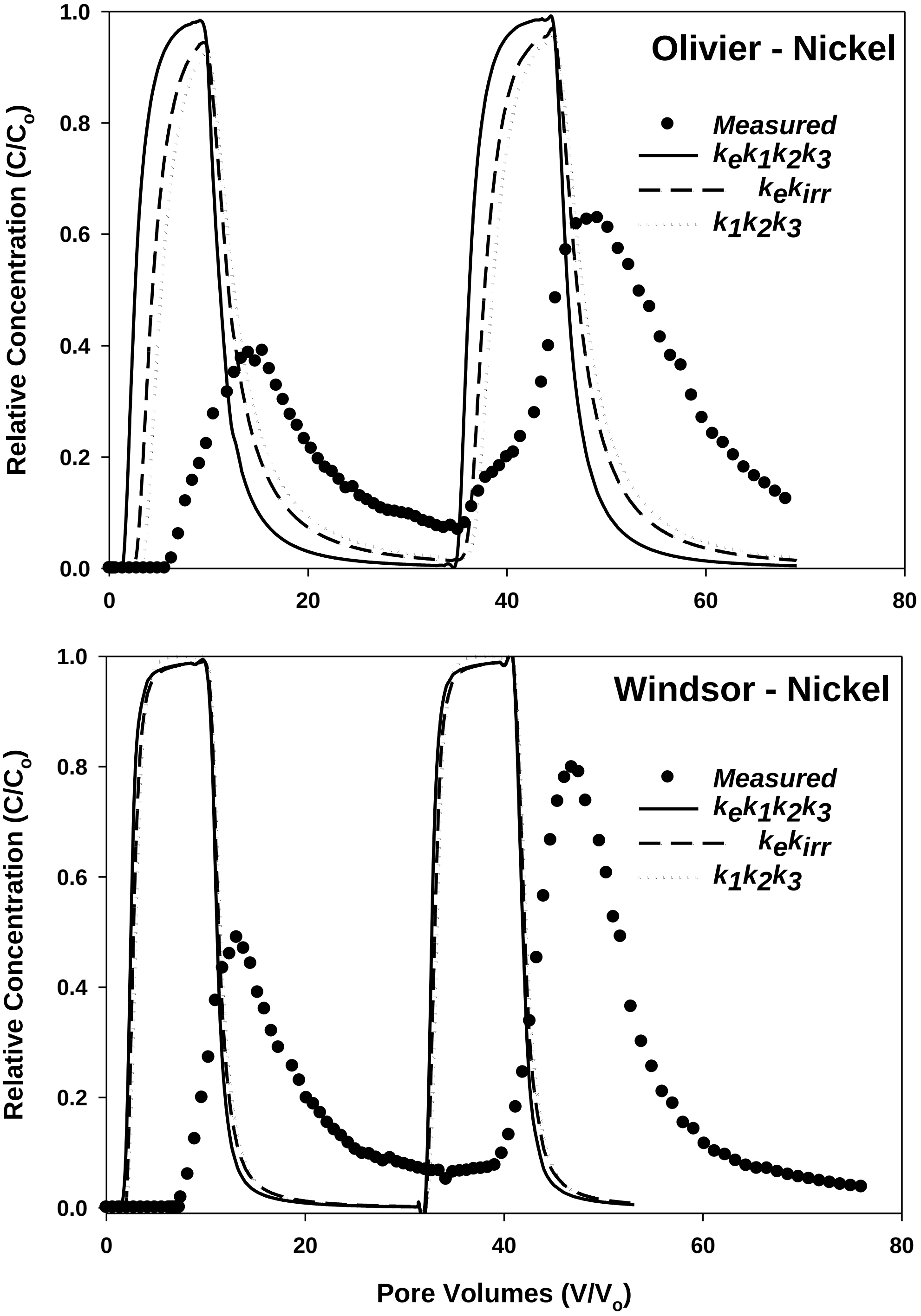

Figure 4.6. Nickel breakthrough curves (BTCs) results from two applied Ni pulses for Windsor and Olivier soils. Solid and dashed curves are multireaction transport model (MRM) predictions where model parameters were those from the batch kinetic experiment.

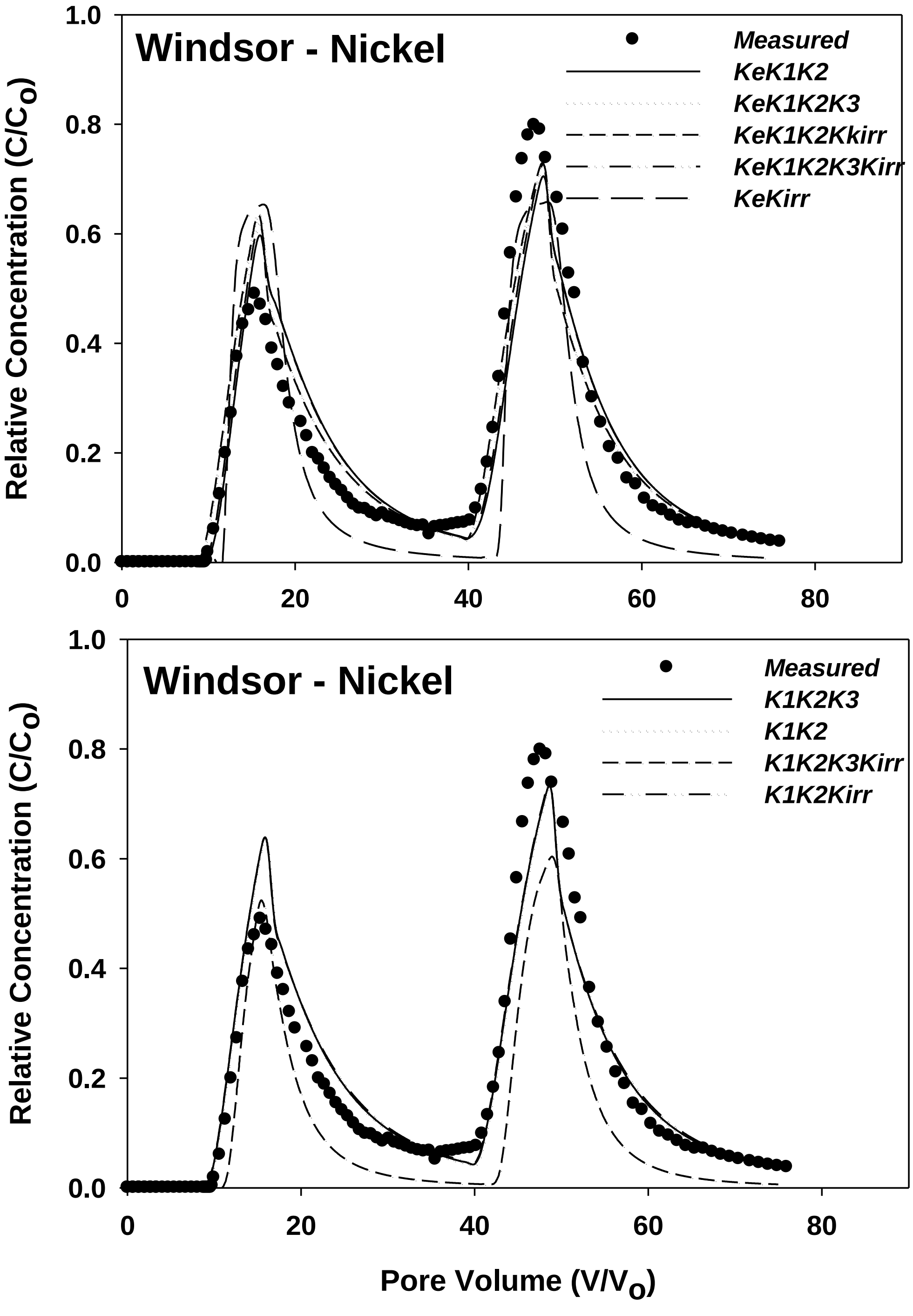

Figure 4.7. Nickel breakthrough curves (BTCs) results from two applied Ni pulses for Windsor soil. Solid and dashed curves are multireaction transport model (MRM) predictions where model parameters were those from nonlinear inverse modeling.

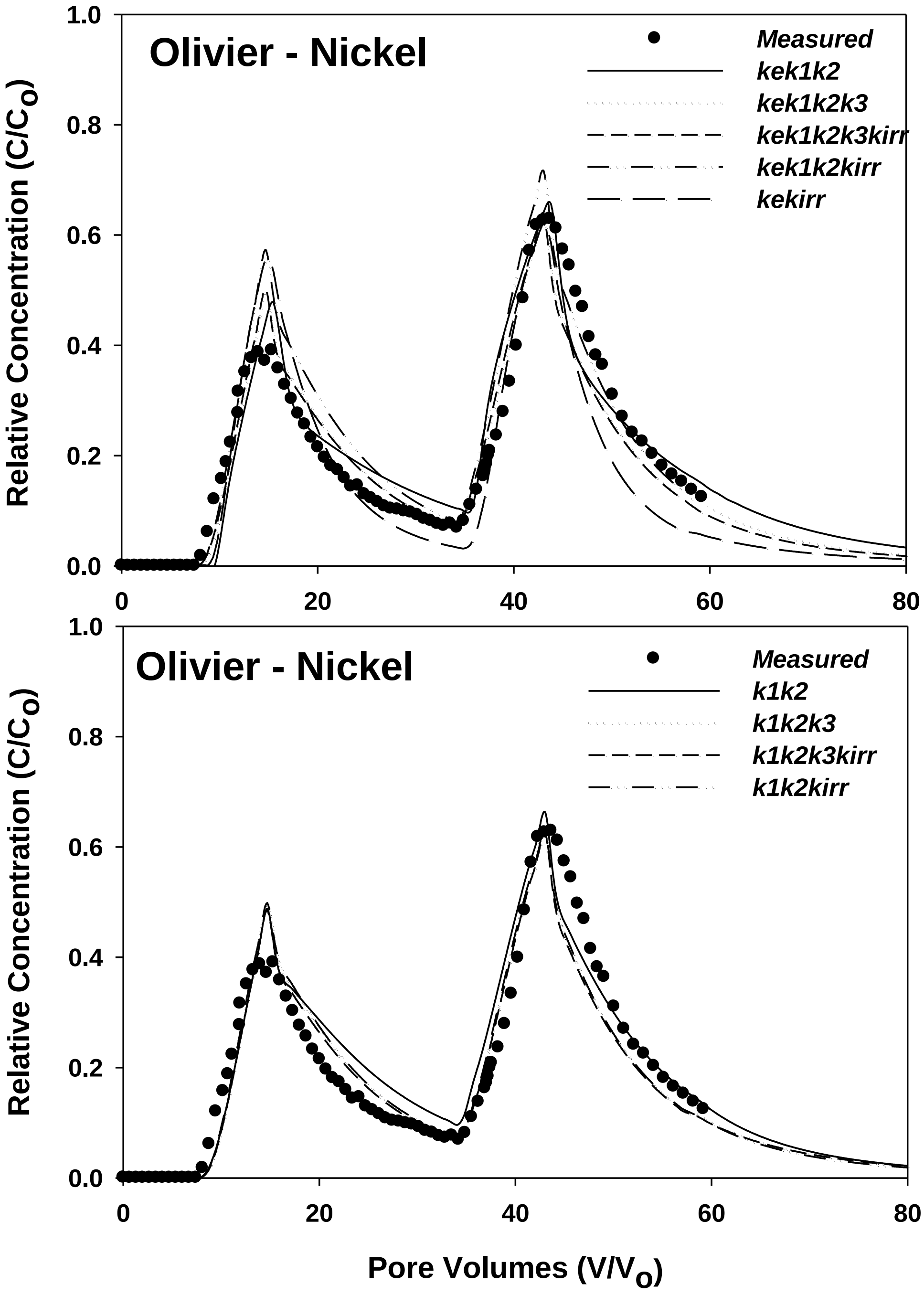

Figure 4.8. Nickel breakthrough curves (BTCs) results from two applied Ni pulses for Olivier soil. Solid and dashed curves are multireaction transport model (MRM) predictions where model parameters were those from nonlinear inverse model.

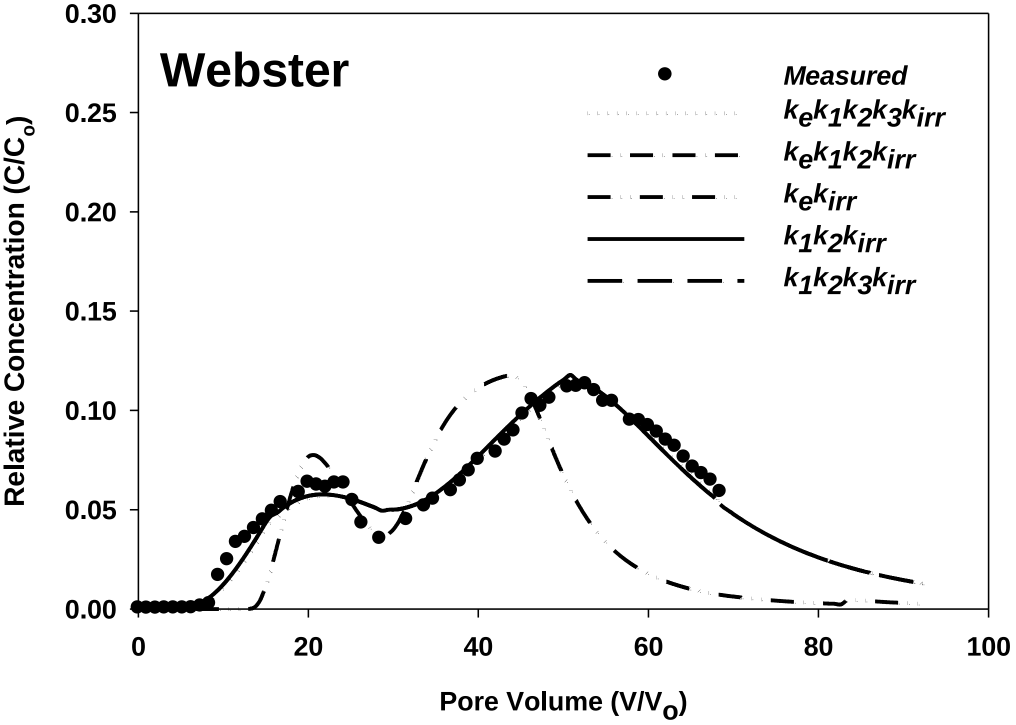

Figure 4.9. Nickel breakthrough curves (BTCs) results from two applied Ni pulses for Webster soil. Solid and dashed curves are multireaction transport model (MRM) predictions where model parameters were those from nonlinear inverse model.

Table 4.5. Comparison the goodness-of-fit and parameters of nine MRM model variations from transport data for Windsor, Olivier and Webster soils.

MRM[a]	RMSE	r^2	k_e	k_1	k_2	k_3	k_{irr}
				-------------------------------h^{-1}--------------------------------			
				Windsor			
M1	0.0535	0.936		0.3901±0.0199	0.0327±0.0020		
M2	0.0537	0.937		0.3875±0.0202	0.0323± 0.0020	0.0000±0.00001	
M3	0.1723	0.566		0.4353±0.0866	0.0122±0.0031	0.0004±0.0013	0.0000±0.0122
M4	0.0535	0.938		0.3836±0.0191	0.0310±0.0022		
M5	0.0951	0.848	19.71± 0.64				0.0090±0.0008
M6	0.0622	0.915	0.0008±1.1931	0.5157±0.0442	0.0392±0.0032		
M7	0.0541	0.937	0.0005±0.5359	0.3871±0.0268	0.0322±0.0024	0.0000±0.0002	
M8	0.0540	0.937	0.0002±0.2059	0.3819±0.0211	0.0310±0.0023		0.0007±0.0006
M9	0.0587	0.925	0.0003±0.8306	0.4864±0.0338	0.0370±0.0029	0.0002±0.0002	0.0000±0.0003
				Olivier			
M1	0.0582	0.888	-	0.3598±0.0168	0.0245±0.0014	-	-
M2	0.0519	0.899	-	0.3771±0.0171	0.0276±0.0017	0.0008±0.0001	-
M3	0.0527	0.900	-	0.3773±0.0177	0.0271±0.0018	0.0009±0.0002	0.0000±0.0000
M4	0.0527	0.896	-	0.3712±0.0185	0.0296±0.0022	-	0.0026±0.0006
M5	0.0741	0.855	2.49±0.80	-	-	-	0.0067±0.0006
M6	0.0589	0.875	0.94±1.26	0.2234±0.0194	0.0158±0.0016	-	-
M7	0.0522	0.899	0.0015±0.1237	0.3768±0.0172	0.0275±0.0017	0.0008±0.0001	-
M8	0.6650	0.895	0.0004±0.4035	0.3710±0.0211	0.0296±0.0024	-	0.0000±0.0006
M9	0.0528	0.898	0.0024±0.0003	0.3635±0.0309	0.0266±0.0022	0.0008±0.0001	0.0000±0.0001
				Webster			
M3	0.0055	0.978	-	0.3145±0.0169	0.0205±0.0013	0.0000±0.0001	0.0478±0.0004
M4	0.0055	0.978	-	0.3145±0.0168	0.0205±0.0013	-	0.0478±0.0003
M5	0.0219	0.748	30.21±1.15	-	-	-	0.0548±0.0012
M8	0.0055	0.978	0.1473±0.0897	0.3121±0.0505	0.0204±0.0023	-	0.0477±0.0004
M9	0.0057	0.978	0.2028±0.0308	0.3306±0.0598	0.0210±0.0027	0.0000±0.0314	0.0478±0.0004

[a] Required model parameters for different MRM formulations are as follows: M1= k_1 and k_2;; M2 = k_1, k_2, and k_3; M3 = k_1, k_2, k_3 and k_{irr}; M4 = k_1, k_2 and k_{irr} M5 = K_e and k_{irr}; M6 = K_e, k_1 and k_2;; M7 = K_e, k_1, k_2, and k_3;; M8 = K_e, k_1, k_2, and k_{irr}; M9 = k_e, k_1, k_2, k_3, and k_{irr} .

However, based on RMSE and r^2 as well comparison of predicted vs observed BTCs, for Olivier and Windsor soils it was not possible to determine whether the dominant irreversible reactions are concurrent (S_{irr}) or consecutive (S_s) (see Figs 4.7 and 4.8). On the other hand, in all model variations, incorporation of equilibrium retention (S_e) was not necessary to describe the measured BTC results for all model variations.

For Webster soil, several model variations produced good model predictions of the applied Ni pulses as shown by the BTC presented in Fig. 4.9. MRM model variation that accounted for equilibrium and concurrent irreversible reactions (S_e and S_{irr}) provided poor model predictions of measured Ni retention than other model variations. All other model variations provided equally good predictions as long as the kinetic phase (S_k) and concurrent irreversible reactions (S_{irr}) were incorporated into the model. Incorporation of additional mechanisms; i.e., the equilibrium sites (S_e) or consecutive irreversible reactions (S_s) did not provide additional improvements in model predictions as shown in Fig. 4.8. Based on simulation results for the various model variations, values for RMSE and r^2 were not significantly altered when S_e and S_s phases were incorporated into the model. These results are consistent with the batch data where irreversible reactions were considered as the dominant mechanism.

Differences in affinity for Ni and the observed concentration in effluent may be related to soil organic matter, iron oxides and the clay mineralogy of the different soils. Windsor soil is an Entisol and contains parent material that has not been completely weathered to second minerals and hence has lower sorption capacity for Ni (Hinz and Selim, 1994). Sparks (1995) argued that in soils where of kaolinite and illite minerals are dominant, sorption is due to ion exchange (electro-static) and Ni may form out-sphere complexes. Sorbed Ni as outer-sphere complexes is considered mobile, leading much higher percentage of Ni recovered from effluent. Whereas strong affinity of heavy metals due to inner-sphere complexes is expected when smectitic type clay is dominant as is the case for Webester soil (Serrano et al., 2005), leading lower Ni recovered from effluent. Moreover, we can associate kinetic phase (S_k) as specific sorption phase, whereas (S_{irr} or S_s) may be associated with irreversible or slowly irreversible sorption. Tsang and Lo (2005) suggested that heavy metal sorption with organic matter and iron oxides forms more specific complexes, which required a much longer reaction time to reach equilibrium. This time-dependent sorption of Ni may be responsible for the observed retardant BTCs of Ni and the associated significant S_k phase in our model description for Olivier and Windsor soil columns. Singh et al. (1992) found that major proportions of the Ni in the soils were concentrated with the iron oxides, and the dissolution kinetics of these elements indicate that some may be present in the structure of the iron oxides, which is partially irreversible or slowly reversible. This provided the evidence that iron oxides may be responsible for partially irreversible phase (S_{irr} or S_s) described in the MRM model for Olivier and Windsor soils.

For Webster soil, strong irreversible Ni retention is clearly evident by fact that low recovery of Ni in the effluent where 81.1% of applied Ni was retained in the soil column at the termination of the miscible displacement experiment (see Table 4.4). This was expected since Webster soil is a fine loamy Haplaquoll with 3.7% $CaCO_3$. Businelli et al. (2004) found that calcium carbonate contributes to Ni retention through the formation of a strong complex via co-precipitation that involves Ni/Ca carbonate double salt or mixed Ni/Al hydroxides and carbonates formation. Ni/Al layered double hydroxides was observed at pH or 6.5 or higher (Scheidegger et al., 1998). Moroever, Ni/Al layered double hydroxides are highly stable and irreversible; and resistant to dissolution in dilute HNO_3 (Scheidegger et al., 1998). On the other hand, contrary to the transport data for Webster soil, batch results indicated that the use of reversible reactions of the equilibrium type (S_e) was better to describe Ni kinetic sorption. It is conceivable that fundamental differences between batch and column experiments are perhaps responsible. Therefore, additional research is needed on the machanisms of adsorption of Ni during transport in soils. Such knowledge is needed to provide the improvements of the MRM model presented here.

In Fig. 4.10, we present measured results of Ni retained by the soil with depth for individual soil columns following the termination of the miscible displacement transport experiments. The solid curves are predictions of Ni sorbed distribution with soil depth using the MRTM model. Extensive heterogeneity is manifested for all soils as demonstrated by the values of the different replications. All samples were taken at the middle depth within each layer and lack of uniformity during column packing may also have contributed to the observed variability.

Results shown in Fig. 4.10 show that for Olivier and Webster soils, the amount of nickel retained by the soil decreased with depth. This is indicative of strong sorption of the Ni applied to the soil surface. This strong sorption was also manifested by the low recovery of Ni from column effluents which were only 18.9% and 50.4% of Ni applied for Webster and Olivier soils respectively (see Table 4.4). The Ni recovery was from the soil digestion using DEENA. For Windsor soil, Ni sorbed in the soil increased with depth (Fig. 4.10). This pattern indicates downward movement of nickel from the soil surface to lower depths, i.e., a leaching pattern. These distribution results are in agreement with our batch experimental data, where Windsor soil exhibited lowest affinity for Ni retention and thus higher mobility of Ni in Windsor soil column was expected. This is in contrast to the observed high amount of Ni retained near the soil surface for Webster soil due to its high retention capacity for Ni. Such accumulation patterns were observed by Sukkariyah et al. (2005) for Ni, Cu, and Cd in a clay loam soil. Based on their results, they concluded that the movement of trace metals through the soil profile is negligible and there is little risk of contamination of the ground water at their experimental site.

The MRTM model was utilized in a predictive mode to predict the amount of Ni sorbed with depth shown in Fig. 4.10. For modeling purposes, we regarded these results as an independently measured data set where the extracted Ni from the soil was assumed to represent the total amount of Ni sorbed (S). No inverse modeling was carried out here, rather these predictions we utilized were obtained using previously derived model parameters that provided best descriptions of Ni BTCs. As illustrate in Fig. 4.10, the distribution of Ni retained in soil depth described by the model. We recognize that Ni concentration in effluent and retained in soil column are not strictly independent. However, for predictive modeling, one may regard the as quasi independent. Although improvement in prediction capabilities are needed, the use of the nonlinear multireaction model presented here is recommened for providing estimates of the levels of Ni retained by the soil with depth.

The movement and distribution of Ni in the soil profile is of considerable interest due the potential contamination of land and water resources. Two patterns for the movement of Ni in soils have been observed: a leaching pattern (downward movement) and accumulation pattern (heavy metal retained near the surface soils). In the accumulation pattern, Ni is strongly sorbed by the soil matrix (Sukkariyah et al., 2005). Therefore it is believed that irreversible or slowly reversible mechanisms are dominant with little release of heavy metals with time. This pattern was observed by Sukkariyah et al. (2005) who investigated the distribution and mobility of Ni in a clay loam soil. They reported that due to a one time application of biosolids from a wastewater treatment plant some 17 y earlier, 85% of Ni applied remained near the surface (0-10 cm).

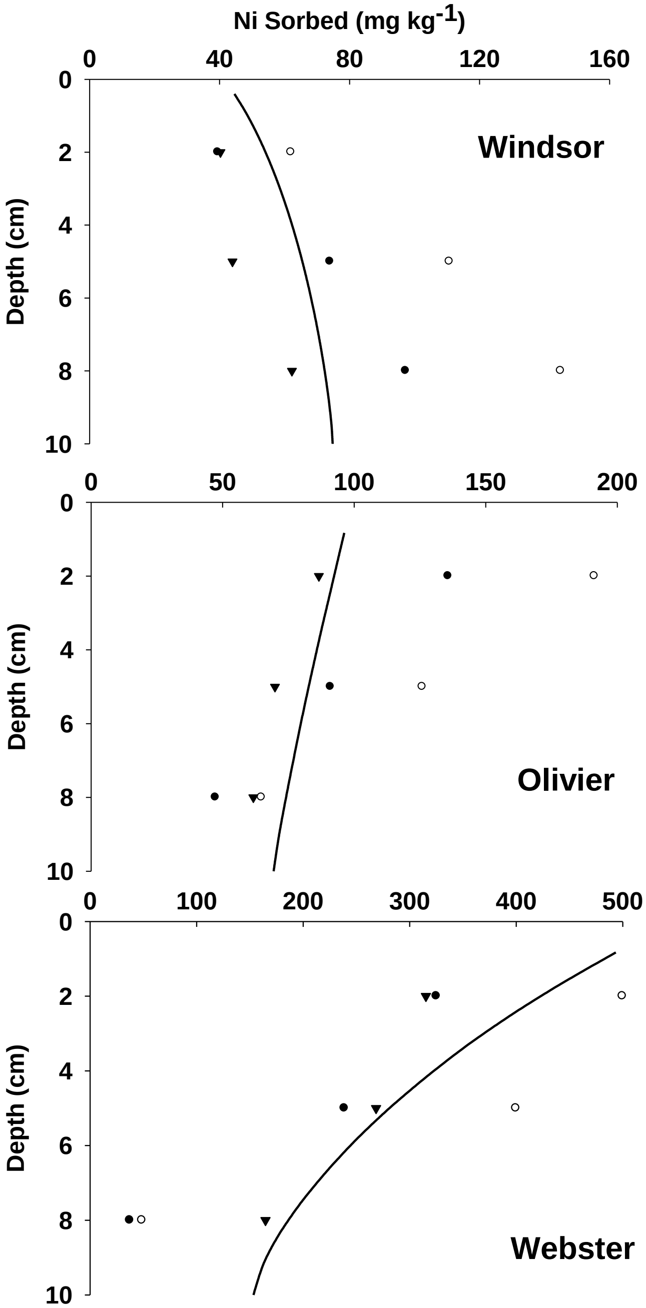

Figure 4.10. Distribution of Ni concentration with depth in the columns of Windsor, Olivier and Webster soils. Solid lines are MRM predictions and symbols are measured Ni extracted by digestion of soils after the termination of transport experiment.

