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Christoph Hinz

Louisiana State University and Agricultural & Mechanical College

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Sorption, kinetics, and transport of selected heavy metals in soil: A laboratory study and modelling approaches

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The Louisiana State University and Agricultural and Mechanical Col., 1992

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SORPTION, KINETICS, AND TRANSPORT OF SELECTED HEAVY METALS IN SOIL:
A LABORATORY STUDY AND MODELLING APPROACHES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Agronomy

by

Christoph Hinz
Dipl.-Geol., Rheinisch-Westfälische Technische Hochschule Aachen, Federal Republic of Germany, 1986
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ABSTRACT

The retention and transport behavior of heavy metals in soils is affected by soil chemical heterogeneity. The objectives of this study were to evaluate (i) the effects of heterogeneity on solute transport of heavy metals under steady water flow, (ii) the applicability of single solute and ion exchange isotherms to model Zn and Cd transport in soil columns, (iii) the modelling of the sorption kinetics of Zn under batch and flow conditions, and (iv) the effects of organic matter and iron oxide removal on the kinetics of Zn sorption in soils.

A sensitivity analysis showed that site affinity distribution functions describing chemical heterogeneity in soils are directly related to breakthrough behavior of reactive solutes. The general Langmuir-Freundlich and the Rothmund-Kornfeld equations adequately described heavy metal sorption and transport in soil columns for conditions of variable ionic strength. The modelled and measured Zn breakthrough curves in an acidic sandy soil agreed quantitatively whereas Cd transport was qualitatively predicted. Zn and Cd transport in a weakly acidic silt loam soil was only qualitatively described by mass transfer kinetics.

The kinetics of Zn retention as measured under batch conditions were described using a multireaction model and a two-site second-order models and were successful only for a narrow concentration range. Based on noncompetitive high affinity and competitive low affinity sorption sites describing Zn-Ca ion exchange a new model was proposed. This model successfully described Zn sorption kinetics in an acidic soil at initial concentrations varying from 0.