On the other hand, Antoniadis and Alloway (2003) reported that there is a risk of heavy metal movement downward in the soil profile in cases of excessive loading of heavy metals which are considered “mobile”, e.g., Cd, Ni, and Zn, and where heavy metals have been applied on low sorptive capacity soils. In their study, downward movement of Ni to 80 cm of soil profiles was observed where sludge was deposited for decades on a sandy soil. The evaluation of Ni mobility was also related to adsorption and desorption parameters in 21 soils (Businelli et al., 2009). They concluded that adsorption with strong hysteresis (irreversible or partially reversible) limited the leaching of heavy metal through the soil profile. In contrast, when adsorption is not completely hysteretic, there is potential mobility and risk of groundwater (leaching through soil profile). These findings are consistent with our results, where Windsor sandy soil having the lowest affinity for Ni exhibited a leaching pattern whereas Oliver loam and Webster loam soils, with higher affinities, exhibited an accumulation patterns. Moreover, both patterns were well described by the MRM model.

4.5 Summary

In summary, we evaluated the nonlinear equilibrium kinetic MRM for its prediction capability of Ni retention as well as transport in three soils having different soil properties. Results from kinetic batch experiments indicated that Ni sorption by all soils was highly nonlinear and time independent. Based on MRM predictions, the use of two concurrent, nonlinear reversible and one irreversible is recommended for describing Ni kinetic sorption by soils. Column transport experiments indicated extensive Ni retardation followed by slow release of the BTCs. The extent of Ni retardation during the solute transport followed the sequence of Windsor < Olivier < Webster. The inverse MRM provided a good prediction of Ni transport in soils and it is capable for describing Ni distribution with depth in soil columns.

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CHAPTER 5: COMPETITIVE KINETICS OF NI AND CD ADSORPTION AND DESORPTION IN SOILS

5.1 Introduction

Application of fertilizers, sewage sludge, liming materials, and industrial waste materials introduces nickel into the natural environment and frequently causes other contaminates to be co-deposited (McIlveen and Negusanti, 1994). Therefore simultaneous presence of several heavy metals is common in contaminated soils. This situation can create considerable difficulty in assessing the impact of heavy metals contamination if only a single element in contaminated soils is considered. In this study the focus is Ni and Cd competitive kinetics of adsorption and desorption. These two heavy metals were chosen because they are considered relatively mobile in the soil and water environments (Tang and Lo, 2006; Atanassova, 1999).

The competitive sorption of Cd and Ni at equilibrium (short term) condition has been extensively investigated (Echeverría et al., 1998; Antoniadis and Tsadilas, 2007; Vega et al., 2009; Voegelin et al., 2001). However, there is no agreement on the selective preference of these two trace metals. The selective preference of heavy metal sorption was found to be related to several factors, including charge to radius ratio, electronegativity, softness parameter, and first hydrolysis constant (Tsang and Lo, 2006; Sposito, 1989; Echeverría et al., 1998; Antoniadis and Tsadilas 2007). According to the ionic radius and ionization potential for metal to form covalent bonds, Sposito (1989) defined selective preference of Cd over Ni. Echeverría et al. (1998) and Antoniadis and Tsadilas (2007) reported that Ni adsorption was stronger than Cd, which was related to hydrolysis of divalent ions capable of forming inner-sphere complexes with clay lattice edges. Schulthess and Huang (1990) showed that Ni adsorption by clays is strongly influenced by pH as well as silicon and aluminum oxide surface ratios. Voegelin et al. (2001) pointed out that greater difference in the sorption behavior of Cd and Ni must be expected at neutral to basic condition compared to that in acidic condition.

Most of above studies focused on competitive effect on adsorption. Few studies investigated the competitive effect on desorption or release of heavy metal soils, however, adsorption and desorption isotherms, together, show whether sorption is irreversible or partially irreversible. Often, desorption and adsorption isotherms fail to coincide, thus showing hysteresis (Kan et al., 1994; Strawn et al, 1999; Vega et al., 2009). Competiton may also affect observed hysteresis. Atanassova (1999) found that there is competitive effect which enhanced the release of heavy metals at low affinity sites. This finding was based on investigation of competitive effect of Cu, Zn, Cd and Ni on adsorption and desorption in soil clay fraction of Bulgaria soils. Moreover, whatever for desorption or adsorption, the utility of results from short duration (equilibrium) studies for accurately describing kinetic (time-dependent) behavior of heavy metal in soil environment were questioned (Voegelin et al., 2001, Pang and Close, 1999).

Kinetic or time-dependent sorption of Cd and Ni behavior were frequently observed and related to soil heterogeneity, slow diffusion to reaction sites within the soil matrix, rate-limited reactions and precipitation at mineral surfaces (Voegelin and Kretzschmar, 2005; Pang and Close, 1999; Jeon et al., 2003; Eric et al., 2001). Jeon et al. (2003) reported that Ni and Cd kinetic sorption by hematite was instantaneous followed by a relatively slow stage that continued for 5 days, reported by. Also they found that the extent of retention of metal ions by hematite was Ni > Cd. Under neutral to alkaline conditions, Ni was found to form multinuclear complexes on several mineral phases including Pyrophyllite, Montomorillite, gibbsite, Illite, Kaonilite and even on natural soils using extended X-ray fine structure (EXAFS) spectroscopy (Eric et al., 2001; Scheidegger et al., 1996; Scheidegger et al, 1998). Moreover, this slow buildup of multinuclear complex was highly time-dependent and irreversible or weakly reversible. Such a slow release or no release was observed following leaching by dilute HNO_3 at pH 3 when competitive ions were absent. However, Voegelin and Kretzschmar (2005) observed that Ni nucleate complex became relative non-stable and easier to be dissolved in presence of Zn compared to that in the absence of Zn in column experiment. The rate-limited sorption may give the potential discrepancy on adsorption and desorption of Ni and Cd in the presence and absence of competition.

The purpose of this study was to understand the competitive effect on sorption-desorption kinetics of Ni and Cd in several soils and define their selective preference between Ni and Cd. The multireaction model (MRM) was used to evaluate the competitive effect between Ni and Cd during kinetic sorption in soils. Moreover, a hysteresis index was used to characterize the relationship of adsorption and desorption for Ni and Cd in the presence and absence of competitive ions.

5.2 Materials and Methods

5.2.1 Soils

Surface soils of Olivier loam, Webster Loam, and Windsor sand were used in this study. Olivier loam is a common alluvium soil occurring in the lower Mississippi River basin in Louisiana and southern Mississippi. Webster loam was sampled in Story County, Iowa State. It consists of very deep, poorly drained, moderately permeable soils formed in glacial till or local alluvium derived from till on uplands. Windsor sand is a fine sandy soil formed on glacial outwash plains, deltas of the northeast region of the U.S. Soil samples were air dried and passed through 2 mm sieves for analysis. Soil properties such as soil pH, cation exchange capacity

(CEC), and particle size analysis were determined earlier in previous study (Liao and Selim, 2009) and listed in Table 5.1.

Table 5.1 Selected physical and chemical properties of the soils studied.

Soil		Olivier Loam	Webster Loam	Windsor Sand
pH		5.80	6.92	6.11
TOC[a]	%	0.83	4.03	2.03
CEC[b]	cmol kg^{-1}	8.6	27.0	2.0
Sand[c]	%	5	39	77
Silt	%	89	39	20
Clay	%	6	22	3
Selective extraction by				
Ammonium oxalate (pH 3.0)				
Fe	g kg^{-1}	0.32	0.98	0.36
Al	g kg^{-1}	0.08	0.89	0.69
Citrate-bicarbonate-dithionite (CBD)				
Fe	g kg^{-1}	4.09	4.42	3.68
Al	g kg^{-1}	1.29	0.77	3.65

[a] TOC = total organic carbon. [b] CEC = cation exchange capacity. [c] Grain size distribution: sand (2.00-0.05 mm), sslt (0.05-0.002 mm), and clay (<0.002 mm).

5.2.2 Adsorption and Desorption

Kinetic retention using the batch method descried by Amacher et al. (1988) was used to quantify adsorption and desorption isotherms for Ni and Cd by all soils at constant room temperature of 25 °C. Triplicate 3-g samples of each soil were place in Teflon centrifuge tubes and mixed with 30-mL solution. Here reagent-grade $Cd(NO_3)_2$ and $Ni(NO_3)_2$ were used to prepare solutions with different Cd/Ni molar ratios in a background solution of 0.005 M $Ca(NO_3)_2$. Specifically, for Ni initial concentration at 0.10mM, the concentrations of the competing ions (Cd) were 0, 0.047, 0.235, and 0.766 *mM*. As an example, for one set of Ni sorption in the presence of Cd, the amounts of Ni and Cd added, expressed as (*mM* Ni/*mM* Cd) were 0.100/0, 0.100/0.0240, 0.100/0.237, and 0.10/0.760. The mixtures were continuously shaken on a reciprocal shaker and then centrifuged at 5000 g for 10 minutes prior to sampling. After 2, 6, 12, 24, 72, 168, 336 and 504 hours of reaction time (for Windsor and Olivier and extended to 672 h for Webster), a 1-mL aliquot was sampled and was analyzed using ICP-AES (Spectro Citros CCD). Amounts of Ni or Cd sorbed by the soil matrix were determined by the difference between the concentrations of the supernatant and that of the initial solutions.

Desorption or release experiments were conducted to assess the release of nickel as well as the extent of hysteretic behavior of heavy metal in the different soils. Sequential or successive dilutions were initiated immediately after the last adsorption step for all initial concentrations. Each desorption step was carried out by replacing the supernatant, followed by adding 30 mL of 0.005 *M* $Ca(NO_3)_2$ background solution and shaking for 48 h. Six desorption steps were carried out. The amount of Ni released/desorbed was calculated from the difference between concentrations of the supernatant and that of the amount initially sorbed at each desorption step.

5.3 Results and Discussion

5.3.1 Single Element Sorption Isotherms

Single-metal sorption isotherms for Ni and Cd by the three soils, exhibited similarity in shape after 504 h of reaction (Fig. 5.1), which belonged to L type depicted by high nonlinear with strong affinity at low heavy metal concentration loading and low affinity at higher added metal concentration (Sposito, 1989). For Windsor and Olivier soil, the discrepancy between Ni and Cd isotherms at higher concentration level were larger than that at lower concentration. Nonlinearity and competition are often regarded as characteristics of site-specific adsorption processes.

The Freundlich equilibrium approach was utilized to describe the nonlinear adsorption behaviors,

$$S_i = K_i C_i^{n_i} \qquad (5.1)$$

where S_i represents the (total) amount of sorbed (μg kg^{-1}), K_i is the Freundlich distribution or partition coefficient (L kg^{-1}), and n_i is a dimensionless reaction order commonly less than one. Isotherms for Ni and Cd for the three soils were well described by the Freundlich Eq [5.1] with coefficients of correlation *(r^2)* ranging from 0.992 to 0.999 (Table 5.2). The n_i *v*alues for Windsor, Olivier and Webster soil were 0.58, 0.52 and 0.59 for Cd and 0.48, 0.50 and 0.52 for Ni, respectively.

Table 5.2. Estimated Freundlich and SRS parameters for competitive adsorption of Ni and Cd for the different soils.

Soil	Ni Isotherms			Cd Isotherms			SRS parameters §			
	K (L kg^{-1})	*n*	r^2	*K* (L kg^{-1})	*n*	r^2	$\alpha_{Ni\text{-}Cd}$	$\alpha_{Cd\text{-}Ni}$	r^2	RMSE §§
Windsor	5.363 ± 0.452	0.48 ± 0.050	0.992	9.325 ± 0.19	0.58 ± 0.01	0.993	5.07	0.221	0.999	0.015
Olivier	17.053 ± 1.114	0.50 ± 0.026	0.997	20.888 ± 0.70	0.52 ± 0.01	0.999	3.53	0.362	0.996	0.006
Webster	42.998 ± 1.100	0.52 ± 0.007	0.993	27.116 ± 2.06	0.59 ± 0.02	0.997	3.56	11.00	0.979	0.060

§ SRS = Shenindrof-Rebhun-Sheituch parameters. §§ RMSE = Root mean square error.

Figure 5.1 is a representation of single ion isotherms for Ni and Cd for each soil and indicates that Cd adsorption was larger than Ni for Windsor and Olivier soils. This is also well illustrated by the respective K_i values: 9.325 and 5.363 L kg^{-1} for Cd and Ni on Windsor soil, and 20.888 and 17.053 L kg^{-1} for Cd and Ni on Olivier soil (see Table 5.2). Estimated K_i values from the Freundlich equation represent the bonding strength between chemical and sorbent. Higher K_i values indicate higher bonding strength. For Ni and Cd reaction for Olivier and Windsor soils, K_i values for Cd were larger than that for Ni, demonstrating that the bonding strength for Cd by Windsor and Olivier soils were larger than that for Ni. This result was in line with previous study when equilibrium batch was used to estimate the competition of Ni and Cd in soils (Liao and Selim, 2009) and attributed to their ionic radii and chemical properties.

Webster soil with a neutral pH exhibited higher affinity for Ni than Cd (see Fig. 5.1 and Table 5.2). This result was also observed by Antoniadis and Tsadilas (2007). They found that adsorption preference of Ni over Cd on a soil having pH of 6.89, and were related to metal-ion hydrolysis. The *pK* values for metal hydrolysis: $Me^{2+} + H_2O = MeOH^+ + H^+$, are 10.08 and 9.86 for Cd^{2+} and Ni^{2+}, respectively. The lower *pK* value for Ni is indicative of stronger specific sorption (Antoniadis and Tsadilas, 2007). If hydrolysis of metal ions, either in solution or at the soil surface, is a primary adsorption mechanism for metal ions on adsorbent, higher affinity for Ni is expected. Earlier, Gomes et al. (2001) reported an adsorption sequence of Ni > Cd for two soils with pH higher than 6.0. They also reported that, for acidic soils, the adsorption of Cd was larger than Ni which is in agreement with our results illustrated in Fig 5.1. Increased metal sorption with increasing pH is attributed to changes in the hydrolysis state of ions in solution (Harter, 1983; Echeverrí a et al., 1998).

5.3.2 Competitive Effect when 504 h

Ni or Cd competitive adsorption at 504 h in the presence of Cd or Ni respectively were illustrated in Fig. 5.2 for all three soils. Here the amount of ion sorbed (*mmol* per kg soil) is presented versus a range of input concentration of the competing ion. As shown in Figure 5.2 (top), sorption of Ni substantially decreased with respect to concentration increasing of competing Cd present in system. Similar effects due to competitive interactions were observed for Cd when a range concentrations of Ni present (Fig. 5.2 bottom) for all three soils. In general, as the initial metal concentration were increased, competition between metals for exchange sites was enhanced, resulting in decreasing of metal sorbed in competing system compared to that in .

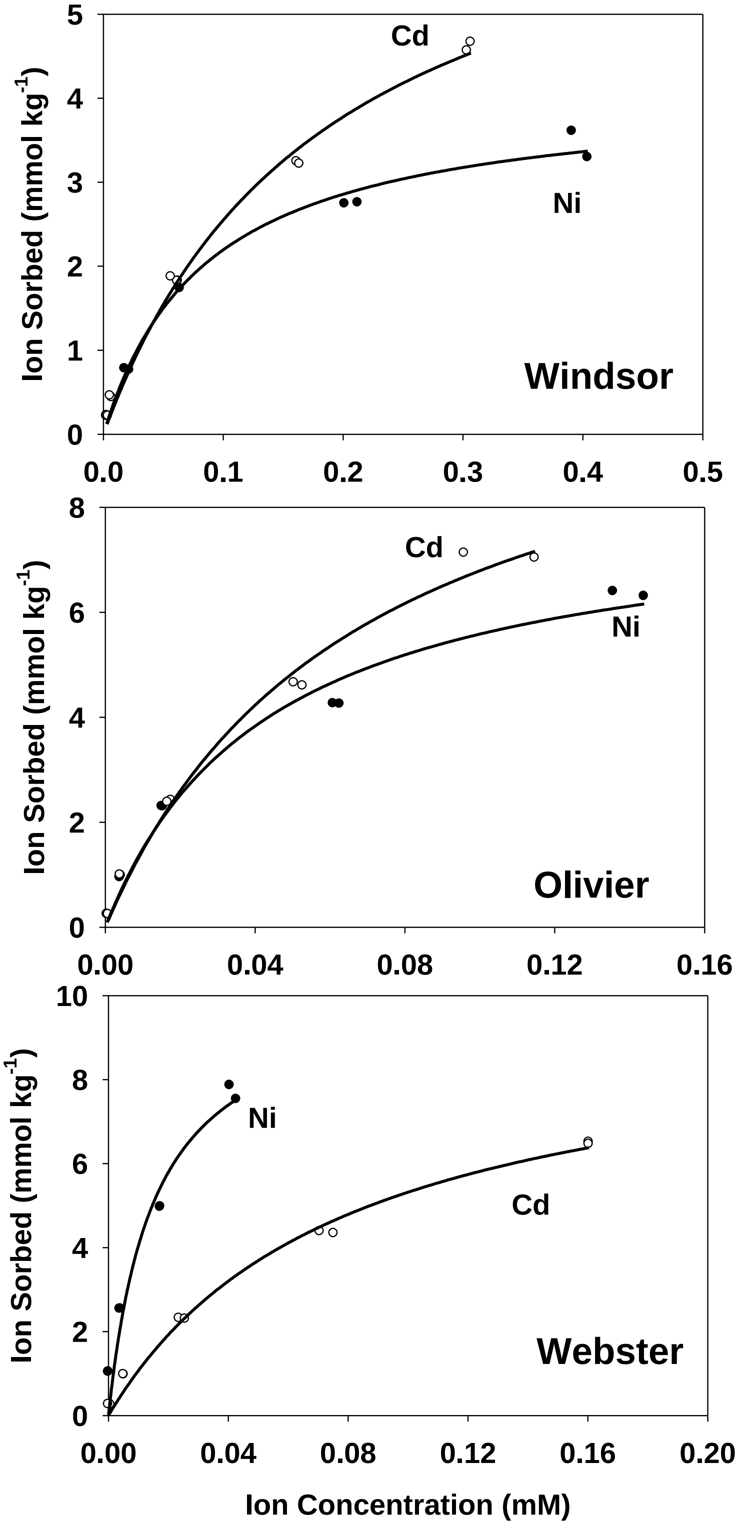

Figure 5.1. Adsorption isotherms for Ni and Cd for Windsor, Olivier and Webster soils. Solid curves are Freundlich model predictions.

single element system (Bibak, 1997). Moreover, for Windsor and Olivier soils the presence of Ni tended to reduce Cd sorption, but to a less degree than that of Cd on Ni sorption, and is indicated by the percent reduction of metals sorption. When 0.760 mM Cd was added, the amounts of Ni adsorbed were reduced by 26.3 and 12.9% for Windsor and Olivier soils, whereas, when 0.760 mM Ni was added, the amounts of Cd adsorption were reduced by 17.3 and 9.3% for Windsor and Olivier soils, respectively.

For Webster soil, the effects of Ni on Cd are stronger than that of Cd on Ni as shown by 2.2% reduction of Ni sorption in the presence of Cd at 0.760mM and 8.0% reduction of Cd sorption in the presence of Ni. These results are in line with earlier studies of competitive equilibrium sorption of 24 h (Liao and Selim, 2009), but the reduction degree is lower than those results (up to 45%) due to initial input concentration lower than that of applied concentration. An excess of surface sites for metal cations negated competition, explaining why the competitive effect was not strong or even not necessarily observed at low heavy metal loading (Tsange and Lo, 2006; Voegelin and Kretzschmar, 2005). Tsang and Lo (2006) also suggested that the competitive effect of sorption depends on the number of available sorption sites and the extent of saturation of those sites by competing ions, so the competing concentration is lower, weaker competitive effect is expected.

When more than one competing ions is present in the solution, Shenindrof-Rebhun-Sheituch (SRS) equation was often used to evaluate the competitive sorption of Ni and Cd in soils (Sheindorf et al., 1981). The derivation of SRS equation is based on the assumption of an exponential distribution of adsorption energies for each component. A general form of the SRS equation can be written as

where the subscripts *i* and *j* denote metal component *i* and *j*, *l* is the total number of components, and $\alpha_{i,j}$ is a dimensionless competition coefficient for the adsorption of component i

$$S_i = K_i C_i \left(\sum_{j=1}^{l} \alpha_{i,j} \ C_j \right)^{n_i - 1} \qquad [5.2]$$

in the presence of component j. The parameters K_i and n_i are the Freundlich parameters representing a single component system i as described in Eq [5.1] above. By definition, $\alpha_{i,j}$ equals 1 when $i = j$. If there is no competition, i.e., $\alpha_{i,j} = 0$ for all $j \neq i$, Eq [5.2] yields a single species Freundlich equation for component i identical to Eq [5.1]. Freundlich K and n given in Table 2 for Cd and Ni isotherms, where no competing ions were present, were utilized as input parameters in the SRS Eq [5.2]. Estimates for best-fit $\alpha_{i,j}$ using nonlinear least square optimization are given in Table 5.2. Generally, the competitive effect suppressed the sorption of Ni and Cd for each other on all soils, whereas the extent of the effect varied for both heavy metal ions and varied among soils. In the presence of Cd, the estimated α for Ni adsorption, were larger than that for Cd on Windsor and Olivier soils, indicating that the suppress effect for Ni was stronger than Cd, that is, Ni was largely affected by Cd compared the effect of Ni over Cd. In contrast, α for Ni adsorption on Webster soil was less than that for Cd, which implies that Ni adsorption on Webster soil was least affected in a competitive Ni-Cd system. These results on Webster soil are in agreement with the competitive sorption reported by Antoniadis and Tsadilas (2007) that Ni was only slightly affected by competition in the presence of Cd. Similar results of competitive effect of Ni and Cd was obtained in earlier study (Liao and Selim, 2009) that Ni was stronger influenced by Cd compared to the suppression effect Ni over Cd for Windsor and Olivier soils. In contrast, for Webster soil, Ni adsorption was less affected in a competitive Ni-Cd system in comparison to the other two soils.

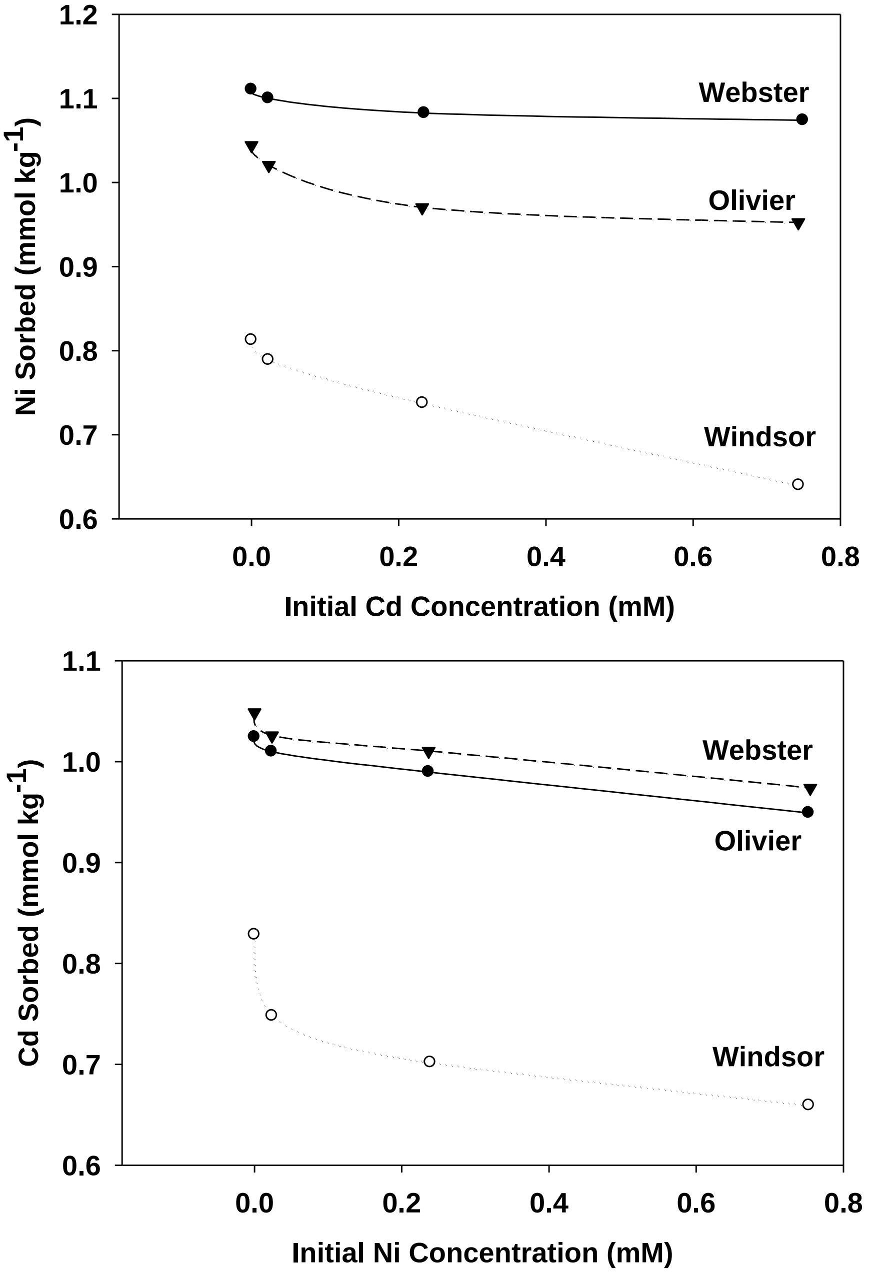

Figure 5.2. Competitive sorption of Ni and Cd in the presence of various input concentrations of competing ion for Windsor, Olivier and Webster soil at 504 h. Top: initial concentrations of Ni was 0.10 *mM*. Bottom: initial concentrations of Cd was 0.10 *mM.*

Another method to quantify competitive sorption was the relative preference estimated by selectivity coefficient, which may be expressed as

$$K_{Ni-Cd} = \frac{S_{Ni}C_{Cd}}{S_{Cd}C_{Ni}} \tag{5.3}$$

where $K_{Ni\text{-}Cd}$ is the selectivity coefficient of Ni over Cd; S represents the amount of adsorption of metal ion on the soil; C is the metal concentration in solution. Selectivity coefficient $K_{Ni\text{-}Cd}$ is less than 1, which indicated preferential adsorption of Cd over Ni. From Fig. 5.3, the average values of $K_{Ni\text{-}Cd}$ for Windsor and Olivier soils were less than 1, representing that selective adsorption of Cd over Ni. However, preferential adsorption Ni over than Cd was observed for Webster soil with the $K_{Ni\text{-}Cd}$ values larger than 1. These results were consistent with competitive coefficient derived from SRS equation for Ni and Cd mention above and reported by Liao and Selim (2009), represented that Ni is preferential element than Cd for Webster soil, therefore less affected by Cd in competing system.

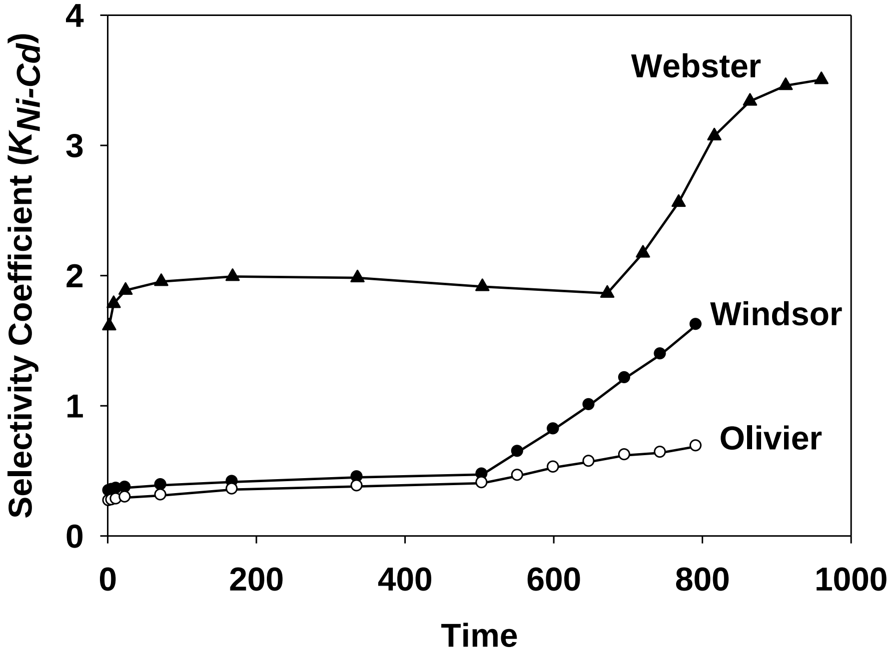

Figure5. 3. Selectivity coefficients of Ni over Cd as a function of reaction time for Webster, Olivier and Windsor soils at Ni/Cd concentration ratio of 0.10/0.237 mM.

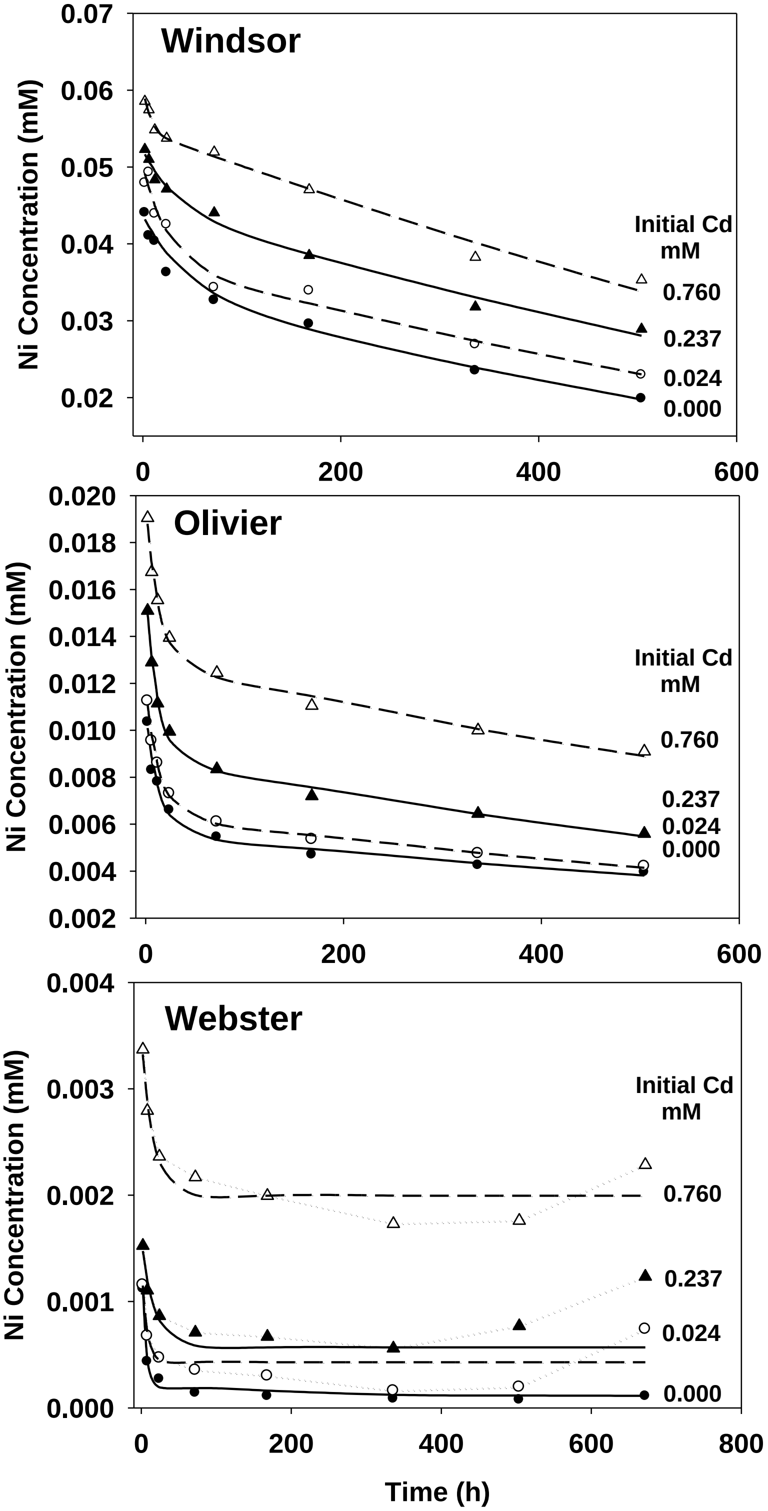

Figure 5.4. Ni concentration in solution with reaction time in the presence of various concentrations of input Cd. The initial concentration of Ni was 0.10 mM. The lines were the results from MRM simulation.

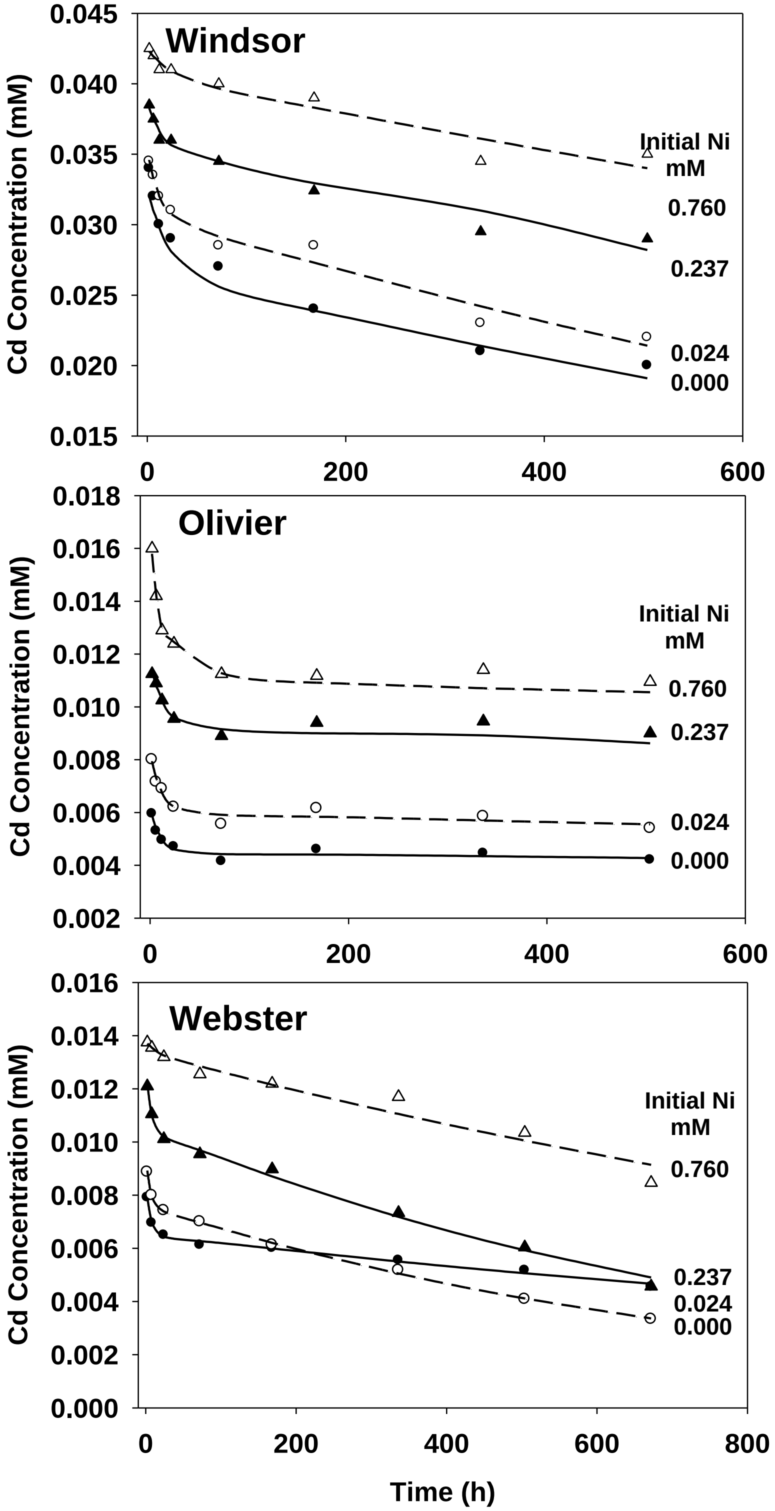

Figure 5.5. Cd concentration in solution with reaction time in the presence of various concentrations of input Ni. The initial concentration of Cd was 0.10 mM. The lines were the results from MRM simulation.

Competition for specific adsorption sites is likely the major cause for the observed competitive or selective preference between Ni and Cd sorption behavior. In acidic soils (Windsor and Olivier), the electronegativity (X) values and conventional hard-soft acid-base (HSAB) principle showed that selective preference Cd over Ni (Liu et al., 2006; Sparks, 1995; Puls and Bohn, 1988). Whereas, for Webster soil, the hydrolysis condition is the main reason (mentioned above) for adsorption of Ni and Cd, adsorption preference of Ni is expected (Antoniadis and Tsadilas, 2007).

5.3.3 Competitive Kinetics

To account for competitive kinetics, the time dependent sorptions of Ni or Cd at initial concentration of 0.10mM in the presence of various concentrations of competing ions are shown in Fig. 5.4 and 5.5. In general, as the concentration of Cd increased in a competing system, Ni sorbed by all soils was significantly reduced. Similarly, the extent of Cd sorbed by all three soils was decreased as concentration of Cd in the applied solution increased (Fig. 5.5). These competitive effects also exhibited strong time-dependent behavior for either Cd or Ni sorption on the three soils. As mentioned above, the competitive effect of sorption depends on the extent of saturation of sorption sites by competing ions (Smith et al., 2002). This saturation process occurred either by applying high concentration of metals or low concentration for continuous reaction for longer time.

An important mechanism for kinetics behavior of heavy metal is its diffusion into soil matrix, which was due to two-phase process: reaction occurring instantly on liquid-mineral interfaces and slow penetration or intraparticle diffusion. In our study, the reaction time ranged from 2 h to 3 weeks, the soils matrix was continuously absorbing Ni or Cd in mono- and binary system, which indicated that sorption sites were not saturated in short terms and slow penetration diffusion occurred. Therefore, Ni or Cd reaction with soils exhibited highly time-dependent in competitive system and in single element system.

The extent competitive effect with time varied among the different soils. Fig 5.3. clearly demonstrates that selectivity coefficients did not change over time for Windsor and Olivier, and implied that the selective preference did not change between Ni and Cd for Windsor and Olivier soils with time. Whereas the coefficient of $K_{Ni\text{-}Cd}$ for Webster soil increased at first several adsorption steps following a plateau and then slightly decreased after 336 during adsorption. This decrease of $K_{Ni\text{-}Cd}$ after 336 was due to Ni concentration increased after 336 h in binary system, which was illustrated by Fig. 5.4 (Webster soil). This Ni concentration increasing in solution was not observed in the absence of Cd. Some scientists proposed that Ni may form poly-nuclear surface complexes on mineral phase at alkali condition or neutral pH (Scheidegger et al., 1996). And further evidence from XAFS scatter scan proved that induced Ni-Al layered double hydroxide (Ni-Al LDH) was formed after 48 hours and developed with time on mineral, clay fraction and whole soils at pH higher than 7 (Eric et al., 2001; Scheidegger et al., 1996; Scheidegger et al, 1998). But the above studies were based on single element condition. The competitive effect may slow down the nuclear process or facilitate the release Ni during sorption. Voegelin and Kretzschmar (2005) investigated formation and dissolution of single and mixed Zn and Ni precipitates in soil by using column and XAFS techniques. They found that only 23% of the retained Ni was leached in experiments with Ni alone, whereas 87% of the retained Ni were released upon acidification in the presence of Zn. EXAFS analysis revealed that the Zn-Ni LDH phases formed in the Ni-Zn mixed condition had been completely dissolved, while the LDH phase formed in the Ni only condition was still present. This finding indicated that competitive effect facilitates the release of nucleate complexes of Ni.

In our study, the release of Ni was observed during competitive sorption represented by Ni concentration increased in solution after 336 h (Fig. 5.4). The above experiment was conducted at input concentration of 0.10 mM for Ni and 0.760 mM to 0.023 mM for Cd. Ni concentration jump as describing above was not observed in system containing 0.760 mM Ni and 0.10 mM Cd (not shown). An excess of surface sites for metal cations negated competion, explaining why the competitive effect was not necessarily observed at low heavy metal concentrations (Tsang and Lo, 2006). Here in the circumstance of selective preference Ni over Cd on Webster soil and Cd concentration is relatively low compared that of Ni, the weaker competitive effect of Cd on Ni sorption was expected. But, we need to point out that, in considering Cd, comparatively weakly sorbing ion than Zn and no evidence showed that Cd can form nucleate precipitation on soils or any minerals, further studies and evidence needed for sure whether Ni nucleate process will be slowed down or the release of Ni nucleate form will be facilitated in the presence of Cd.

5.3.4 Competitive Effect Evaluated by MRM

Multireaction model along with a nonlinear least-squares optimization (Zhang and Selim, 2006) was utilized to describe the kinetic results for Ni and Cd for three soils in the presence or in the absence of competing ion, the simulation results of which were visually illustrated by the lines shown in Fig. 5.4. This multipurpose model accounts for several concurrent and consecutive type retention reactions of heavy metals in soils, include equilibrium and kinetic mechanisms of the reversible and irreversible types, which can be presented by the following formulation:

$$S_e = k_e\left(\frac{\theta}{\rho}\right)C^n \qquad (5.4)$$

$$\frac{\partial S_k}{\partial t} = k_1\left(\frac{\theta}{\rho}\right)C^m - [k_2 + k_3]S_k \qquad (5.5)$$

$$\frac{\partial S_s}{\partial t} = k_3 S_k \qquad (5.6)$$

$$\rho\frac{\partial S_{irr}}{\partial t} = k_{irr}\theta C \qquad (5.7)$$

where S_e is the amount retained on equilibrium-type sites (mmol/kg) and has a low binding energy, S_k is the amount retained on kinetic-type sites (mmol/kg) through strong interactions with the soil matrix, and S_s and S_{irr} represent the amount retained irreversibly (mmol/kg). The coefficient k_e is an equilibrium constant (dimensionless) associated with instantaneous reactions, whereas k_1 and k_2 (h^{-1}) are the forward and backward reaction rate coefficients associated with the kinetic-type sites, respectively. The parameter k_3 (h^{-1}) is the irreversible rate coefficient associated with the kinetic sites and k_{irr} (h^{-1}) is the irreversible rate coefficient associated with the soil solution. The parameters n and m are the reaction orders (dimensionless) associated with S_e and S_k, respectively, θ is the soil water content (cm^3/cm^3), and ρ is the soil bulk density (g/cm^3). We assumed m = n and was derived from Freundlich parameter N given in Table 5.2 for all three soils.

The goodness of fit and estimated parameters with a range concentration of competing ions was listed in Table 5.3 and 5.4. In previous chapter, we evaluated nine model variations of MRM with a number of reactions, we found that nonlinear reversible along with consecutive or concurrent irreversible reaction were the dominant mechanisms for describing time-dependent Ni retention in soils. Earlier study (Selim et al., 1992) of Cd transport and retention also compared model variation to describe Cd retention in soils, which concluded that five-parameter variations consisting of one reversible and one irreversible mechanism provided better predictions of Cd time-dependent behavior based on r^2 and RMSE. The kinetic sorption of Cd in this study was well described by several MRM model variations, which resulted in similar predictions. We finally utilized a simpler variation with nonlinear reversible along with consecutive irreversible reaction to describe Cd retention as compared with Ni time-dependent sorption behavior. From Table 5.3 and 5.4, either in single element or in binary element system, k_e values of Ni kinetic adsorption are lower than those of Cd for Windsor or Olivier soils, whereas the values for Webster soil showed the opposite trend that is k_e values for Ni are higher than those for Cd. The effect of the presence of Cd at different concentration on competitive Ni sorption is well depicted by the multireaction model. The rate coefficients k_e associated with reversible reaction (S_e) for Ni on all three soil exhibited significant decrease as Cd concentration in solution increased. This Ni concentration decrease in solution with Cd applied increasing was well illustrated by Fig 5.4, in which, the lines were the simulation form MRM.

Table 5.3. Estimated MRM parameters for the kinetic adsorption of nickel in the presence of various concentrations of Cadmium

Cd_o^a mM	Ke	k_1 h^{-1}	k_2 h^{-1}	k_3 h^{-1}	r^2
Windsor					
0	1.47±0.04	0.0009±0.0004	0.0163±0.0109	0.0035±0.0016	0.998
0.024	1.35±0.07	0.0017±0.0008	0.0304±0.0178	0.0029±0.0008	0.997
0.237	1.26±0.07	0.0008±0.0004	0.0223±0.0134	0.0047±0.0015	0.999
0.760	1.00±0.07	0.0021±0.0021	0.1050±0.0910	0.0079±0.0030	0.999
Olivier					
0	3.58±0.03	0.0057±0.0005	0.0470±0.0044	0.0016±0.0002	0.999
0.024	3.50±0.05	0.0059±0.0008	0.0467±0.0070	0.0014±0.0003	0.998
0.237	3.10±0.03	0.0062±0.0006	0.0564±0.0052	0.0018±0.0002	0.999
0.760	2.79±0.04	0.0043±0.0008	0.0561±0.0097	0.0019±0.0003	0.999
Webster					
0	6.84±0.10	0.0254±0.0006	0.0308±0.0047	0.0013±0.0000	0.938
0.024	6.94±0.53	0.0124±0.0037	0.0397±0.0067	0.0039±0.0007	0.940
0.237	6.44±0.50	0.0110±0.0048	0.0292±0.0012	0.0000±0.0000	0.951
0.760	5.27±0.22	0.0096±0.0006	0.0696±0.0033	0.0016±0.0000	0.999

Similar competitive effect of Cd kinetic retention in the presence of Ni was also observed and demonstrated in Table .4 and Fig. 5.5. This S_e is the amount retained on equilibrium-type sites associated with a low binding energy. The coefficient k_e is an equilibrium constant (dimensionless) associated with instantaneous reactions, so competition of Ni and Cd on this site is expected. Values of kinetic coefficient of k_1 were relatively stable with concentration change of competing ions for Windsor and Olivier. However, this value for Webster decreased as competing ion in solution increased for both Ni and Cd sorption. k_1 is the forward reaction rate coefficients associated with the kinetic-type sites. Decreasing of this value implied that less Cd or Ni was absorbed on soils due to competitive effect.

Table 5.4. Estimated MRM parameters for the kinetic adsorption of cadmium in the presence of various concentrations of nickel

Ni_o^a mM	Ke	k_1 h^{-1}	k_2 h^{-1}	k_3 h^{-1}	r^2
Windsor					
0	1.94±0.05	0.0014±0.0006	0.0366±0.0173	0.0030±0.0009	0.999
0.024	1.82±0.06	0.0018±0.0010	0.0682±0.0351	0.0045±0.0017	0.998
0.237	1.73±0.08	0.0010±0.0013	0.0546±0.0074	0.0019±0.0016	0.997
0.760	1.57±0.06	0.0014±0.0001	0.0325±0.0067	0.0063 ± 0.0008	0.998
Olivier					
0	7.29±0.35	0.0027±0.0003	0.0183±0.0027	0.0000±0.0000	0.970
0.024	4.51±0.11	0.0055±0.0019	0.0709±0.0194	0.0005±0.0002	0.998
0.237	4.02±0.07	0.0046±0.0013	0.0667±0.0162	0.0006±0.0003	0.999
0.760	3.59±0.05	0.0025±0.0008	0.0570±0.0150	0.0002±0.0001	0.999
Webster					
0	4.00±0.08	0.0072±0.0022	0.1240±0.0249	0.0048±0.0003	0.999
0.024	3.75±0.25	0.0071±0.0008	0.1400±0.0111	0.0046±0.0020	0.995
0.237	3.34±0.12	0.0055±0.0035	0.1360±0.0586	0.0049±0.0014	0.998
0.760	3.30±0.05	0.0004±0.0001	0.0554±0.0425	0.0069±0.0026	0.998

5.3.5 Desorption Hysteresis – Effect of Competition

Following the last step of adsorption, metal ions retained by the soils was desorbed by successive dilution with Ni or Cd free solution. The release curves of metal ions were presented as the concentration in solution of metal ions vs the amount of metal ions retained by soils in the presence of various concentrations of competing ions (Fig. 5.6 and 5.7). The competitive effect was that it suppressed the adsorption of Ni or Cd in the soils, whereas, the competitive effect enhanced the release of Ni or Cd from soils were well illustrated by Fig 5.6 and 5.7. At the same initial input concentrations of 0.10 mM Ni or Cd respectively, the amount of Ni or Cd retained by each soil was significantly decreased with the applied competitive ions concentration increased, represented that more Ni or Cd was released in competitive system compared that in single element system. Sorption and desorption isotherms, together, show whether sorption is reversible or, on the contrary, wholly or partially irreversible (hysteresis). The discrepancy between adsorption isotherms is larger, which indicated that hysteresis is stronger (Kan et al., 1994; Strawn et al, 1999; Vega et al., 2009). Due to competitive effect, additional metal was released compared to that in the absence of competition, which may cause less discrepancy between adsorption and desorption isotherms under competitive effect. Therefore, the hysteresis could be diminished upon competitive effect.

The families of desorption isotherms of Ni or Cd by Olivier soil were given out as an example to illustrate the hysteresis behavior at single and binary system (Fig. 5.8 and 5.9). According to the concept of hysteresis (Kan et al., 1994; Strawn et al, 1999), if heavy metal sorption was fully reversible, desorption isotherms would not be significantly different from the corresponding sorption isotherms. From Fig. 5.8 and 5.9, in the presence of competing ion Ni or Cd at 0.10mM respectively, the hysteresis is weaker compared to that in the absence of competing ions. This is well depicted by the degree of discrepancy between sorption and desorption isotherms in Fig 5.8 and 5.9.

Some indices were proposed to account for sorption hysteresis as based on the following prosperities: sorbed concentration, Freundlich equation dimensionless coefficient n, the bulk distribution coefficient Kd and the area between the sorption and desorption isotherms,

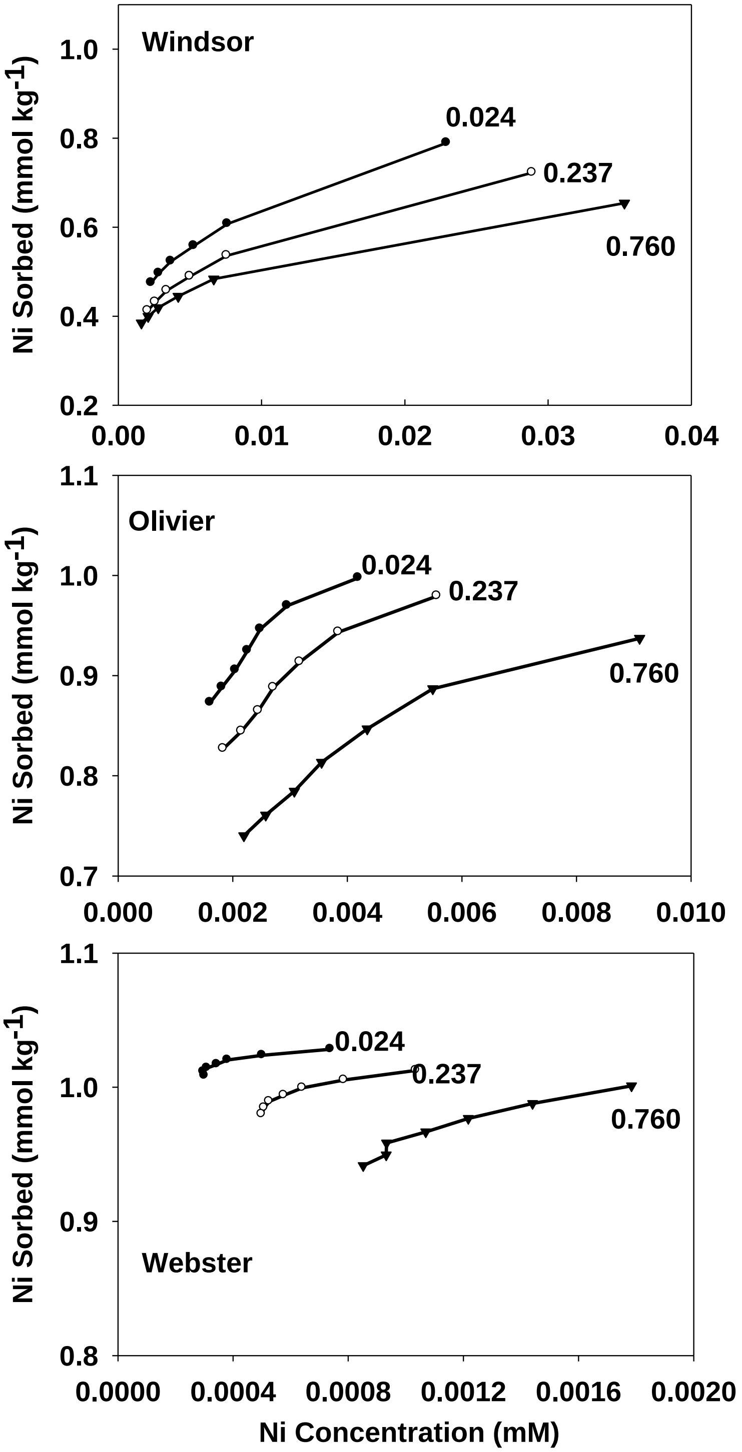

Figure 5.6. Desorption isotherms of Ni in the presence of various concentrations of input Cd for Windsor, Olivier and Webster soils. The initial concentration of Ni was 0.10 mM.

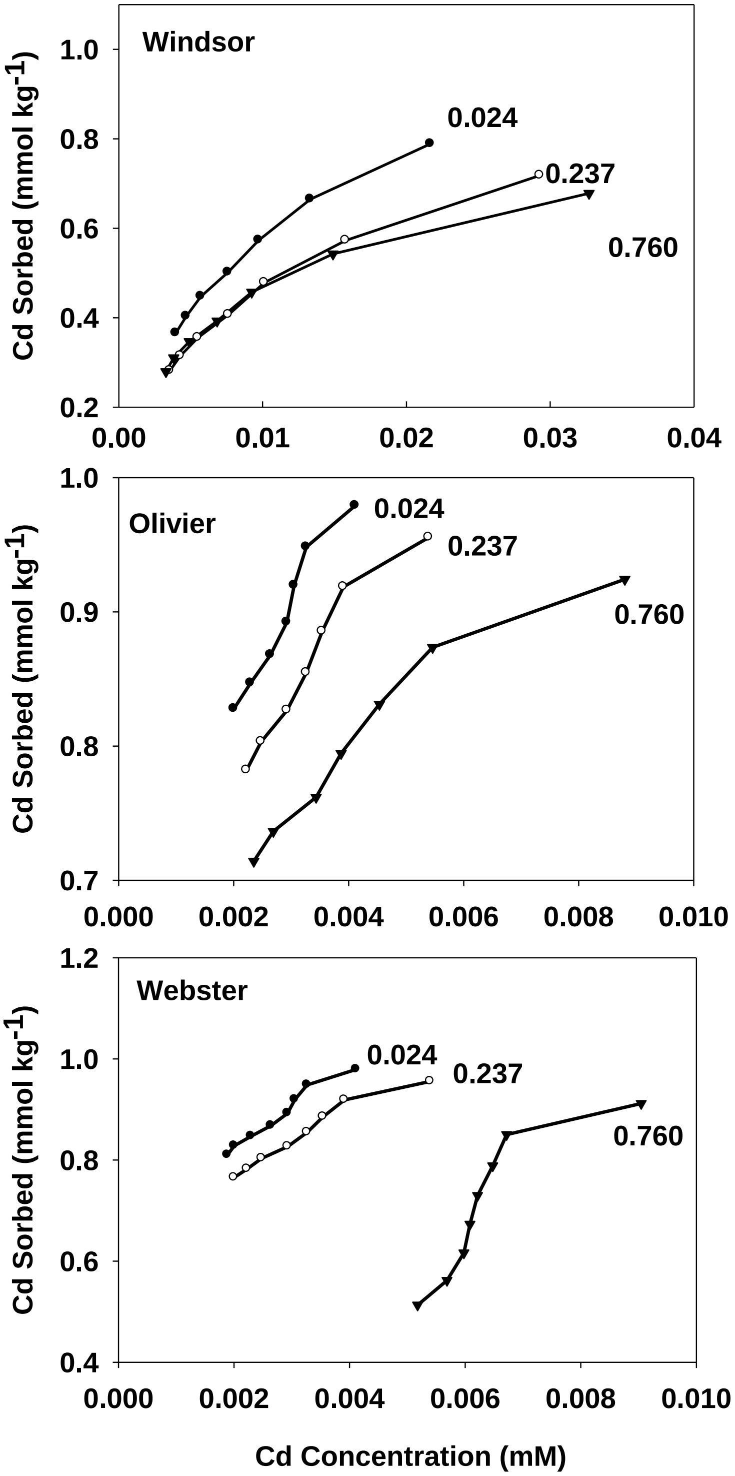

Figure 5.7. Desorption isotherms of Cd in the presence of various concentrations of input Ni for Windsor, Olivier and Webster soils. The initial concentration of Cd was 0.10 mM.

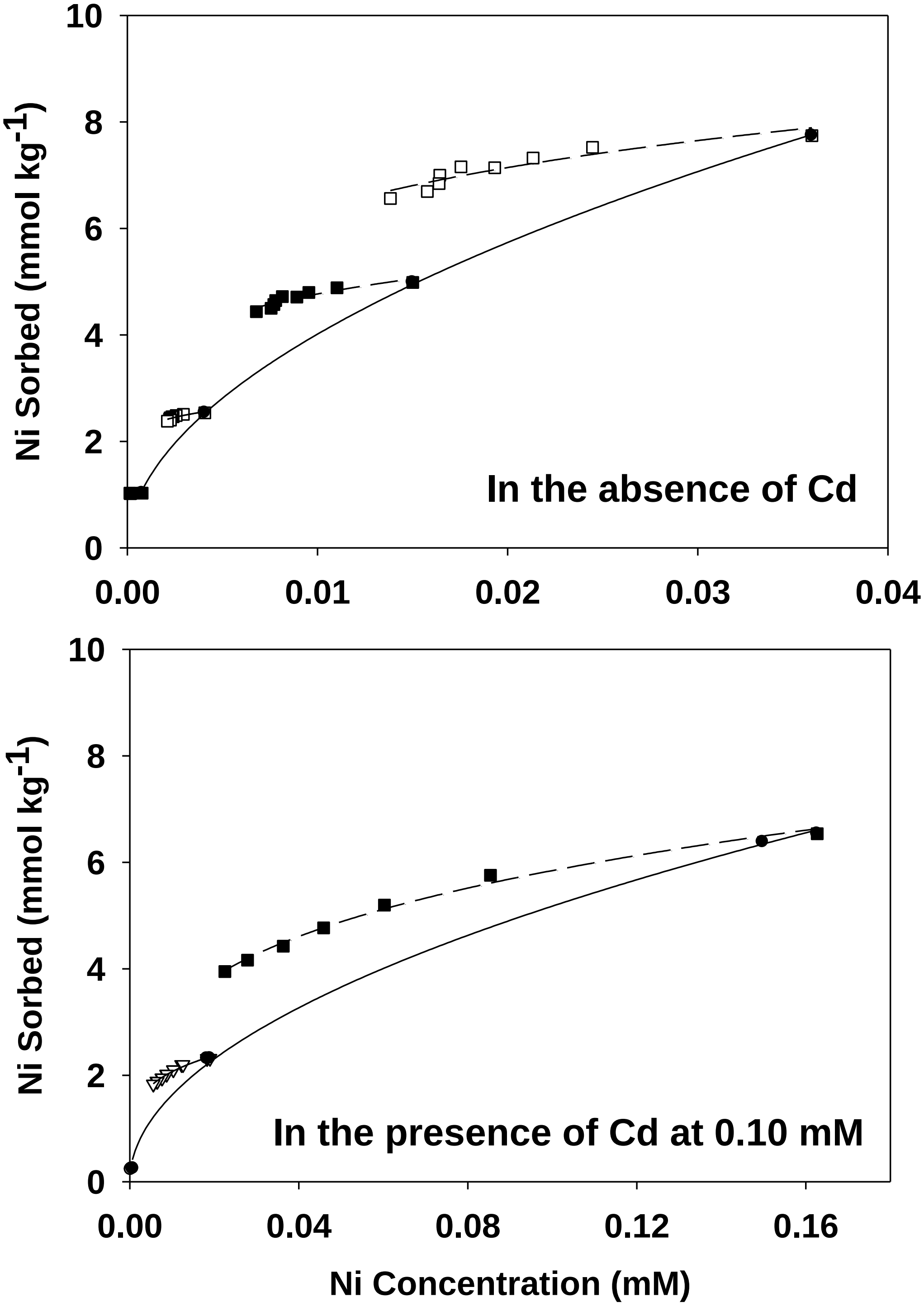

Figure 5.8. Adsorption-desorption hysteresis of Ni by Olivier soil in the absence (Top) and presence of Cd (Bottom). The solid curve is the adsorption isotherms at 504 h. The dash lines are desorption isotherms. Symbols are for different initial concentrations.

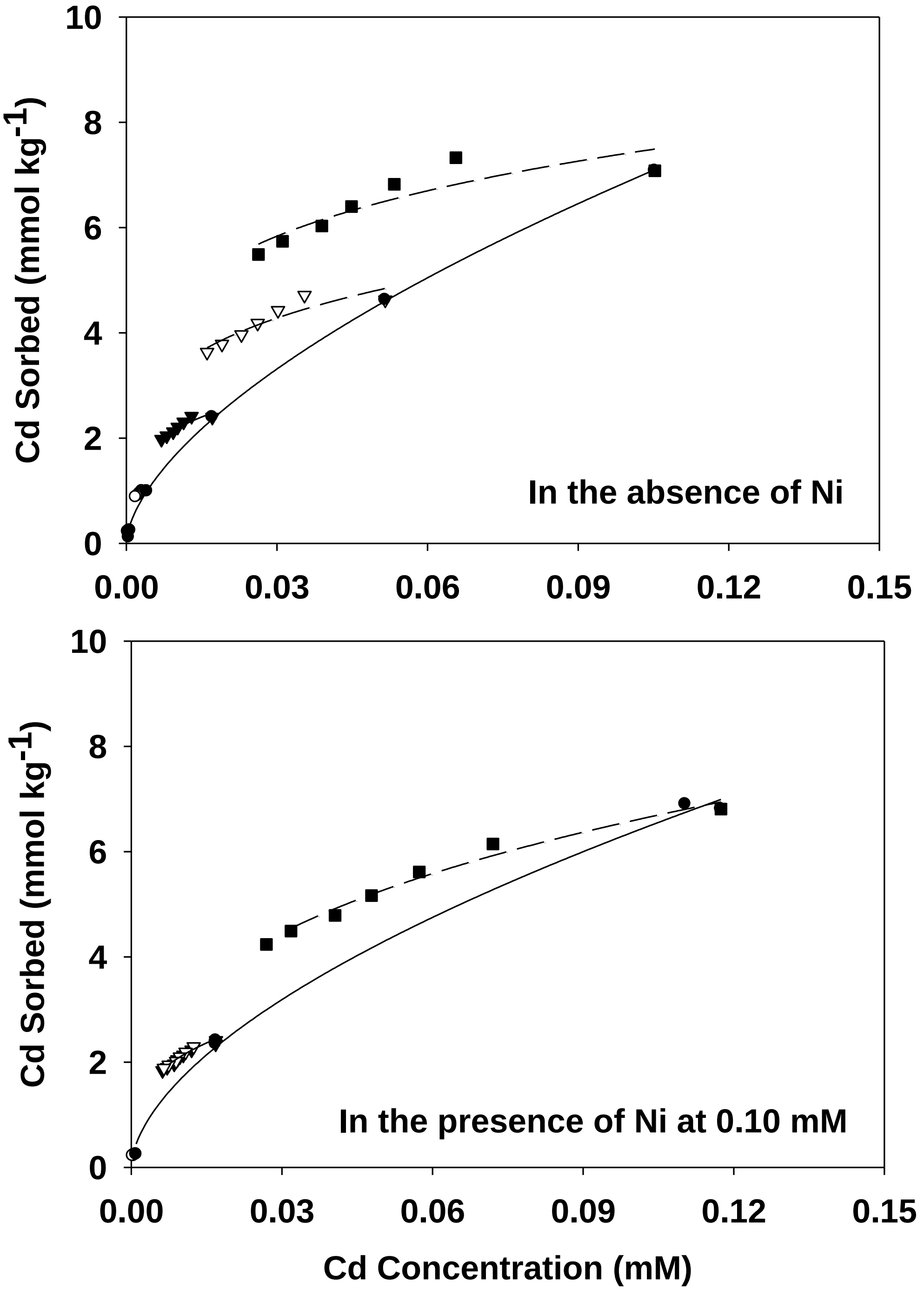

Figure 5.9. Adsorption-desorption hysteresis of Cd by Olivier soil in the absence (Top) and presence of Ni (Bottom). The solid curve is the adsorption isotherms at 504 h. The dash lines are desorption isotherms. Symbols are for different initial concentrations.

which was described by Vega et al. (2009). They recently proposed a hysteresis index (HI) to evaluate and to compare the hysteresis of the sorption of Cd, Cu and Pb form single metal and multi-metal solution. HI was defined as

$$HI = \frac{Kr}{Ks} \tag{5.8}$$

Where Ks were defined as the slope of a regression equation

$$Ks = \frac{Ss}{Si} \tag{5.9}$$

Ss is the amount of metal sorbed (mmol kg^{-1}) by soil at equilibrium, and Si is the initial input amount of metal, the amount of metal in the solution before contact with the soil, likewise per gram of soil. Ks is dimensionless and varies from 0 for totally nonsorbed soils to 1 for an ideal soil that completely eliminates metal form solution. Kr is defined as the associated value from heavy metal retained on soil after desorption. Kr is then 0 for a soil that completely releases all sorbed metal. HI would be unity if sorption were totally irreversible and zero if all sorbed metal were released. By using HI, we estimated the hysteresis change of heavy metal reaction with soils in the presence of competitive ions. In this study, we calculated Ks based on the amount of metal sorbed at last step of sorption and Kr based on last step of desorption. The calculated HI was presented against various concentrations of competitive ions applied in solution, shown in Fig. 5.10. All of HI for all soils are far larger than 0 and less than 1, implying that Ni sorption by all soils are partially irreversible, but the degree of hysteresis vaired among soils. The average of HIs of Ni for Webster soil were highest among soils and close to 1, which indicated that Ni sorption by Webster soil exhibited strongest hysteresis and much more irreversible than that for Olivier soil. Sorption-desorption hysteresis of Ni for Windsor is much weaker than other two soils. HIs for Cd followed the sequence of Windsor < Webster < Olivier.

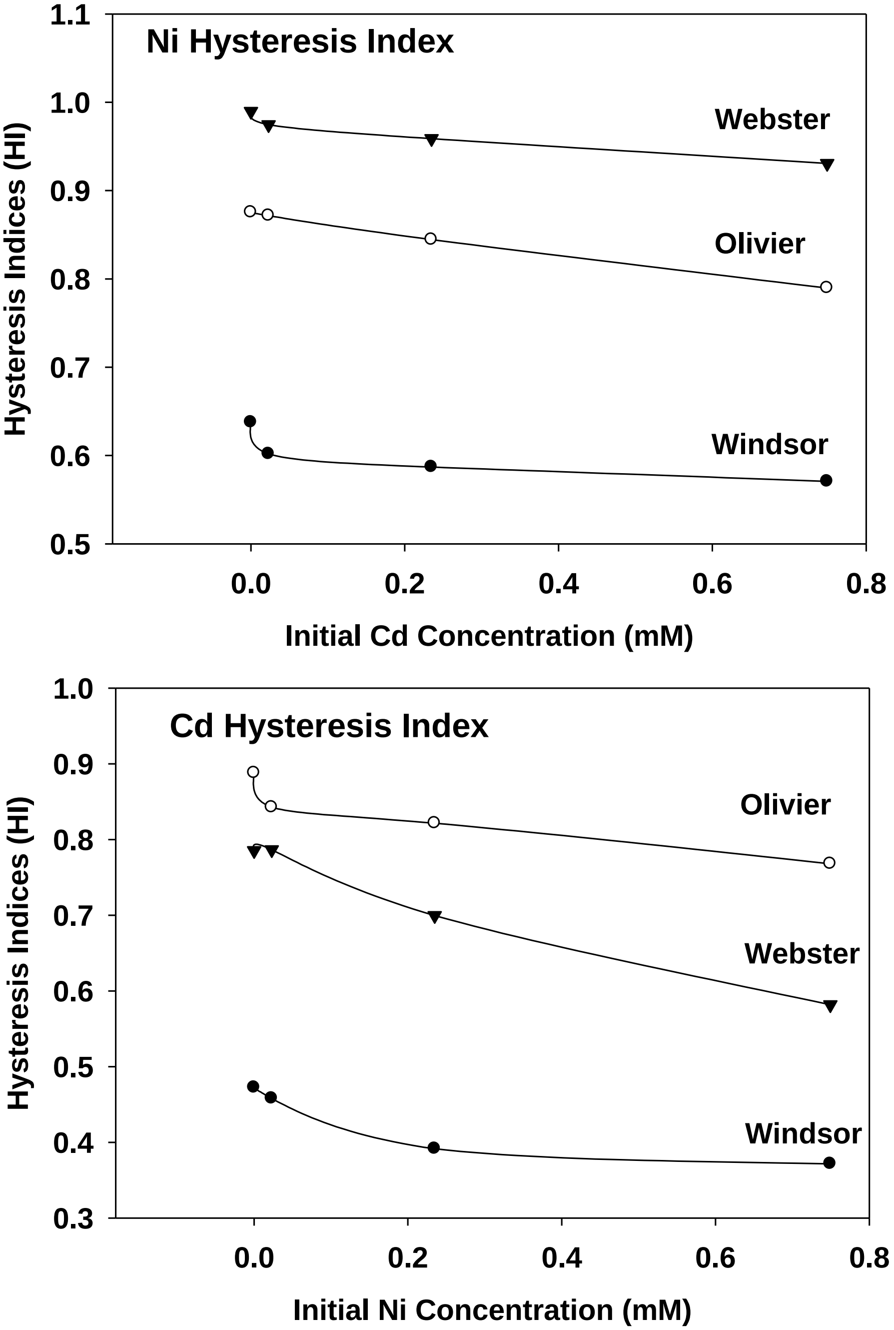

Figure 5.10. Hysteresis Index (HI) of Ni or Cd for all three soils in the presence of several initial concentrations of competing ions.

These HIs sequence difference between Ni and Cd are in line with sorption distribution coefficient K_i. The distribution coefficients (K_i) of Ni are larger than that of Cd for Webster soil, discussed in earlier section.

Based on the concept of HIs by Vega et al., (2009), the higher HIs of heavy metal ions are, the more irreversible the sorption of heavy metal ions are. In this study, HIs of Ni or Cd calculated when there is no competitive ions of Ni or Cd for all soils are significantly higher than that in the presence of competitive ions of Ni or Cd, respectively. And more, the HIs for all soils were significantly reduced as concentration of competing ion in the applied solution increased (Fig. 5.10), which represented that heavy metal ions sorption with soils became more reversible when competitive ions present. These results are agreement with results from Vega et al. (2009). They study hysteresis in the individual and competitive sorption of cadmium, copper, and lead by soil horizons and find that HIs of Cd sorption in multimetal solution are much lower than that in single element system.

5.4 Summary

The single-solute isotherms of Ni and Cd by three soils exhibited highly nonlinear and varied among three soils. The sorption affinity of Ni was higher than that of Cd for Webster soils, whereas sorption affinities of Ni were lower than that of Cd for Windsor and Olivier soils. The results from kinetics of competitive adsorption-desorption experiment demonstrated that the competition between Ni and Cd has the potential of increasing the mobility for each other in nature soils. These were presented by sorption of Ni or Cd significantly reduced and release enhanced in multi-metal system. And sorption decreasing or desorption increasing of heavy metal by soils become stronger by increasing concentration of competing ions. During the kinetic sorption, the selective preference of Cd over Ni did not change with time on Olivier and Windsor soils, but the preference of Ni over Cd increased with time for Webster soil. The highly time-dependent sorptions of Ni or Cd by three soils were successfully described with multireation model (MRM). The new proposed HIs of Ni and Cd clearly demonstrated that competitive effect can diminish the degree of hysteresis of Ni and Cd sorption by soils, therefore enhance the reversible and mobility of Ni and Cd in soils.

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CHAPTER 6: COMPETITIVE TRANSPORT OF NI AND CD IN SOIL COLUMNS: EFFECT OF SUPPRESSION AND ENHANCEMENT

6.1 Introduction

Pollutions originated from agricultural use of sewage sludge, application of fertilizers, smelters and mining emission cause serious threats to soil quality and ecosystem health. Typically, contaminated soils contain several metal contaminants. It has been well documented that nickel (Ni) and Cadmium (Cd) are weakly sorbed and can be rather mobile in acidic soils (Atanassova, 1999). A consequence of heavy metals ions such as Cd and Ni, is that ion competition may result in their enhanced mobility in the soil environment.

Extensive studies were performed to investigate the competitive effect between Ni and Cd where equilibrium coniditon was assumed (Atanassova, 1999; Antoniadis and Tsadilas (2007; Echeverrí a et al., 1998). However, due to the heterogeneous nature of soils, information on competitive effect is somewhat contradictary. When cation exchange was considered as the major sorption mechanism for both ions, Cd was less affected by Ni and the Cd of was selective preference over Ni, which was contributed to corresponding charge-to-radius ratio, electronegativity and softness parameter (Gomes et al., 2001; Echeverrí a et al., 1998; Papini et al., 2004). In contrast, the selective preference of Ni over Cd was related to hydrolysis of divalent ions capable of forming inner-sphere complexes with clay lattice edges (Jeon et al., 2003; Antoniadis and Tsadilas, 2007). All arguments indicated that metals are sorbed via different mechanisms on heterogeneous soils components with a range of bonding strength (nonspecific and specific) and characteristics (electrostatic and covalent).

Earlier in 1984, Tiller et al. proposed the procedures for the separation of sorbed metals into fraction of lower and higher affinity for soil surfaces, which recently have been considered that it can provide better insight into competitive sorption. Antoniadis and Tsadilas (2007) found that competitive effect of Ni and Cd suppressed overall sorption for each other on soils without separating the specific or nonspecific sorption. Agbenin and Olojo (2004) found that the specific sorption of Zn on a Nigeria soil was depressed by Cu which was specifically sorbed on clay minerals, amorphous hydrous oxides. Conversely, competition of Pb and Cd at nonspecific or low affinity sites suppressed the overall sorption (the sum of specific sorption and nonsepecific sorpiton) but it promoted the Cd sorption at specific sites or higher affinity sites (Serrano et al., 2005). Atanassova (1999) found that for one Netherland clay soil, Cu specific sorption decreased as a result of competition with Zn, Cd and Ni for low affinity sites at high percentage saturation of the CEC. Moreover, he also suggested that the degree of competitive effect should take the surface coverage into account. Saha et al. (2002) found that, in batch systems, the competition affected metal adsorption only when high metal concentrations are introduced to the soil system. The competitive degree of sorption depends on the number of available sorption sites and the extent of saturation of sorption sites by the competing ions (Tsang and Lo, 2006). Most of the above studies focused on competitive sorption of heavy metals in soils where equilibrium equilibrium condition was assumed; the effect of kinetics on specific reaction sites were ignored.

Few studies investigated competitive transport of heavy metals during miscible displacement experiments, which was mimic the behavior of contaminants in heterogamous geological material (Tsang and Lo, 2006; Voegelin et al., 2001; Voegelin and Kretzschmar, 2005). Antoniadia et al. (2007) found that Ni mobility used a column infiltration technique, increases in the presence of Zn and Cu contributed to competition for the common sorption sites on the soil. The breakthrough curves (BTCs) of Ni exhibited a leftward shift of their front compared with their single-element infiltration. Tsang and Lo (2006) reported that during column experiments, competitive effect of Cu and Cd reduced the nonspecific sorption on soil as well as decreased more specific sorption of Cd on oxide and organic matter fractions by Cu. Such suppress effect of Cu to Cd on both sorption resulted in equilibrium transport of Cd whereas its transport in single element system are nonequilibrium and time-dependent. The specific sorption and transport of Cu was less affected by Cd and displayed a lower degree of competition than non specific sorption. This discrepancy of competitive effect between nonspecific and specific sorption was expected since nonspecific sorption occurs in 1 min and reaches equilibrium with 30 min, whereas the specific sorption could range from days to months. Voegelin et al. (2001) found that the competitive transport of Cd, Zn and Ni could be described only when competitive nonspecific cation exchange and competitive specific sorption were taken into account. Due to heterogeneity in nature of sorption sites on soil surfaces (nonspecific sites and specific sites co-exist) to heavy metals, the competitive effect may influence not only the extent of sorption (retardation of breakthrough) but also the release behavior (tailing or symmetrical BTCs). The information about competitive effect to release process of BTCs was limited.

The objective of this investigation was to study the competitive retention and release of Ni and Cd during transport in saturated soil columns. Sequential extraction procedure was used to estimate nonspecific and specific sorption that affects competitive ions. The distribution with soil depth in the soil columns and the mobility of Ni and Cd assessed.

6.2 Experimental Section

Surface soils of Olivier loam and Windsor sand were air-dried and passed through a 2-mm sieve. These soils samples were collected form Louisiana(Olivier) and New Hampshire(Windsor). Soil properties such as soil pH, cation exchange capacity (CEC), and particle size analysis were determined earlier in our laboratory (Liao and Selim, 2009) listed in Table 6.1.

Table 6.1. Selected physical and chemical properties of the soils studied.

Soil		Olivier Loam	Windsor Sand
pH		5.80	6.11
TOC[a]	%	0.83	2.03
CEC[b]	cmol kg^{-1}	8.6	2.0
Sand[c]	%	5	77
Silt	%	89	20
Clay	%	6	3
Selective extraction by			
Ammonium oxalate (pH 3.0)			
Fe	g kg^{-1}	0.32	0.36
Al	g kg^{-1}	0.08	0.69
Citrate-bicarbonate-dithionite (CBD)			
Fe	g kg^{-1}	4.09	3.68
Al	g kg^{-1}	1.29	3.65

[a] TOC = total organic carbon. [b] CEC = cation exchange capacity. [c] Grain size distribution: sand (2.00-0.05 mm), silt (0.05-0.002 mm), and clay (<0.002 mm).

6.2.1 Column Experiment

Competitive transport of Ni and Cd in soils was investigated using the miscible displacement technique as described by Selim et al (1992). Six columns of internal diameter 6.4 cm and length 10 cm were uniformly packed with the soil. The resulting bulk density, porosity and experimental condition associated with each column are given in Table 6.2. The soil columns were slowly saturated with an upward-flowing background solution of 0.005 *M* $Ca(NO_3)_2$ at a low Darcy flux. Input solutions of 0.005 *M* $Ca(NO_3)_2$ were applied for several pore volumes using a variable speed piston pump, and the fluxes were adjusted to the desired flow rates. A constant ionic strength and effluent pH were maintained after 20 to 30 pore volumes of 0.005 *M* $Ca(NO_3)_2$ were applied to each column before introduction of Ni or Cd pulse solutions. Single or binary metal solutions of Ni or Cd were prepared by dissolving $Ni(NO_3)_2$ or $Cd(NO_3)_2$ in the background solution of 0.005 *M* $Ca(NO_3)_2$. A 0.80 m*M* Ni input pulse was followed immediately 0.8 m*M* Cd input pulse for column 101 and 201, whereas, for column 102 and 202, 0.8 m*M* Cd input pulse was followed by 0.8 m*M* Ni input pulse. A pulse of mixed solution of 0.8 m*M* Cd and 0.8 m*M* Ni were injected into 103 and 203 columns. For any column, each pulse of Ni or Cd or mixture of Ni and Cd was approximately 10 to 12 pore volumes and was subsequently eluted by 0.005 *M* $Ca(NO_3)_2$. Column effluent was collected using a fraction collector (model Retriever II, Teledyne Isco, Inc., Lincoln, NE). The concentrations of Fe, Al, Ca, Ni and Cd in effluent were analyzed using ICP-AES (Spectro Citros CCD). The level of Fe and Al indicated negligible dissolution of mineral oxides during the breakthrough of Ni and Cd.

Table 6.2. Column soil physical parameters for Ni and Cd competitive miscible displacement experiments.

Column	Soil	ρ	θ	ν	D	Ion	Pulse Input		Recovery (%) from effluent	
		mg m^{-3}	%	cm h^{-1}	cm^2 h^{-1}		Ni	Cd	Ni	Cd
100	Olivier	1.30	0.49	0.37	0.78 ± 0.07	Ni only			58.0%	
101	Olivier	1.32	0.50	0.70	0.81 ± 0.110	Ni→Cd	8.2	10.7	80.50	62.70
102	Olivier	1.37	0.49	0.70	1.00 ± 0.005	Cd→Ni	11.2	10.4	79.69	69.22
103	Olivier	1.33	0.49	0.75	1.00 ± 0.006	Ni &Cd	10.1		82.32	82.21
200	Windsor	1.38	0.48	0.38	0.78 ± 0.004	Ni only			68.32	
201	Windsor	1.49	0.44	0.76	1.00 ± 0.005	Ni→Cd[i]	10.7	9.6	88.02	75.01
202	Windsor	1.35	0.49	0.74	1.00 ± 0.004	Cd→Ni[ii]	10.5	8.4	82.94	74.08
203	Windsor	1.29	0.51	0.61	1.00 ± 0.006	Ni &Cd[iii]	8.43		95.89	65.16

[i] Ni pulse followed by Cd pulse. [ii] Cd pulse followed by Ni pulse. [iii] Ni and Cd mixture pulse.

6.2.2 Sequential Extraction

A sequential extraction procedure (Tessier et al., 1979) was conducted here to investigate the amount of nickel retained at various binding phases following the termination of miscible displacement transport experiments. Columns were sectioned into 3 equal sections of 3.3 cm in length and the soil was air dried. Four fractions were quantified which was exchangeable, bound to Fe-Mn oxide, bound to organic matter, and residual. Those fractions were extracted by $MgCl_2$ (pH 7.0), $NH_2OH^{\cdot}HCl$ in 25% HOAc (pH~2), H_2O_2/HNO_3 (pH~2) and subsequently NH_4OAc, and HNO_3 in hot water bath respectively. Following each extraction, the samples were centrifuged at 5000 g for 10 min and the Ni concentrations in supernatant were analyzed using ICP-AES (Spectro Citros CCD). The samples were washed with deionixed water prior to the next extraction step.

6.3 Results Description

The breakthrough curves (BTCs) were illustrated by plotting relative concentration (effluent concentration/influent concentration) versus dimensionless time (pore volume) (Fig. 6.1- 6.3). Figure 6.1 demonstrated the transport of Ni and Cd in Olivier soil column (101) and Windsor soil column (201), where Ni pulse was applied prior to Cd pulse. From the BTCs, both Ni and Cd were strongly retarded and asymmetrical, showing excessive tailing at the desorption side (right side) in both columns during the transport, where in the first 0-8 pore volumes, no Ni was detected and no Cd was detected within 10 pore volumes after Cd applied. A significant concentration drop of Ni in the effluent was observed in both soil columns after Cd was applied into column for 4-5 pore volumes. This may indicate that application of Cd promotes the retention of Ni, leading less Ni was leached in the effluent.

Figure 6.2 illustrated the BTCs of Ni and Cd during the transport in Olivier soil column (102) and Windsor soil column (202), where Cd pulse was applied prior to Ni pulse. No Cd was detected during the first 10 pore volumes and even after Ni was applied for 10 pore volumes, which cause that no Cd was detected during first 20 pore volumes in both columns. Cd BTCs in 102 and 202 were more retarded compared to Cd BTCs in 101 and 20. Ni application at 10 pore volume seems to promote the sorption of Cd instead of increasing the concentration of Cd in effluent. The concentration of Cd started to increase in the effluent at similar time with Ni when the background solution was applied.

The mixture pulse of Ni and Cd was injected into column 103 and 203 shown in Figure 6.3. Competition significantly reduced the retardation of Ni and Cd transport in soils when Ni and Cd simultaneously present in soil columns, as represented by instant sharper front of both Ni and Cd BTCs compared to BTCs of Ni or Cd in column 101, 102, 201 and 202. Simultaneous presence of Ni and Cd in soil column also resulted in less tailing BTCs of Ni and Cd (desorption site or right side) compared to other soil columns representing by narrow and symmetrical Ni and Cd BTCs, whereas the less tailing phenomena was not observed in column 203 (Olivier soil). For Windsor column (203) (Fig. 6.3), the effluent of Ni had a peak concentration that exceeded the input concentration ($C/C\text{o} \approx 1.2$). This overshooting phenomenon of Ni appears to arise by the competitive sorption of Cd. The relatively weakly sorbing Ni migrated ahead of Cd due to a much smaller retardation, and therefore, initially sorbed on the soil in the absence of Cd competition. However, part of sorbed Ni was then remobilized due to its displacement by the subsequent breakthrough of Cd, leading to normalized effluent concentration greater than unity. This Ni overshooting phenomenon was not observed during the competitive Cd and Ni transport in Olivier soil column 103. This may be due to higher sorption affinity of Ni on Olivier soil compared to that on Windsor soil observed in previous study (Liao and Selim, 2009), therefore initial sorbed Ni on Olivier soil was not strongly mobile as that on Windsor soil.

6.4 Discussion

Generally, highly sorbed and retarded transports of Ni and Cd was observed in soil columns (101, 102, 201 and 202), which agreed with the results of Antoniadis et al. (2007) and (Puls and Close, 2009), attributed to rate limited or time-dependent adsorption–desorption behavior of Ni and Cd by soils. The kinetic or time-dependent sorption behavior o Ni and Cd was observed in previous chapter as well as also reported by (Scheidegger et al., 1998; Selim et al., 1992). The observed prolonged tail of BTCs for Ni or Cd in column 101, 102, 201 and 202) may be due to their nonlinear nature (or heterogeneity) of sorption in soil, respectively, where the N values were less than 1, derived from Freundlich equation in previous chapter. The parameter N represents the energy distribution or the heterogeneity of sorption-site, where the highest energy sites are preferentially sorbed at low concentrations, and as the concentration increases, successively lower energy sites become occupied (Sheindorf et al., 1981). In our columns study, Ni or Cd sorbed at lower affinity sites of soil were first released and followed by slow or gradient release of Ni and Cd sorbed at higher affinity sites, leading to prolonged tailing for BTCs of Ni or Cd. Nonlinearity and competition are often regarded as characteristics of site-specific adsorption processes (Spark, 1995).

Commonly, competition reduced the retardation of heavy metal ion transport in soil when the competitive cations were simultaneously present in soils (Tsang and Lo, 2006; Antoniadis et al., 2007). Such reduction of retardation of Ni or Cd transport due to competition effect was also observed in column 103 and 203 in our studies. With co-existence of both metal ions in soil columns, the instant competition at low affinity sites each other, leading to rapid increase of Ni and Cd concentration in effluent (less retardation). Atanassova (1999) found that the competition of Cu, Zn, Ni and Cd at low affinity sites in soil clays decreased the sorption of heavy metal during batch experiment study. Generally, the sorption of heavy metal decreased in multi-component system as result of competitive sorption of heavy metals at low affinity sites in soils, which was considered as the generally accepted results of heavy metal competition (Antoniadis and Tsadilas, 2007) and are in line with our results from column 103 and 203.

However, two phenomena of the observed Ni concentration drop in column 101 and 201 due to the following Cd pulse application and the more retardation of Cd BTCs in 102 and 202 due to Ni pulse application were in contrast to those results but in agreement with Serrano et al. (2005) and Mesquita and Viera a Silva (2002). In their batch studies, the Langmuir parameter k was used to estimate the competitive effect of heavy metal of Cd and Pb in 4 soils (Serrano et al., 2005). The higher k values have been related to specifically sorbed metals at high energy surfaces, whereas, lower k values appear to be related to sorption at low energy surfaces. They found that k values of Cd or Pb in binary system were larger than that in single system. They suggested that competition for sorption sites promotes the retention of Cd and Pb on more specific sorption positions having higher affinity. Further investigation about competitive kinetics found that initial Cd sorption rate increased in the presence of Pb, which indicated that the competitive Pb sorption forces Cd retention on sorption sites with greater affinity or more specific for this metal. In our study, Ni seems sorbed more when Cd pulse was applied into soil column 101 and 201 for 3-4 pore volumes. According to Serrano et al. (2005), Cd forced Ni retention in more specific sorption sites, leading to concentration drop in the effluent at sorption sites (right site). In column 102 and 202, Cd was input prior to Ni application, which seemed not cause the release of Cd, but promoted Cd sorption onto soil. The retardation of Cd are even stronger in 102 and 202 columns compared Cd in 101 and 201 as shown by concentration maintaining at non-detectable level within 20 pore volumes. Sorption of heavy metal ions on more specific sites requires a much longer reaction time (Tsang and Lo, 2006) referred as rate-limited sorption, which is the reason of observed retardation phenomena for heavy metal ions transport in soil (Pulse and Close, 2007). Here, according to Serrano et al. (2005), we assume that Ni application forced Cd to more specific sorption, which resulted in Cd sorption requires a much longer reaction time to reach equilibrium compared that in single element system,

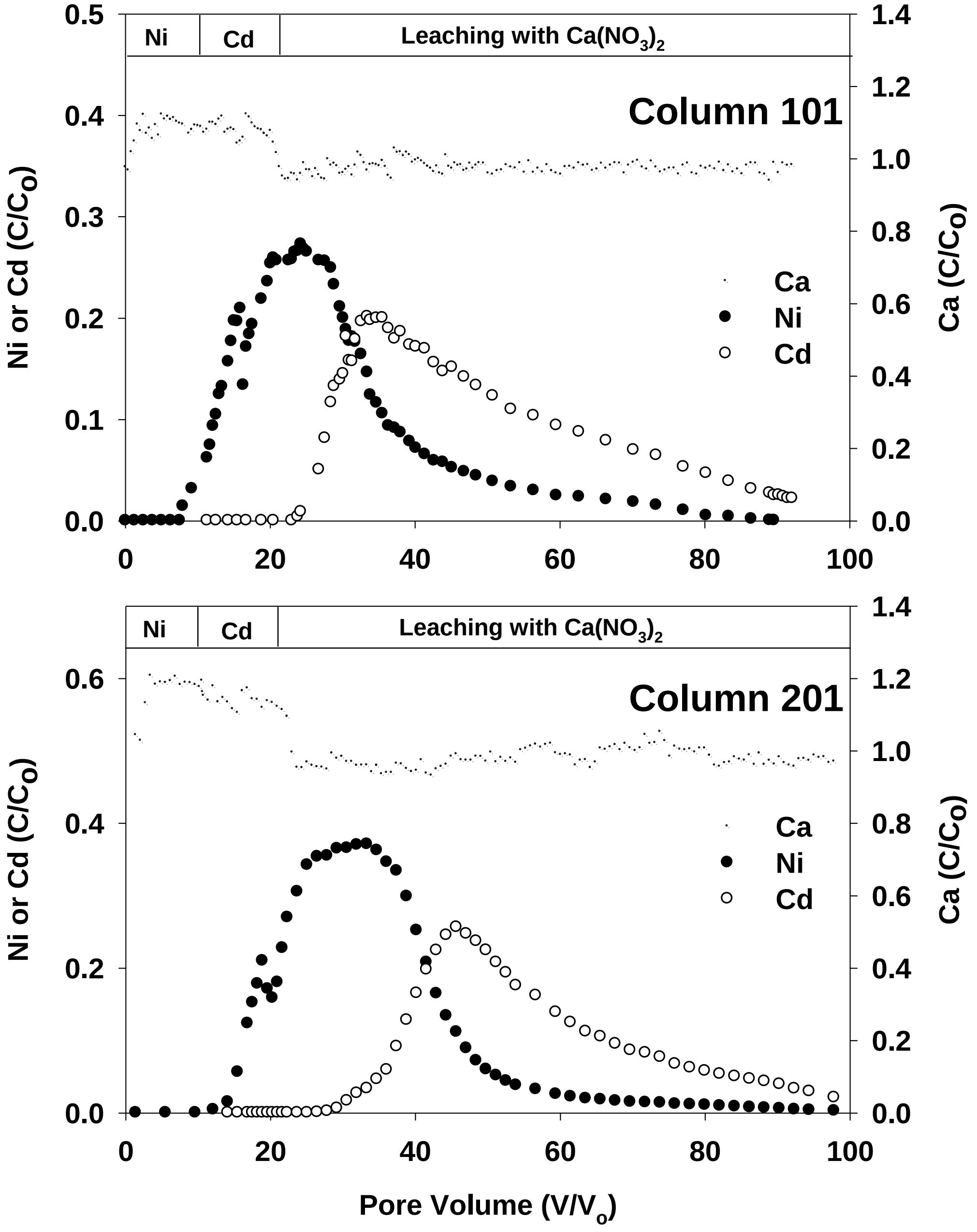

Figure 6.1. Breakthrough curves for Ni and Cd competitive transport in soil column 101 and 201. Ni pulse was applied at 0 pore volume followed by Cd pulse at 10 pore volume. Background solution was 0.005 *M* $Ca(NO_3)_2$. Symbols are for different elements respectively.

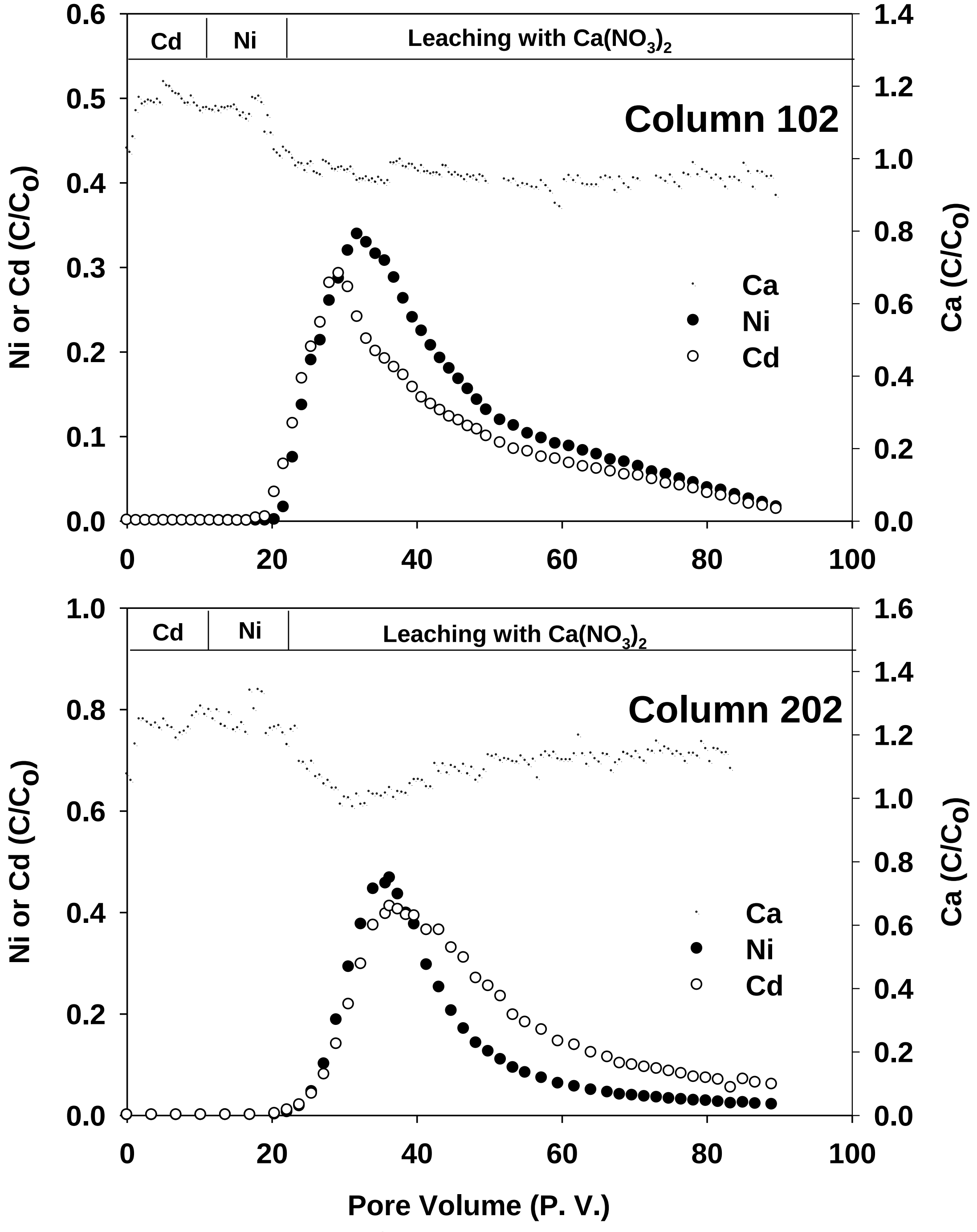

Figure 6.2. Breakthrough curves for Ni and Cd competitive transport in soil column 102 and 202. Cd pulse was applied at 0 pore volume followed by Ni pulse at 10 pore volume. Background solution was 0.005 *M* $Ca(NO_3)_2$. Symbols are for different elements respectively.

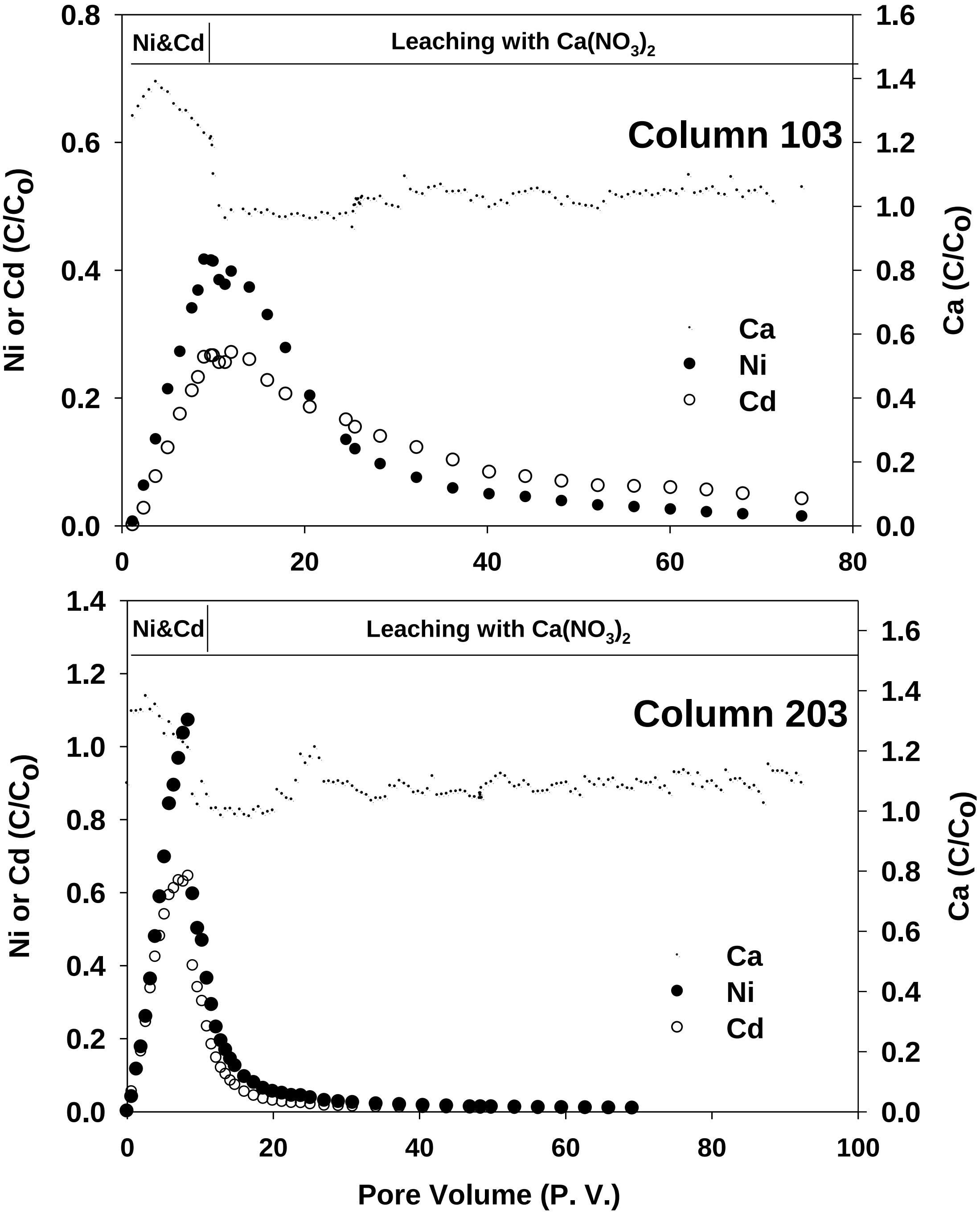

Figure 6.3. Breakthrough curves for Ni and Cd competitive transport in soil column 103 and 203. Mixture pulse of Ni and Cd was applied at 0 pore volume. Background solution was 0.005 *M* $Ca(NO_3)_2$. Symbols are for different elements respectively.

therefore, the more retardant Cd BTCs were observed in column 102 and 202. Nevertheless, both observed Ni concentration drop and Cd retardation are due to competition forcing Ni or Cd for each other to higher affinity sites or more specific sites, in line with the results of Pb and Cd competition (Serrano et al., 2005).

Moreover, compared to the increment of Ni and Cd sorption (concentration drop of Ni and more retardation of Cd) in column 101, 201, 102 and 202 with the reduction of Ni and Cd sorption (less retardation) in column 103 and 203, we would take the time-dependent sorption as well as saturation status of the competitive sites as consideration to discuss the reason of either increasing the retardation or decreasing the retardation due to competition. Saturation process occurred either by applying high concentration metals or low concentration continuous reaction for longer time.

Take column 101 as example, Ni was applied into column for 10 pore volumes, which is 5 days. In the absence of Cd, Ni was spontaneously sorbed on exchangeable sites (low affinity sites) and with the Ni pulse continued for 5 days, Ni was gradually sorbed at higher affinity sites. Cd application at the sixth day and competed with Ni initially sorbed at low affinity sites, which is highly depend on the availability of sorption sites. Tsang and Lo (2006) suggested that the competitive effect of sorption depends on the number of available sorption sites and the extent of saturation of those sites by competing ions. At low surface coverage, the sorption decrease due to competition effect were not necessarily observed, where the competition was weak due to sorption sites available. Whereas at higher surface coverage or saturation condition, the competition between sorption sites is stronger, expressing by sorption of heavy metal decreased (Tsang and Lo, 2005). Here, Ni reacted with soil for 5 days, Ni may bond with higher affinity sites, therefore when Cd applied, the competition at low affinity sites may be weak and cause no significant Ni desorbed and be observed. Whereas, according to Serrano et al. (2005), the competitive effect of Cd forced the Ni to be sorbed on more specific sorption sites therefore the retention of Ni increased, leading significant concentration drop in the effluent being observed. For column 103, the simultaneous presence of Cd and Ni resulted in higher surface coverage, therefore the instant competition of Ni and Cd at low affinity sites suppress the sorption for each other and resulted in sharp front of Ni and Cd BTCs observed in column 103 and 203. At this situation, the competition of Ni and Cd at low affinity may also force each other to be sorbed at higher affinity sites, but this phenomenon may be covered because high concentrations of Ni or Cd were in the effluent due to the competition at low affinity sites. As a result of competition at low affinity sites and promotion of sorption at higher affinity sites, the total concentration change in the effluent may not accurately reflect the difference of competitive effect between low and high affinity sites. Further, competitive transport experiments of heavy metal were commonly conducted by saturation soil with one cation and then replacing it with other cations (Voegelin et al., 2001). Under this condition the heterogeneity nature of sorption sites was diminished and the competition effect was enlarged at most for significant results showed up.

In column systems, where the steady-state condition is adsorption site saturation by the given metal, competition affects metal adsorption even if the added metal concentration is low. During our transport experiments, soil columns were saturated by Ca. When Ni or Cd pulse was applied into soil columns 101, 102, 201 and 202, the effluent concentration of Ca exceeded the influent concentration by 20% due to competitive effect of Ni or Cd. The stronger effect of Ni and Cd mixture to Ca was observed when Ni and Cd were simultaneously present at soil columns (Fig. 3), represented by some 40% higher of Ca in effluent than that of influent. However, this significant concentration increase may level off or cover the effect of competition at higher energy level.

Earlier in 1984, Tiller et al. started to concern the study of higher-affinity reactions of Cd, Zn and Ni ions with soil clay and described the procedures for the separation of sorbed metals into fraction of lower and higher affinity for soils surfaces. This work was meaningful specially at identifying the mechanisms of competitive sorption of heavy metal in soils. Traditionally, the competition effect during bath experiments was evaluated by comparing the total amount sorbed metal on soils in single and multi-component system, the results of which often showed that the sorption amount of heavy metals was decreased due to competitive effects (Antoniadis and Tsadilas, 2007; Atanassova, 1999). This is in somehow can evaluate the competition effect for general results. However, heavy metals of Cu, Zn, Pb, Cd and Ni were considered more specific sorption with soil matrix compared with Ca, Mg and Na. The competition may have effect not only at exchangeable phase but also at specific phase. Mesquita and Vieira e Silva (2002) separated the exchangeable sorption and specific sorption of Cu and Zn by 4 soils in single and binary elements system using batch experiment. From their experimental data, the exchangeable sorption of both ions significantly decreased in binary system for all soils compared that in single element system; whereas, the specific sorption of Zn increased on two soils with higher clay contents, organic matter and CEC and decreased on other two soils with lower CEC. Moreover, total amount sorbed on soil (the sum of exchangeable and specific sorption) decreased in binary system compared that in single system. The total amount of sorbed Zn did not reflect the sorption difference at specific sorption sites in single and binary system. The sorption increment of Zn by two soils at more specific sorption sites in binary system were in line with the assumption of Serrano et al (2005) that competition at low affinity sites forces heavy metal to sorbed at sites with higher affinity or more specific sites. Therefore, the use of total sorbed heavy metal to evaluate the competition effect was questioned.

In Serrano et al (2005) studies, they found that k values in binary system were equal or less than that in single binary for one soil having low affinity with Pb and Cd, which indicated that competition did not force Pb or Cd sorbed on more specific sites on this soil. This trend was also demonstrated by Mesquita and Vieira e Silva (2002), where, the specific sorption amount of Zn decreased in the present of Cu in two soils with low organic matter and clay contents. From the observed results of Serrano et al. (2005) and Mesquita and Vieira e Silva (2002), we made assumption that the promotion of retention at more specific sites due to competition at low affinity sites depends on the availability of higher affinity sites for metals on soil surfaces. At certain surface coverage, if there are specific sorption sties available, the competition at low affinity sites forces the sorption to higher affinity sites but competition can only happened at low affinity sites when no specific sites available. By using this assumption, we try to explain that no tailing of Ni and Cd BTCs in column 203 (Windsor soil) was observed as well as the prolonged tailing were still observed in column 103 (Olivier soil) although the competition significant reduced the retardation of BTCs in both columns. Windsor soil has lower sorption affinity with Ni and Cd than Olivier soil does, observed in previous study (Liao and Selim, 2009). At the same surface coverage (Ni and Cd simultaneously present) for both columns, Olivier soil has more high affinity sites available compared to Windsor soil. With Ni and Cd continuous application for 5 d, Ni and Cd was forced to sorbed at higher affinity sites in Olivier soil. Due to the nonlinear or heterogeneity of sorption, Ni or Cd sorbed at low affinity sites was released before that sorbed at high affinity sites. The slow release of Ni and Cd at higher affinity sites resulted in the prolonged tailing in Olivier soil, where as for Windsor soil, due to not availability of higher affinity sites at higher surface coverage, the competition may only happen at lower affinity sites and no Ni or Cd was forced to higher affinity sites, which caused Ni and Cd BTCs symmetrical and narrow in Windsor column.

The competitive transport of Ni and Cd in soil columns can not be explained solely by the concentration of Ni or Cd in effluent during column experiments that lead to the following evaluating of the competitive effect on fractionation of soil from column experiments.

6.5 Sequential Extraction

Figure 6.4 presents the results of sequential extraction for soil samples following the termination of miscible displacement transport experiments. Each column was sectioned into 3 equal sections of 3.3 cm in length. In the Fig. 6.4, the results of each fraction were presented by the average of this fraction of 3 sections in each column. The competitive effect on non-specific and specific sorption was then evaluated with sequential extraction, of which the four fractions from exchangeable to residual are defined. In terms of increasing metal binding strength, sorption on the first fraction is weak and regarded as nonspecific, while sorption on the latter three fractions is of high binding strength and considered specific. From Fig. 6.4, the exchangeable fraction (or nonspecific sorption) of Ni sorbed on soils were reduced due to competition with Cd, reflecting by lower percentage of exchangeable Ni in column 101, 102, 103 and 201, 202, 203 and 200 (with competition of Cd)) compared to columns of 100 and 200 (without competition), respectively. This sorption reductions of Ni on soils were also reflected by higher percentage of Ni in effluent of columns (101, 102, 103 and 201, 202, 203) compared with lower percentage of Ni recovery from effluent in columns of 100 and 200, which indicated that more Ni was leached out due to competition of Cd in columns of 101, 102, 103 and 201, 202, 203. However, the sorption of Ni on other three fractions (or specific sorption) was enhanced in all columns under competitive condition.

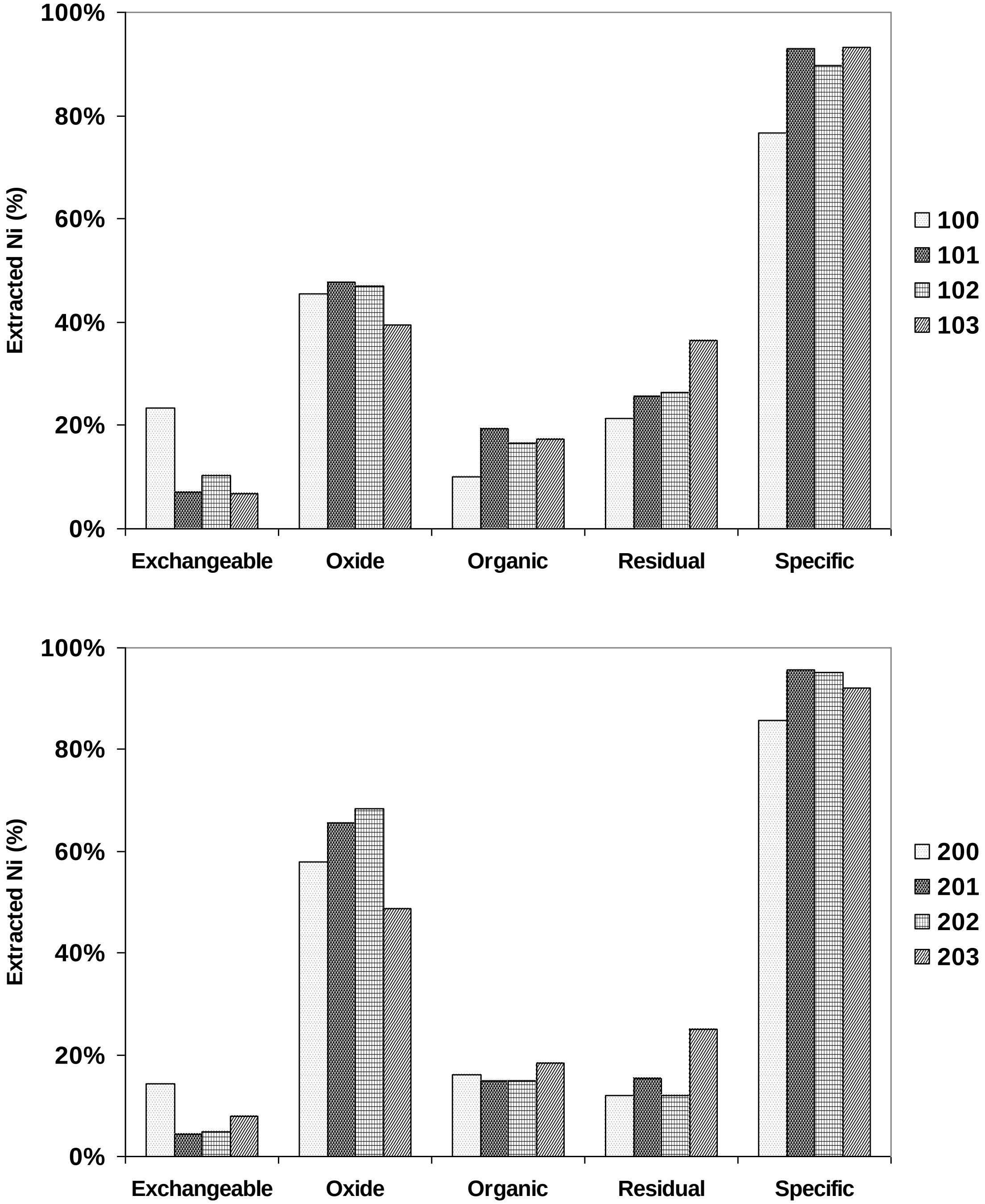

Figure 6.4. Results of sequential extraction of Ni in the soil after heavy metal breakthrough in column experiments of 100, 101, 102 and 103 (Top) and of 200 201, 202 and 203 (Bottom). Specific fractions are the sum of oxide, organic and residual fractions. The results are the average of three sections of each column.

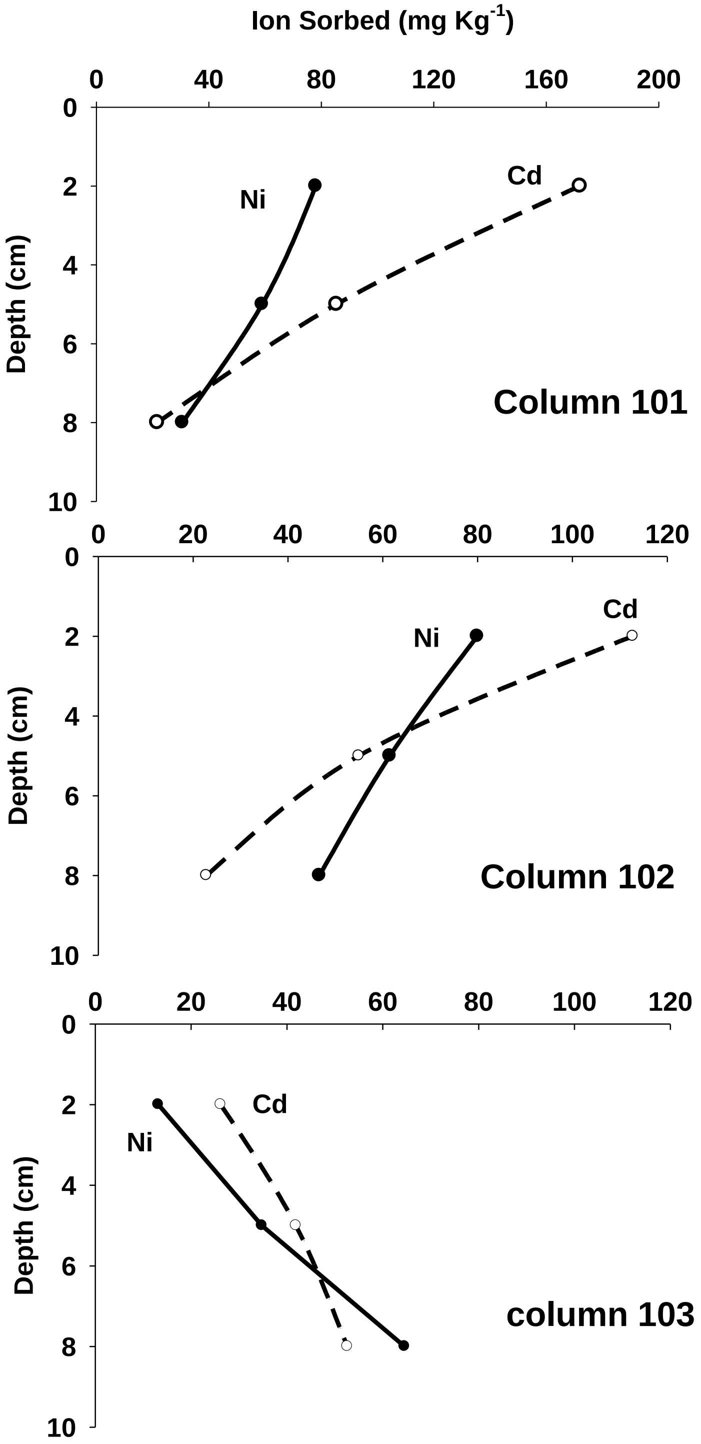

Figure 6.5. Distribution of Ni and Cd concentration with depth in Olivier soil columns of 101, 102 and 103.

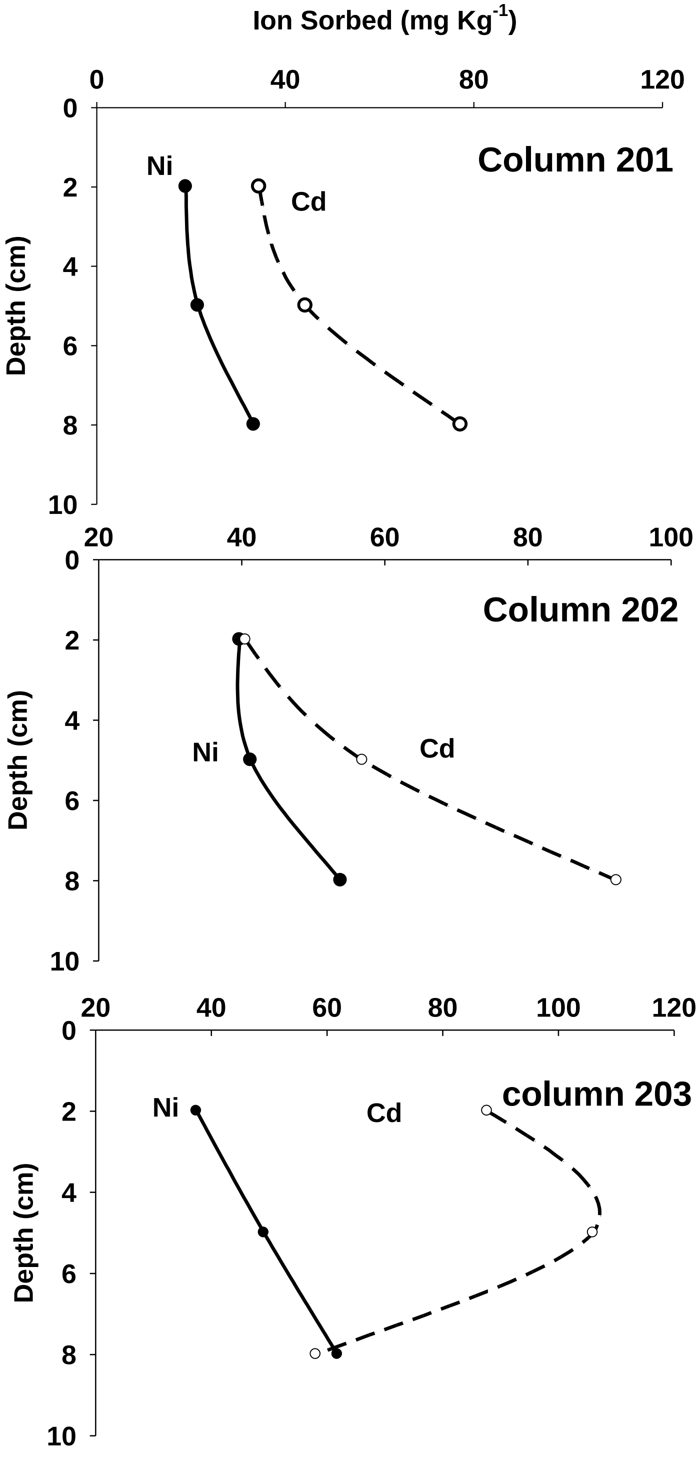

Figure 6.6. Distribution of Ni and Cd concentration with depth in Windsor soil columns of 201, 202 and 203.

These results are in line with the results of Serrano et al. (2005), who reported that the competition at low affinity sites suppresses the sorption of metal at low affinity sites as well as forces the metal to be sorbed on higher affinity sites. We also observed that the oxide fractions of Ni were reduced in column 103 and 203 compared with columns of 100 and 200, respectively. These results were also observed by Tsang and Lo (2005), where Cu and Cd simultaneously present in soil columns also reduced the sorption of Cu on the exchangeable and oxide fractions.

The distribution of Ni and Cd with soil depth in soil columns following the termination of the miscible displacement transport experiments were illustrated in Fig 6.5-6.6. The total Ni and Cd were the sum of all fractions extracted by sequential extraction procedure. Results shown in Fig. 6.5 demonstrate the extent of variability of Ni and Cd distribution with soil depth among three soils. For 101 and 201 soil columns, the amount of Ni and Cd retained by the soil decreased with depth. This is indicative of strong sorption of the Ni and Cd applied to the soil surface, accumulation pattern. For soil column 103, Ni and Cd sorbed in the soil increased with depth (Fig. 6.5). This pattern indicates downward movement of Ni and from the soil surface to lower depths, a leaching pattern. These two different distribution patterns indicated that Ni and Cd have higher mobility in column 103 due to simultaneous presence of Ni and Cd in soils and are in line with the breakthrough curves results, where Ni and Cd were significantly less retardant compared with that in columns of 101 and 102 (Fig 6.1-6.3). At high surface coverage of competitive ions (discussed in earlier section), the competition significantly enhanced the mobility of Ni and Cd in soils. The distribution of Ni and Cd in soil column 201, 202 and 203 presented as leaching pattern, where Ni and Cd concentration in soil increased with soil depth, except for Cd distribution in soil column 203, where Cd increased with depth and then decreased at deeper depth. This pattern was also observed by Al-Soufi (1994).

6.6 Conclusions

The competitive effect of Ni and Cd during the transport in soil columns can suppress the sorption for each other at low affinity sites therefore enhance the mobility of Ni and Cd at low affinity, while this effect can also force the sorption at higher affinity sites. It may cause metal stronger bonding with higher affinity sites. The latter effect highly depends on the availability of higher affinity sites. At certain surface coverage, if there is specific sorption stie available, the competition at low affinity sites forces the sorption to higher affinity sites but competition can only happen at low affinity sites when no specific sites are available. The simultaneous presence of Ni and Cd in soils enhances the mobility for each other, which causes the Ni and Cd distribution pattern changed from accumulation pattern to leaching pattern. The movement and distribution of Ni in the soil profile is of considerable interest due the potential contamination of land and water resources. The leacing pattern has the potential risk of contamination of water resources.

6.7 References

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CHAPTER 7: MERCURY ADSORPTION – DESORPTION AND TRANSPORT IN SOILS

7.1 Introduction

Studies on the fate of mercury (Hg) in the soil environment continue to be of interest to soil scientists, toxicologists, biogeochemists, and terrestrial ecologists (Yin et al., 1997a; Drexel et al., 2002; Gabriel and Williamson, 2004; Kim et al., 2004). The extent of sorption/desorption reactions of Hg in soils strongly influences its toxicity in the soil-water environment. The reactivity of Hg in the soil environment is often represented by a series of complex reactions of organic and inorganic forms under varieties of conditions (Lu and Jaffe, 2001; Gabriel and Williamson, 2004; Haitzer et al., 2002; Ravichandran, 2004). Due to such interactions, the dominant mode of entry of Hg to surface waters begins with soil erosion and subsequent transport with storm runoff water (Cooper and Gillespie, 2001; Gabriel and Williamson, 2004). Therefore, knowledge of adsorption/desorption reactions and transport of Hg in soils is a prerequisite in the understanding of the fate and behavior of Hg in the soil environment and for risk assessment strategies at the field and regional scale.

Studies dealing with heavy metal retention in soils have been extensively reported (Livesey and Huang, 1981; Buchter et al., 1989; Yin et al., 1997b; Miretzky et al., 2005). In most studies, the aim was to quantify the extent of heavy metal adsorption over a short duration, commonly 24 h. Kinetic studies, such as that reported by Amacher et al. (1990), showed that between 24 and 48 h, Hg adsorption reached a quasi-equilibrium state. In another study, Parkpoin et al. (2001) indicated that adsorption of Hg in the sediment exhibited an initial rapid sorption within 1 h, followed by a slower rate of adsorption over a 24-h period. Concentrations of Hg in solution also stabilized after a 24-h equilibration period. Other studies revealed that adsorption and desorption of Hg in soils are often characterized by a biphasic pattern, an initially fast reaction followed by a slow reaction (Yin et al., 1997a). Parkpoin et al. (2001) indicated that the activation energies for Hg desorption in sediments were much larger than those for adsorption, and desorption rates were always slower than adsorption rates.

In terrestrial environments, there are two major types of Hg sorbents: organic matter (humic material) and oxides (Gabriel and Williamson, 2004). Organic matter plays an important role on the sorption of Hg on soils. Yin et al. (1997b) reported that adsorption and desorption rate coefficients were inversely correlated with the soil organic C content. Higher organic C also resulted in higher adsorption of Hg on soils (Yin et al., 1997a; Miretzky et al., 2005). Moreover, the greater the soil organic C content, the higher the fraction of Hg(II) that was resistant to desorption. Yin et al. (1997b) found that for an H_2O_2–treated sandy loam soil, all adsorbed Hg(II) was released after 8 h of desorption. In terms of adsorption capability, metal-oxides and oxyhydroxides are second to organic matter (Gabriel and Williamson, 2004). Kinniburgh and Jackson (1978) reported that more than 90% Hg(II) was absorbed by iron hydrous oxide gel. Cruz-Guzmán et al. (2003) reported that sorption–desorption of Hg(II) followed the sequence: humic acid >> poorly crystallized ferrihydrite > Wyoming Montmorillonite clay.

The primary objective of this study was to quantify rates of Hg(II) retention, release, and mobility in soils. Our objectives were: (i) to quantify time-dependent or kinetic Hg(II) adsorption and desorption or release in soils having different properties, including a reference sand material; (ii) to investigate the effect of organic matter removal from soils on the extent of Hg(II) retention by the different soils; (iii) to measure the mobility of Hg(II) in soil columns during pulse application and subsequent leaching; and (iv) to describe Hg(II) adsorption and mobility based on a nonlinear-equilibrium and kinetic approach.

7.2 Materials and Methods

7.2.1 Soils

Surface soils from the Ap horizon (0–10 cm) of Olivier loam (fine-silty, mixed, thermic Aquic Fragiudalf), Sharkey clay (very fine, montmorillonitic, nonacid, thermic, Vertic Haplaquept), and Windsor sand (mixed, mesic Typic Dipsamment) were used in this study. Soil properties for these benchmark soils such as soil pH, cation exchange capacity, and particle size analysis were determined earlier in our laboratory by Buchter et al. (1989) and Zhang and Selim (2005) and are given in Table 7.1. Washed sea sand (14808–60–7; Fisher Scientific, Pittsburgh, PA) was used as a reference material where no clay and organic matter were present. Zhu and Selim (2002) used this sand material previously as a reference matrix in pesticide retention experiments.

7.2.2 Adsorption-Desorption

A batch equilibration technique was conducted to study Hg adsorption in all soils and reference sand. Six initial Hg(II) concentrations C_o (0.1, 0.5, 1, 5, 10, and 20 mg L^{-1}) as $Hg(NO_3)_2$ were prepared in 0.01 mol L^{-1} $Ca(NO_3)_2$ background solution. For adsorption, 30 mL of the various Hg(II) concentration solutions was added to 3 g of soil in 40 mL Teflon centrifuge tubes in triplicate. The tubes were sealed with Teflon screw caps and placed on a reciprocal shaker. The mixtures were continuously shaken so the soil was in contact with the Hg(II) solution at all times and centrifuged at 5000 × *g* for 10 min before sampling. A 1-mL aliquot was sampled from the supernatant after a 24-h reaction time. Total Hg in the supernatant solution was measured using ICP–AES (Spectro Ciros CCD, Kleve, Germany) and by cold vapor using a Mercury Instruments Analytical Technologies Lab Analyzer Model 254 (Mercury Instruments, Cincinnati, OH). Quality assurance and quality control were strictly adhered to where standard calibration was obtained before Hg analysis.

Table 7.1 Selected physical and chemical properties of the soils studied.

Soil[a]		Olivier Loam	Sharkey Clay	Windsor Sand	Reference sand
pH		5.80	5.77	6.11	6.27
TOC[b]	%	0.83	1.41	2.03	0
CEC[c]	cmol kg^{-1}	8.6	29.6	2.0	0
Sand[d]	%	5	3	77	81
Silt	%	89	36	20	19
Clay	%	6	61	3	0
Selective extraction by					
Ammonium oxalate (pH 3.0)					
Fe	g kg^{-1}	0.32	0.83	0.36	0.23
Al	g kg^{-1}	0.08	0.23	0.69	0.02
Citrate-bicarbonate-dithionite (CBD)					
Fe	g kg^{-1}	4.09	7.77	3.68	0.023
Al	g kg^{-1}	1.29	2.42	3.65	0.043

[a] Soil samples were collected from Louisiana (Sharkey and Olivier) and New Hampshire (Windsor). [b] TOC = total organic carbon. [c] CEC = cation exchange capacity. [d] Grain size distribution: sand (2.00-0.05 mm), silt (0.05-0.002 mm), and clay (<0.002 mm).

For the batch (kinetic) experiments, a standard solution was tested every 15 samples, whereas for samples from our transport column experiments, a standard was run every 30 samples. The recovery of internal standards ranged from 98 to 103%. The detection limit for Hg was 2 $\mu g\ L^{-1}$. Amounts of Hg(II) sorbed on the soil were determined by the difference between the concentrations of the supernatant and that of the initial solutions.

In a separate experiment, all soils were treated with hydrogen peroxide (H_2O_2) to remove the soil organic matter (Kilmer and Alexander, 1949). After the H_2O_2 treatment, each soil was air dried, and 24-h batch adsorption was performed to assess the extent of organic matter removal on Hg(II) adsorption in our soils.

Kinetic desorption was conducted after 24-h adsorption of all (untreated) soils. Desorption was accomplished through sequential or successive dilutions of the slurries to induce Hg(II) desorption or release. Each desorption step was performed by replacing the supernatant with 0.01 mol L^{-1} $Ca(NO_3)_2$ background solution and shaking for 24 h. Ten desorption steps were performed (10 d). The fraction of Hg desorbed from the soils was calculated based on the change in concentration in solution (before and after desorption). During adsorption and desorption, the pH of the mixed solutions were measured after each reaction time using a pH electrode and a standard Multi-pH/millivolt meter; Eh was measured using a millivolt meter along with a Pt and reference electrode. The amount of Hg released/desorbed was calculated from the difference between concentrations of the supernatant and that of the amount initially sorbed at each desorption step.

7.2.3 Transport

The transport of Hg(II) in soils was investigated using the miscible displacement method described by Zhang and Selim (2006). Acrylic columns (10 cm in length and 6.4 cm inner diameter) were uniformly packed with air-dried soil and were slowly water saturated with a background solution of 0.01 mol L^{-1} $Ca(NO_3)_2$ at a low Darcy flux. Input solutions of 0.01 mol L^{-1} $Ca(NO_3)_2$ were applied for several pore volumes using a variable-speed piston pump (model QG6; Fluid Metering Inc., Syosset, NY), and the fluxes were adjusted to the desired flow rates. Column effluent was collected using a fraction collector (Retriever II; Teledyne Isco, Inc., Lincoln, NE). Between 10 and 20 pore volumes of 0.01 mol L^{-1} $Ca(NO_3)_2$ were applied to each column before introduction of Hg(II) pulse solutions. A pulse having a concentration of 8 mg L^{-1} Hg(II) solution in 0.01 mol L^{-1} $Ca(NO_3)_2$ (pH 6) as background solution was introduced to soil and sand columns. The input Hg(II) pulse was approximately 10 to 12 pore volumes for each soil column and 5 pore volumes for the sand column. Mercury pulse inputs were subsequently eluted by 0.01 mol L^{-1} $Ca(NO_3)_2$ Hg-free solution. To obtain independent estimates for the dispersion coefficient (D), a pulse of a tracer solution was applied to each soil column before Hg(II) pulse application. The tracer used was tritium (^3H_2O), which is commonly used for miscible displacement experiments. The collected samples were analyzed using a Tri-Carb liquid scintillation β counter (Packard-2100 TR; Packard, Waltham, MA) by mixing 0.5-mL aliquot with 5 mL cocktail (Ultima Gold; Packard) for 10 min on the liquid scintillation counter. Radioactivity was recorded as counts per minute. The tritium data were described using the classical convection-dispersion equation and best-fit parameters for the dispersion coefficient (D) ($cm^2\ h^{-1}$), and the dimensionless retardation factor R ($=1 + \rho K_d/\theta$) was obtained using nonlinear least-square optimization. Other experimental parameters, such as the soil bulk density (ρ, g cm^{-3}) and soil moisture content (θ, $cm^3\ cm^{-3}$), are given in Table 7.3.

7.3 Results and Discussion

7.3.1 Adsorption Isotherms

The isotherms in Fig. 7.1 show the adsorption of Hg(II) by our three soils and the reference sand. The amount of metal ions adsorbed per gram soil is represented as a function of metal ion concentration in solution. Extremely high Hg adsorption by all soils was observed. Between 93 and 99% of the amount of Hg added was retained by the soil within 24 h (Table 7.2). For the reference sand, the extent of Hg adsorption was significantly lower than that for all soils. A comparison of the adsorption capacities of the different soils shows that Hg sorption followed the sequence: Sharkey clay > Olivier loam > Windsor sand. This sequence is consistent with the clay content sequence in three soils, which is Sharkey clay > Olivier loam > Windsor sand.

Ramamoorthy and Rust (1978) reported that overall Hg adsorption to mineral and organic particles was correlated to the surface area. Due to their large surface area, the finest particles (e.g., colloidal clay particles) have the highest Hg adsorption capacity (Babiarz et al., 2001; Gabriel and Williamson, 2004; Ramamoorthy and Rust, 1978). As a result of the colloids' high affinity for Hg, Hg^{2+} is rapidly removed from the soil solution (Jackson, 1998).

Table 7.2. Freundlich adsorption parameters for Hg for untreated soils and soils after removal of organic matter (OM).

Soil		pH	Eh (mV)	K_f (L Kg^{-1})	N	r^2	% Adsorption†
Windsor	Untreated	5.6-5.8	360-430	1249.49	0.98	0.950	92.8-99.8
	OM removed	5.7-5.9	360-420	125.14	0.88	0.966	79.1-96.1
Olivier	Untreated	6.1-6.4	360-400	10013.19	0.88	0.879	96.8-99.9
	OM removed	5.8-6.1	360-400	970.12	0.85	0.987	93.8-97.9
Sharkey	Untreated	5.9-6.5	360-400		-	-	99.2-99.9
	OM removed	5.9-6.4	360-400	426.98	0.83	0.962	74.2-96.9
Reference sand		5.9-6.5	310-430	1004.63	0.44	0.999	33.7-95.7

†: % of initial Hg added ranging from 0.1-20 mg L^{-1}.

All isotherms for Hg(II) exhibit nonlinear adsorption behavior over the range of concentrations used in our experiment (Fig. 7.1). Nonlinear adsorption is often described by Langmuir equation and/or Freundlich models. Amacher et al. (1990) reported strong nonlinear Hg sorption by several soils where the nonlinear Freundlich coefficient was $N << 1$. S-type isotherms have been used to describe Hg adsorption by soils with high organic matter content (Yin et al., 1997b). S-type isotherms are characterized by limited sorption at low initial concentrations followed by increased adsorption as the concentration in solution increases. The results of Fig. 7.1 indicate that for Olivier and Windsor soils (and to a lesser extent for the Sharkey clay), the isotherms are generally of the S-type. It is postulated that the S-type of isotherms are due to the complexation of metals by dissolved organic matter becuase dissolved organic matter has a strong affinity for Hg. As metal concentration exceeds the complexation capacity of dissolved organic matter, the soil particle surface gains in the competition and begins to adsorb Hg ions significantly (Yin et al., 1997b; Sposito, 1989). S-type isotherms are not commonly described using the Freundlich equation, with N values often greater than 1.0 (Weber, 1995). Nevertheless, the Freundlich model was also used to describe Hg adsorption isotherms for soils from the Amazon (Miretzky et al., 2005), sediments (Parkpoin et al., 2001), and montmorillonite clay (Green-Ruiz, 2005).

For the reference sand material, which is devoid of organic matter, the adsorption isotherm did not exhibit an S-type curve; rather; the shape of the isotherm depicted an L-type curve. Freundlich isotherms are generally used to model nonlinear adsorption behavior of this L-type, having sorption-site energies heterogeneously distributed. Here, the highest energy sites are preferentially sorbed at low concentrations, and, as the concentration increases, successively lower energy sites become occupied. This leads to a concentration-dependent sorption isotherm where the exponent N in Freundlich model is a measure of the extent of the heterogeneity of sorption-site energies. For L-type curves, the exponent N commonly does not exceed 1.

We attempted to describe the adsorption isotherms shown in Fig. 7.1 and 7.2 based on the Freundlich isotherm equation:

$$S = K_f C^N \quad [7.1]$$

where S represents the (total) amount of sorbed Hg (μg kg^{-1}), K_f is the Freundlich distribution or partition coefficient (L kg^{-1}), and N is a dimensionless reaction order commonly less than 1. The Freundlich parameters N and K_f for all soil materials are presented in Table 7.2.

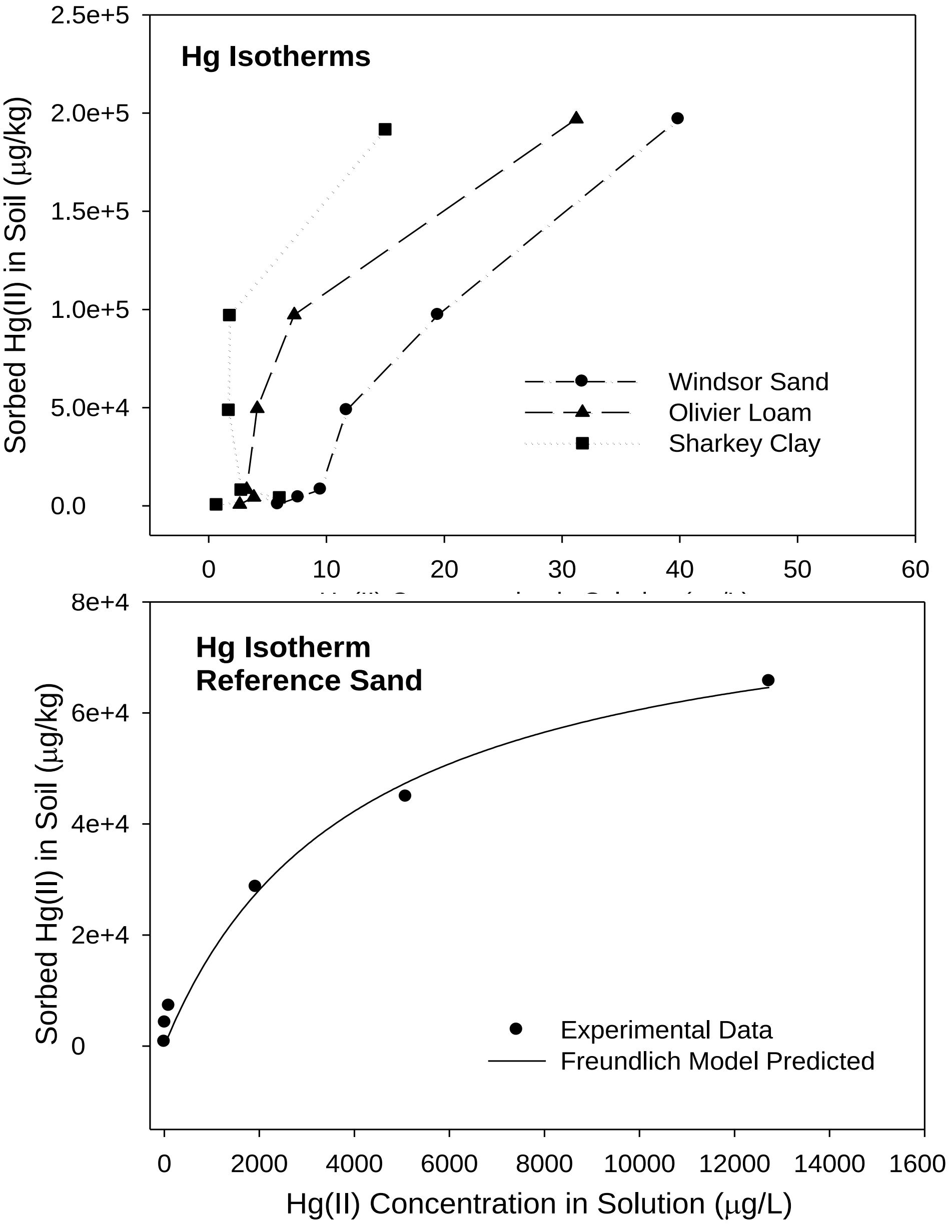

Figure 7.1. Adsorption isotherms of mercury by three soils and reference sand material after 24 h of reaction.

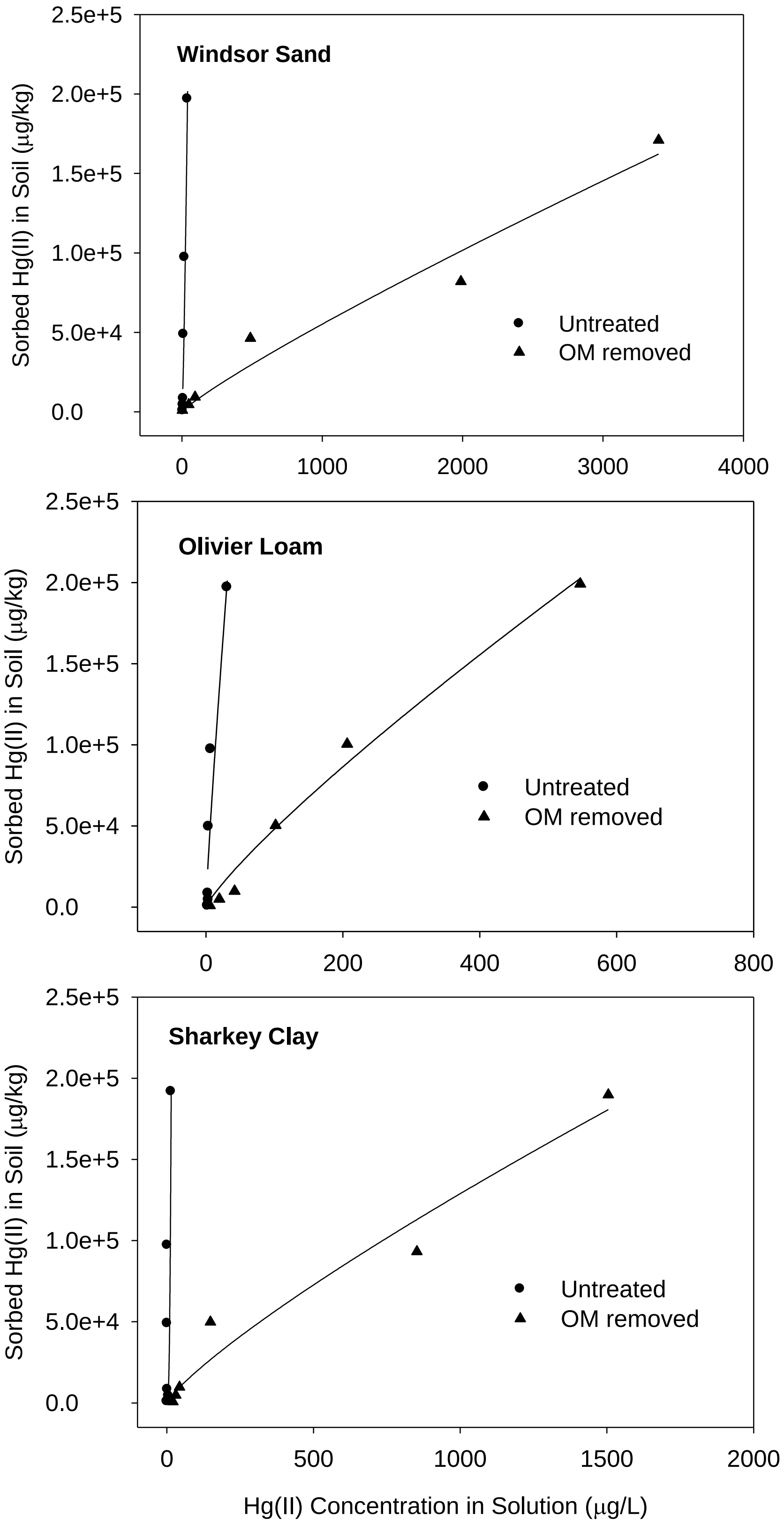

Figure 7.2. Adsorption isotherm of mercury on untreated and organic matter removal soils after 24 h of reaction.

All adsorption data were described with limited success by the Freundlich equation. The r^2 values ranged from 0.879 to 0.999. The Freundlich parameter N for all soils ranged from 0.83 to 0.98 (Table 7.2). The N parameter illustrates the dependence of the sorption process on Hg concentration. Our estimated N values were higher than those (0.52–0.79) reported earlier by Amacher et al. (1990). A possible reason may be the different anions of the background solution used to maintain the constant ionic strength (Cl^- for Amacher's study and NO_3^- in our study). Under acid conditions, the presence of Cl^- could significantly reduce Hg(II) adsorption for soils with low organic matter content (Barrow and Cox, 1992; Yin et al., 1996). Sarkar et al. (1999) demonstrated that for quartz and gibbsite, Hg adsorption was highest in the presence of Cl^- ions. Chloride ions can interfere with the binding of various Hg(II) forms with natural sorbents in soil and sediment media (Gabriel and Williamson, 2004). The N value for the reference sand was 0.44, which is significantly lower than values for the three soils.

The influence of organic matter removal on the three soils is illustrated in Fig. 7.2 (see also Table 7.2). When compared with the untreated soils, the amount of Hg adsorption after organic matter removal decreased by 4, 14, and 25% on Olivier, Windsor, and Sharkey soils, respectively. The N values for all soils when organic matter was removal showed no significant variation when compared with the untreated soils. In contrast, the K_f value significantly decreased, which implies that organic matter removal reduced the binding strength for Hg in the treated soils. This finding is consistent with other reports that showed Hg is closely associated with organic matter in soil (Yin et al., 1996, 1997b). Other researchers reported that the complexing capacity of humic matter is far greater for Hg than for other metals, such as Cd, Zn, Cu, and Pb, because of covalent bonds that commonly form between Hg and organic molecules (Kernorff and Schnitzer, 1980; Gabriel and Williamson, 2004).

7.3.2 Release

Release or desorption rates of Hg after adsorption are presented with time in Fiig. 7.3 and 7.4. As expected, the desorption behavior for the different soils exhibited different affinities for Hg. After the first 3 to 4 d of desorption, more than 48% of the adsorbed Hg was desorbed from the reference sand, whereas less than 8% of the adsorbed Hg was desorbed from the Windsor and Olivier soils. For the Sharkey soil, extremely low Hg concentration prevailed during desorption and was below the limit for detection (2 μg L^{-1}). Similar findings were reported by Amacher et al. (1990). For the reference sand, as the initial Hg concentration in the solution increased from 1 to 20 mg L^{-1}, the amount of Hg desorbed increased from 12.1 to 48.7% of that applied.

This implies that for the reference sand a large amount of Hg was being bound by low-energy sites. In contrast, for Windsor and Olivier, the amount of Hg desorbed decreased from 7.6 to 0.3% for initial Hg concentrations of 0.5 to 20 mg L^{-1}, respectively. This suggests that most of the Hg was bound by high-energy sites in these two soils. It is obvious the Windsor and Olivier soils had more high-energy sites than the reference sand. These high-energy sites may be sites that form extremely stable surface complexes with Hg or be micropores that trap Hg and require high activation energy for Hg release. This finding is consistent with other reports regarding soil affinity for Hg (Yin et al., 1997b).

In most soils, inorganic and organic sorbents for Hg are clay minerals; amorphous oxides; hydroxides; oxyhydroxides of Fe, Mn, and Al (such as FeOOH); amorphous FeS (under reducing conditions); and organic substances in particulate and dissolved phases (i.e., humic and fulvic substances) (Lockwood and Chen, 1973). Of the above sorbents, oxides and organic matter (humic material) have the highest adsorption capacities for Hg^{2+} (Gabriel and Williamson, 2004). Differences in the organic matter content and particle size distribution are the likely reasons for

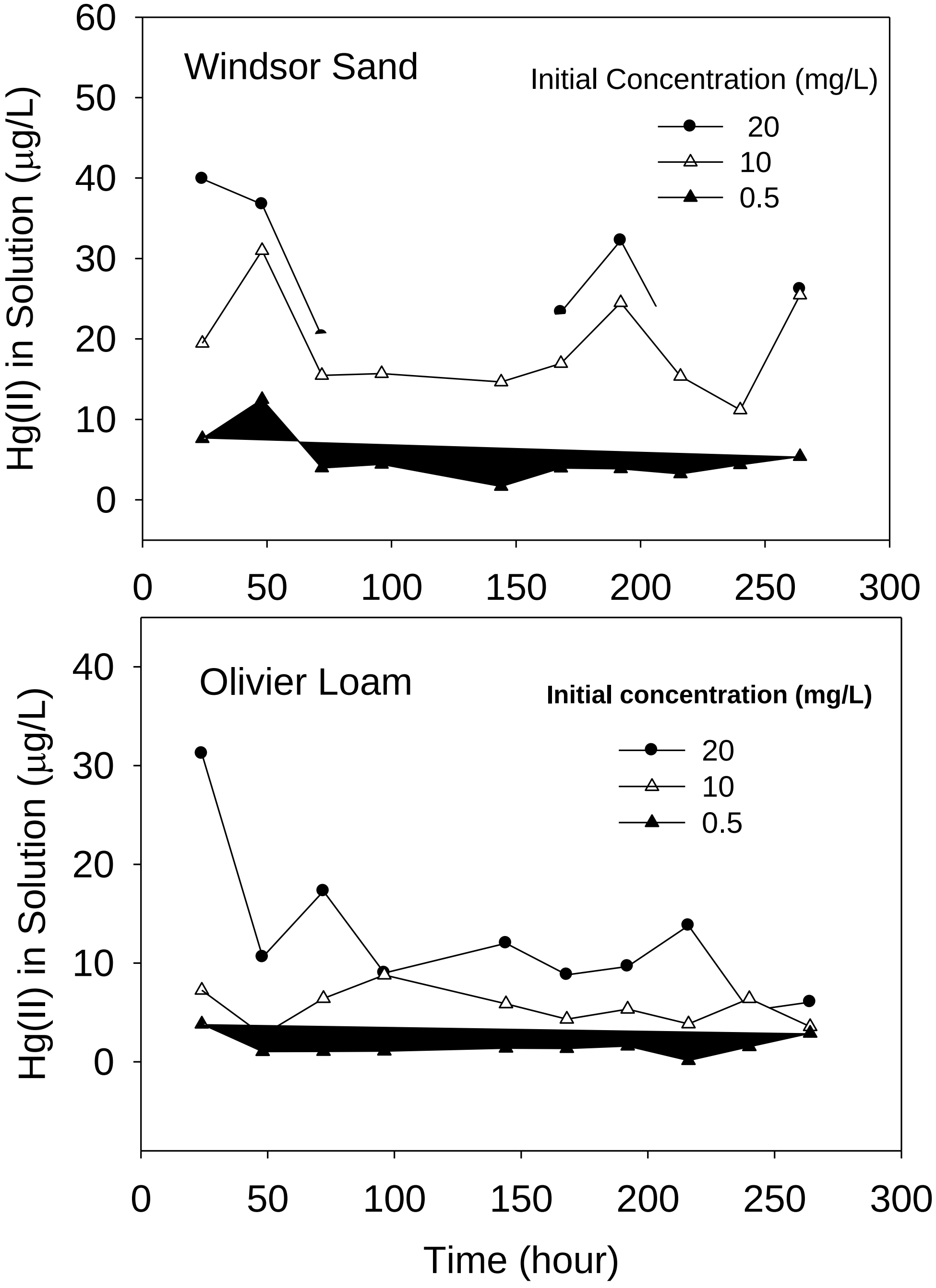

Figure 7.3. Mercury concentration in solution versus time during desorption for Winsor soil (top) and Olivier soil (bottom).

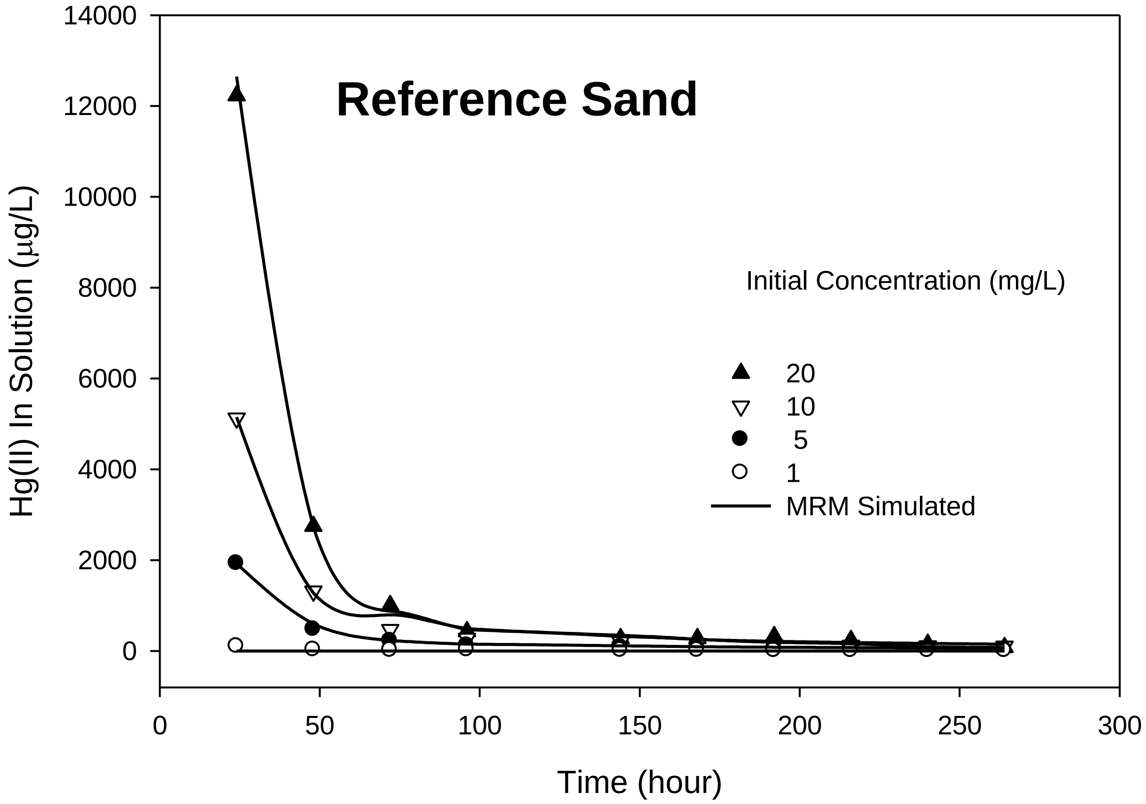

Figure 7.4. Mercury concentration in solution versus time during desorption for different soils. The solid curves are multireaction model (MRM) simulations.

the different Hg adsorption and desorption behavior of the reference sand when compared with the other three soils used in this study. Overall, the total amounts of Hg released, as a percentage of that adsorbed, were 25.0 to 58.5%, 1.0 to 15.2%, and 0.4 to 3.4% for the reference, Windsor, and Olivier soils, respectively. The amount of Hg(II) released was much smaller than that sorbed. Similar results were reported by Yin et al. (1997a), who used a similar kinetic batch technique, and by Miretzky et al. (2005), who performed a soil-column experimental study. These studies demonstrated that the principal causes of the observed irreversibility were the stability of the surface complexes formed and the mechanism through which adsorption occurs.

The reference sand, containing no organic matter and clay, exhibited strong Hg(II) adsorption–desorption hysteresis (Fig. 7.5). Because the reference sand was devoid of organic matter, we suggest that Hg retention is likely due to adsorption by quartz and metal oxides. Strong evidence of Hg adsorption by quartz was reported by Sarkar et al. (1999) over a wide pH range. They postulated that strong Hg sorption by quartz was due to inner- rather than outter-sphere complexation. In addition, the importance of iron oxides for Hg adsorption was extensively reported by several investigators (Kinniburgh and Jackson, 1978; Lockwood and Chen, 1974; Cruz-Guzmán et al., 2003). Gabriel and Williamson (2004) concluded that iron oxides were the second important sorbents for Hg, following organic matter.

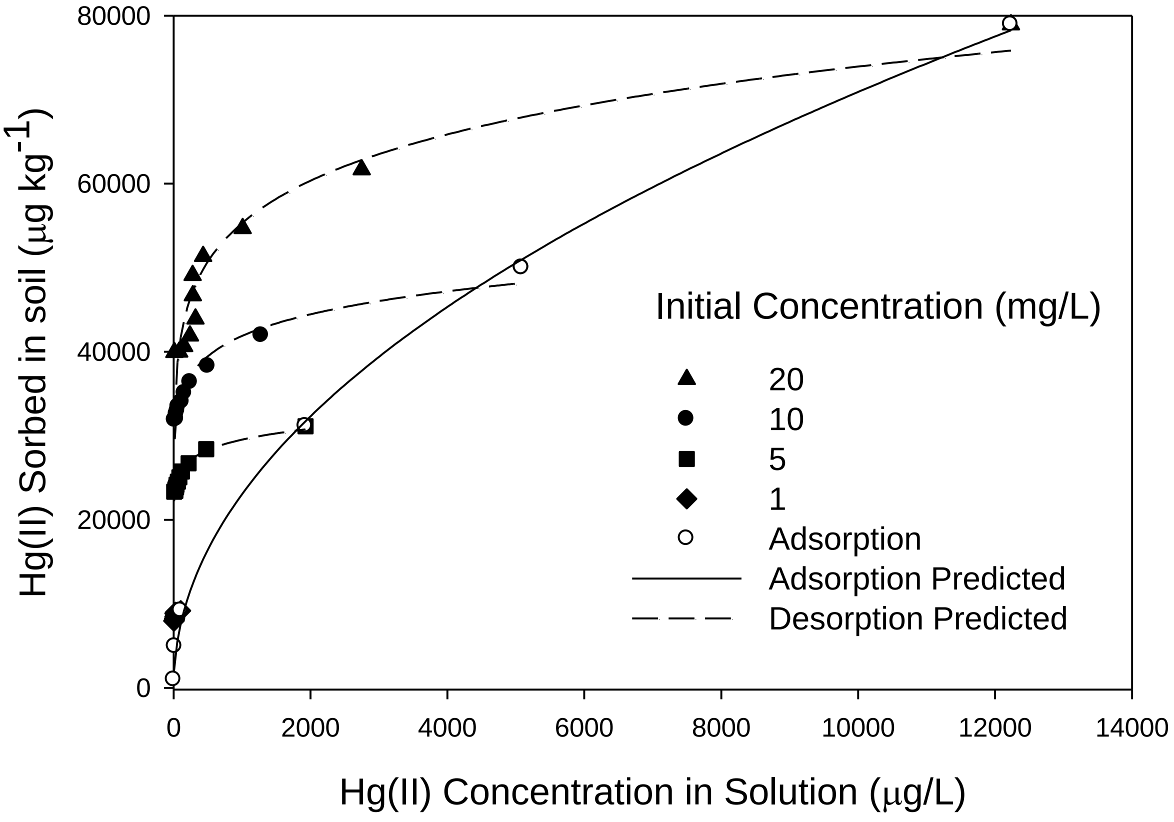

Figure 7.5. Isotherms of mercury desorption from sand based on successive dilution after 24h adsorption for different initial concentrations (Co) of 1, 5, 10, and 20 mg L^{-1}. The solid and dashed curves depict results of curve-fitting with the Freundlich equation for 24-h adsorption and desorption isotherms, respectively.

7.3.3 Multi-reaction Modeling

The simulation data represented by the solid curve shown in Fig. 7.4 are model simulations performed in an effort to describe the kinetic results for Hg retention by the reference sand. The model used was the multi-reaction and transport model described by Zhang and Selim (2006) and given in Fig. 7.6. This multipurpose model accounts for several concurrent- and consecutive-type retention reactions as well as transport of heavy metals in soils. These reactions include equilibrium and kinetic mechanisms of the reversible and irreversible types. The model version chosen in this analysis can be presented by the following formulation:

$$S_e = K_e \left(\frac{\theta}{\rho} \right) C^n \qquad [7.2]$$

$$\frac{\partial S_k}{\partial t} = k_1 \left(\frac{\theta}{\rho} \right) C^m - [k_2 + k_3] S_k \qquad [7.3]$$

$$\frac{\partial S_i}{\partial t} = k_3 \, S_k \qquad [7.4]$$

$$\rho \frac{\partial S_s}{\partial t} = k_s \theta C \qquad [7.5]$$

where S_e is the amount retained on equilibrium-type sites (mg kg^{-1}) and has a low binding energy, S_k is the amount retained on kinetic-type sites (mg kg^{-1}) through strong interactions with the soil matrix, and S_i and S_s represent the amount retained irreversibly (mg kg^{-1}). The coefficient K_e is an equilibrium constant (dimensionless) associated with instantaneous reactions, and k_1 and k_2 (h^{-1}) are the forward and backward reaction rate coefficients associated with the kinetic-type sites, respectively. The parameter k_3 (h^{-1}) is the irreversible rate coefficient associated with the kinetic sites, and k_s (h^{-1}) is the irreversible rate coefficient associated with the soil solution. The parameters n and m are the reaction orders (dimensionless) associated with S_e and S_k, respectively; θ is the soil water content ($cm^3\ cm^{-3}$); and ρ is the soil bulk density (g cm^{-3}). We also assumed m = n = 0.44, which was derived from Freundlich parameter N given in Table 7.2 for the reference sand.

To obtain the simulation shown in Fig. 7.4, we used the multi-reaction model along with a nonlinear least-squares optimization scheme, which provided best-fit of the model to the experimental data. Model parameter estimates were 0.143 ± 0.005, 0.053 ± 0.003, and 0.005 ± 0.001 h^{-1} for k_1, k_2, and k_3, respectively. The goodness of fit of the model to the experimental data as measured by r^2 and RMSE was 0.999 and 0.120, respectively. Based on model calculations, Hg was assumed to be retained in S_k and S_i forms (Fig. 7.6). Both forms may be regarded as somewhat strongly or strongly retained, where S_k is assumed to be slowly reversible and S_i is fully irreversible. In order for the kinetic phase S_k to be considered as slowly reversible or strongly held, the associated forward rate coefficient k_1 must be much greater than the backward rate k_2, as was the case here. As a result, we can assume that S_i is best regarded as strongly retained, which is consistent with our experimental results. When S_s rather than S_i as the irreversible form was considered (Fig. 7.6), the model did not provide significant improvement in the predictions of the retention data ($r^2 = 0.998$; RMSE = 0.151). Moreover, when we used a model version that combined both irreversible forms (S_i and S_s) along with the reversible form S_k, we found that the incorporation of S_s did not improve model predictions. Based on these calculations, kinetic behavior of the irreversible and/or slowly reversible are the dominant mechanisms for the retention of Hg and are best represented by S_k and S_i in the multi-reaction model with k_1, k_2, and k_3 as the associated rates of reactions. Our findings are also consistent with those of Miretzky et al. (2005), who reported much larger forward than backward rates for Hg retention.

Table 7.3. Experimental parameters for miscible displacement experiments for the three soil columns.

Sample	Bulk density ρ_b	Water content θ	Column pore volume p.v.	Darcy flux v	Input pulse (pore volume) (p.v.)	Dispersion coefficient D
	(g/cm^3)	(cm^3/cm^3)	(cm^3)	(cm.h^{-1})		(cm^2.h^{-1})
Reference sand	1.69	0.36	58	0.373	5	0.52
Windsor Sand	1.48	0.44	141	0.364	10	2.33
Olivier Loam	1.19	0.55	177	0.366	10	2.93

7.3.4 Transport

For Windsor and Olivier soils, Hg miscible displacement results indicate strong retention and no distinct peaks or concentration maxima in the effluent solution from the soil columns (Fig. 7.7). The results are presented as breakthrough curves (BTCs) of the relative concentration (C/C_o) versus pore volumes (V/V_o), where C_o is applied (or input) concentration (mg L^{-1}) and V_o is the column pore volume (cm^3). Experimental parameters for the miscible displacement of Hg in the different soil columns are given in Table 7.3. The transport of Hg through the columns was significantly retarded relative to the transport of the conservative tracer (tritium) shown in Fig. 7.8. Generally, Hg breakthrough results exhibited erratic patterns with ill-distinguished peaks, which indicate that Hg is strongly retained and highly immobile in both soils. In fact, after 10 pore volumes of Hg pulse application and the subsequent leaching by 20 to 30 pore volumes of Hg-free solution, the percentages of Hg recovery in column effluents were less than 1% of applied Hg for Windsor and Olivier soils. For Sharkey clay soil, the low concentration of Hg in the column effluent was below the Hg detection limit (2 μg L^{-1}), with 99.9% of applied Hg retained by the soil in the column (results not shown). This observation is consistent with adsorption–desorption results discussed above that indicated that Sharkey had the highest Hg retention capacity whereas lowest retention was observed for the reference sand. Such strong retention of Hg during transport is further evidence of the strong retention as indicated by the adsorption–desorption kinetic data discussed previously.

We recognize that preferential flow is often the dominant mechanism for the transport of dissolved chemicals in many soils. In fact, physical non-equilibrium has been shown to play an important role in the movement of pesticides, phosphorus, and possibly heavy metals (Selim and Ma, 1998). Studies dealing with preferential flow are often performed in the field or where large intact soil columns are used. Breakthrough curves of Fig. 7.7-7.9 indicate that physical non-equilibrium transport conditions for the mobility of Hg the columns were absent.

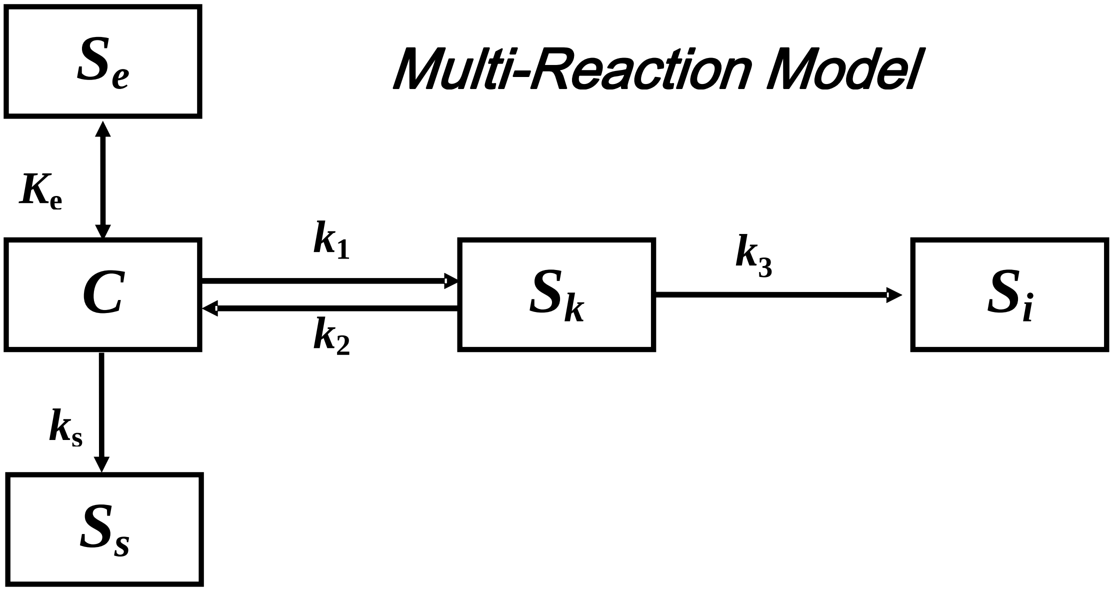

Figure 7.6. A schematic diagram of the multireaction model (MRTM). Here C is concentration in solution, S_e, S_k, S_i and S_s are the amounts sorbed on equilibrium, kinetic, consecutive and concurrent irreversible sites, respectively, where K_e, k_1, k_2, k_3 and k_s are the respective rates of reactions.

This is perhaps due to the fact that our miscible displacement columns were performed in packed columns with disturbed soils where preferential flow conditions are not expected.

One of the few studies that indicated significant Hg mobility in soil columns is that of Miretzky et al. (2005) on alluvial, podozol, and humic gley soils from the Amazon region. The Hg input pulse concentration used was an order of magnitude higher (100 mg L^{-1}) than that used in our present study (8 mg L^{-1}). Such high Hg loading to each soil column is perhaps the main reason for the significant Hg recovery in the effluent solution. Miretzky et al. (2005) reported that Hg retention in soil columns ranged from 17.39 to 62.69% of that applied. Moreover, they reported Hg peaks of their BTCs of as much as 80 mg L^{-1}. In contrast, only in the reference sand, was a noticeable Hg peak observed; this peak did not exceed 2 mg L^{-1} (Fig. 7.9). In fact, for the BTC of the reference sand, which exhibited symmetry, the recovery of Hg from the soil column was only 17.3% of that applied. Therefore, more than 80% of the applied Hg was strongly retained by the reference sand column. Recently, Wernert et al. (2003) reported strong Hg retention in a column experiment of quartz sand (99% quartz and amorphous silica) where continuous Hg pulse application of 100 mg L was maintained. No Hg was observed in the column effluent during the first 100 pore volumes. Approximately 500 pore volumes of Hg application were needed before a concentration maximum of 22 mg L^{-1} was reached. Wernert et al. (2003) did not report the percentage of Hg retained in their quartz column.

Mercury BTC for the reference sand column was successfully described using the multi-reaction model discussed above when coupled with the convective–dispersive equation for reactive solutes in soils (Zhang and Selim, 2006). The simulation is shown by the solid curve in Fig. 7.9, which indicates that the model was successful in describing the BTC (r^2 = 0.979; RMSE = 0.012). Although the complete model described the data well, we found that a fully kinetic

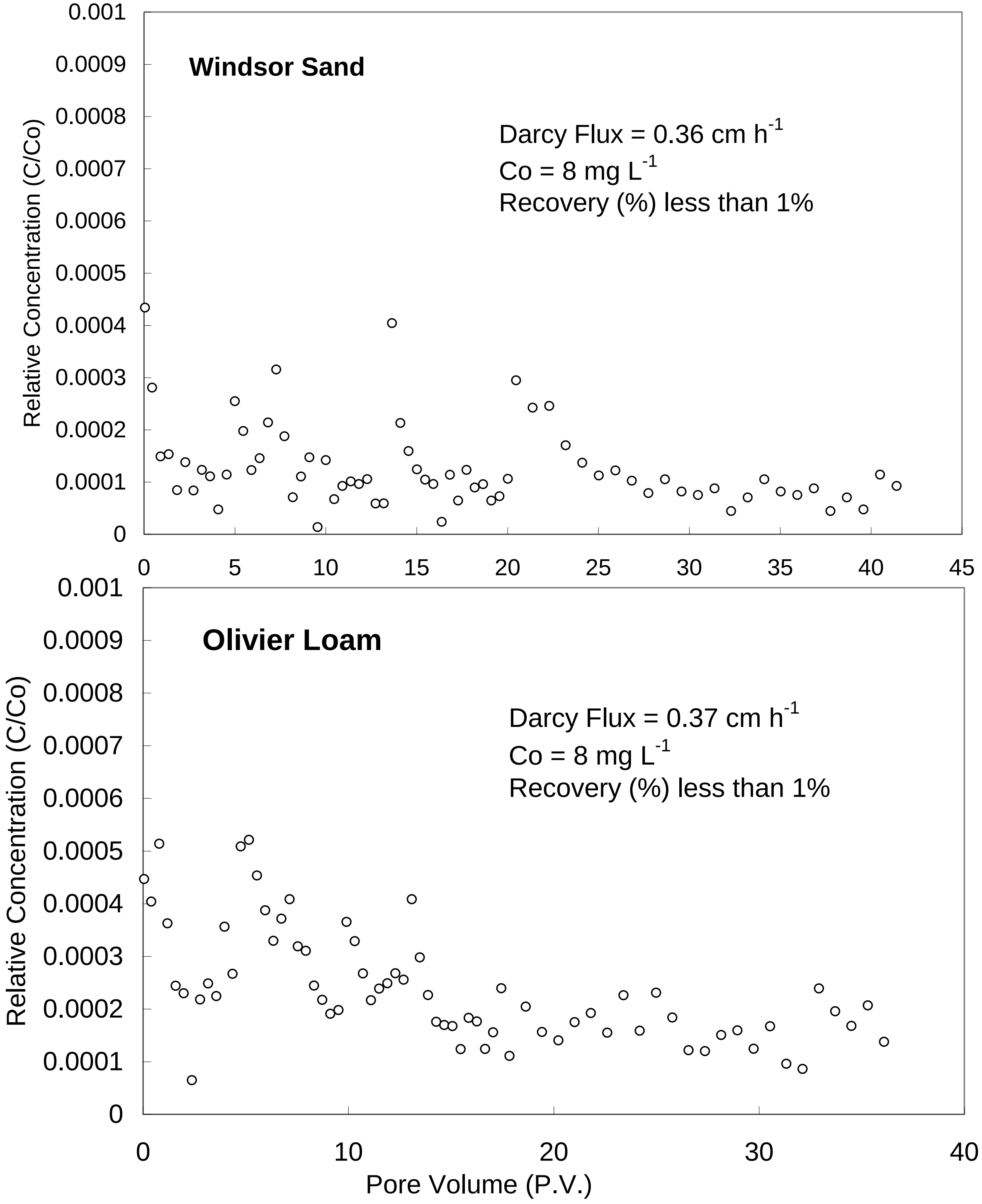

Figure 7.7. Breakthrough curves (BTCs) of applied mercury pulse (Co=8 mg L^{-1}) for Windsor sand (top) and Olivier loam (bottom).

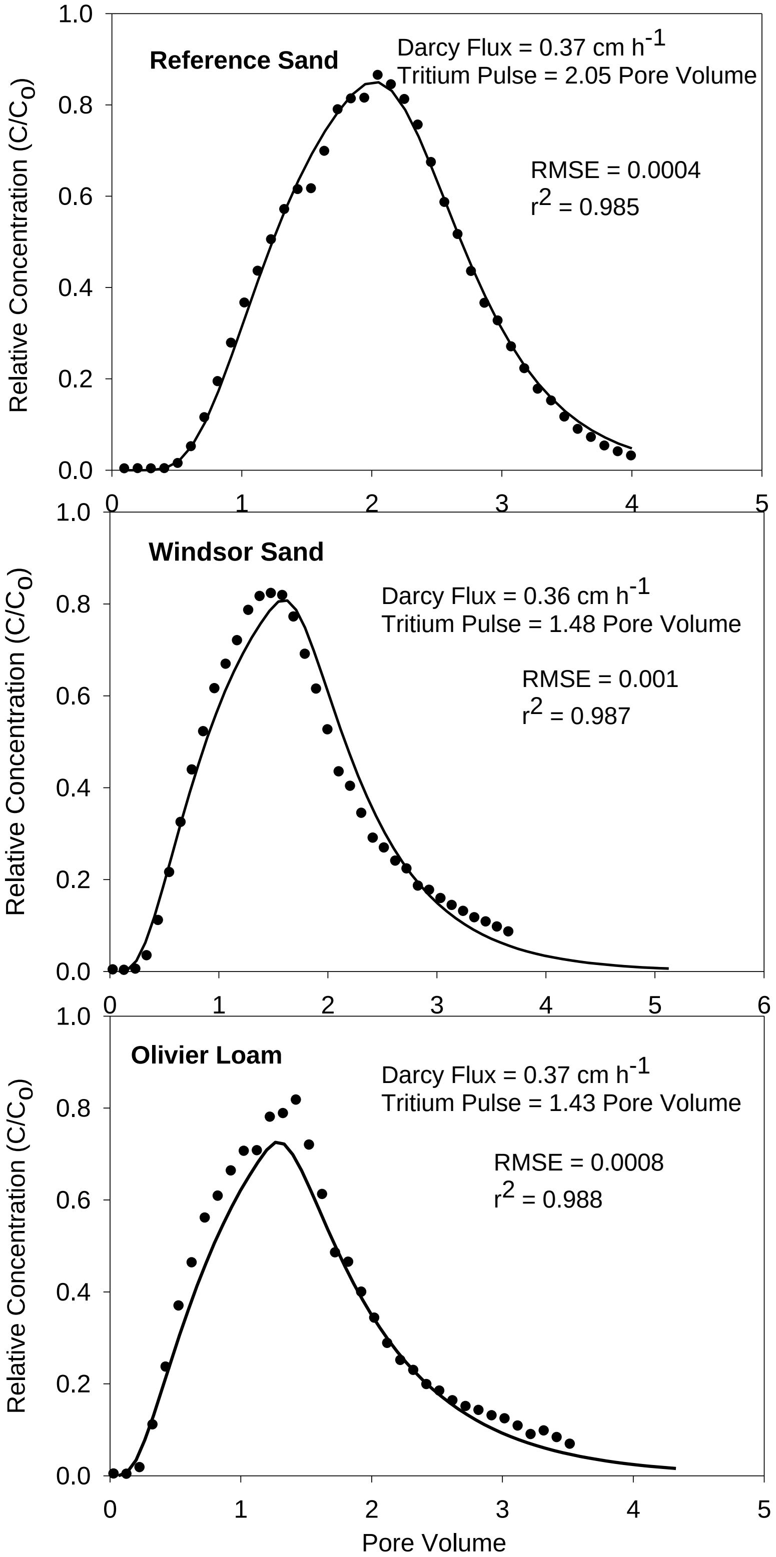

Figure 7.8. Tritium breakthrough curves for the reference sand, Windsor and Olivier soil columns. Solid curves are simulations using the convection-dispersion equation (CDE) for non-reactive solutes (Zhang and Selim, 2006).

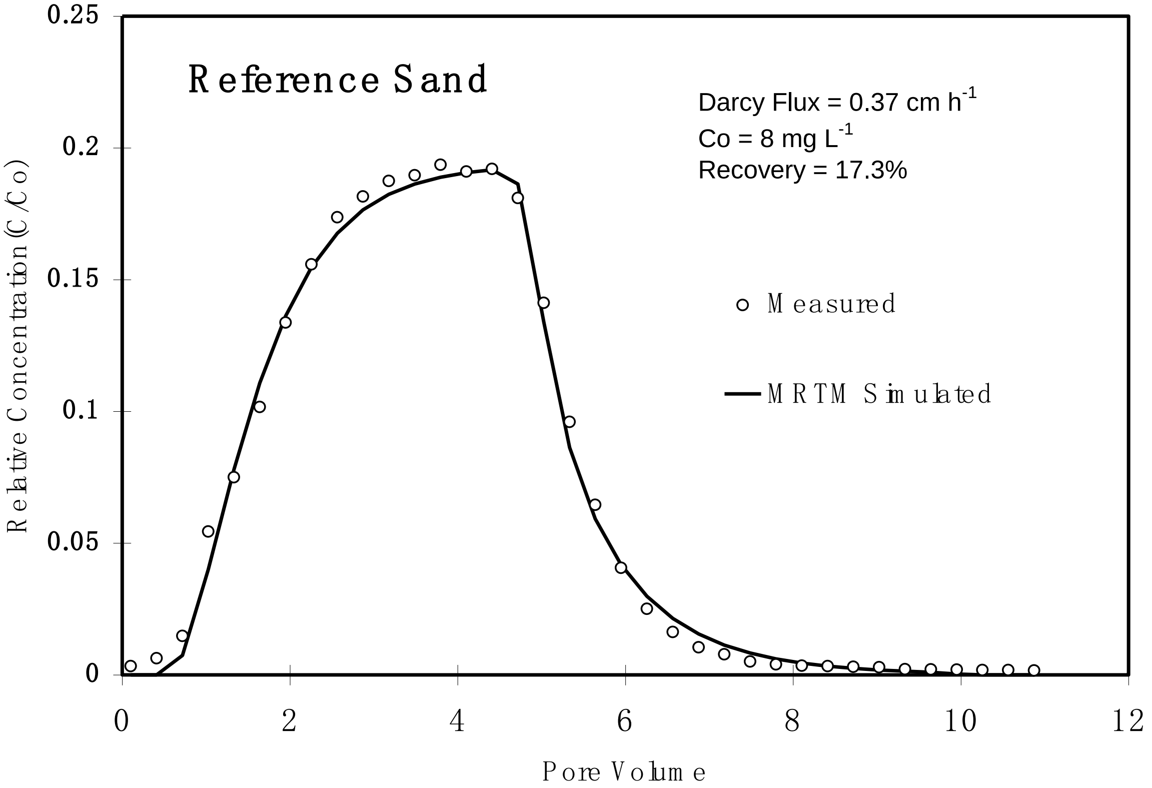

Figure 7.9. Experimental Hg (II) breakthrough curve (BTC) from the reference sand column (Co=8 mg L^{-1}). The solid curve is multireaction model simulation where the rates of reactions were 0.340±0.019, 0.033±0.001 and 0.001±0.001 h^{-1} for k_1, k_2, and k_3, respectively.

model version described the BTC equally well. As a result, a simple model formulation with reversible kinetic and irreversible sites (S_k and S_i) is recommended for the case of the reference sand. Such a finding is consistent with model predictions based on our adsorption–desorption data discussed above and adds credence to the multi-reaction model. Here the irreversible reaction associated with S_i may be considered as inner-sphere complexation, as suggested by Sarkar et al. (1999), in the reference sand. Inter-particle diffusion is another process that is responsible for retention of Hg. Such a process is often considered as a rate-limiting step (Yin et al., 1997a; Miretzky et al., 2005). Nevertheless, model validation and verification are needed, which require further experimental investigation of the processes associated with Hg sorption and transport in soils.

In conclusion, Hg adsorption by all three soils was strongly irreversible where the amounts released or desorbed were extremely small. Moreover, the removal of soil organic matter resulted in a decrease in Hg adsorption in all soils. Adsorption followed S-shape isotherms and was described with limited success using a nonlinear (Freundlich) model. Results from column transport experiments indicated that Hg is highly immobile in all soils investigated. Mercury leaching was only observed in the effluent from a reference sand column. We also conclude that based on adsorption–desorption and transport data, kinetic irreversible and slowly reversible processes are the dominant mechanisms for the retention of Hg by the reference sand.

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CHAPTER 8: CONCLUSIONS

Adsorption-desorption of nickel (Ni) is the primary factor that impacts the bioavailability and mobility of Ni in soils. Adsorption of Ni was highly nonlinear with a Freundlich reaction order *N* much less than 1 for Windsor sand, Olivier loam and Webster loam. Adsorption of Ni by all soils was strongly kinetic, where the rate of Ni retention was rapid initially and was followed by gradual or somewhat slow retention behaviour with increasing reaction time. Freundlich distribution coefficients exhibited continued increase with reaction time for all soils. Desorption of Ni was hysteretic in nature which is an indication of lack of equilibrium retention and/or irreversible or slowly reversible processes. A sequential extraction procedure provided evidence that a significant amount of Ni was irreversibly or partially reversible adsorbed on all soils.
The results of saturated column transport experiments demonstrated that all measured Ni breakthrough curves (BTCs) exhibited extensive asymmetry as illustrated by the difference in the shape of the effluent side from the leaching or desorption side. After extensive leaching, the percentages of Ni mass recovery from column effluent ranged from 68% for Windsor soil to as low as 19% for Webster soil, indicative of irreversible Ni retention. Two distribution patterns of the amount of sorbed Ni with soil depth were observed: a leaching pattern and an accumulating pattern.

A multireaction model (MRM) with nonlinear equilibrium and kinetic sorption successfully described the adsorption kinetics of Ni for all soils. We further evaluated several fomulations of MRM model for its prediction capability of Ni retention as well as transport in soils. Based on root mean square errors, model formulations having kinetic reversible reaction along with a consecutive or concurrent irreversible retention were considered the most favorable in describing Ni retention over time for all three soils. The use of batch model parameters provided poor overall predictions of all BTCs. The use of batch rate coefficients grossly underestimated the extent of Ni retention in Windsor and Olivier soils and overestimated Ni mobility by all model formulations used. We thus concluded that BTC predictions based on batch parameters are not recommended. However, an inverse mode of MRM was was capable of describing Ni BTCs for all soils and the distribution of Ni with soil depth.

The competition between Ni and Cadmium (Cd) has the potential of increasing Ni mobility and bioavailability in natural soil and water environment. The highly nonlinear single-solute isotherms of Ni and Cd were observed for all studied soils. Our results from batch experiments demonstrated that rates and amounts of Ni adsorption by these soils were significantly reduced by increasing Cd additions. The presence of Cd in soils increased mobility of Ni in columns as well as forced Ni sorption at higher affinity (or specific sorption) sites. The simultaneous presence of Ni and Cd also changed the distribution of Ni and Cd from accumulation pattern to leaching pattern in Olivier soil column, which has the potential risk of contamination of groud water.

VITA

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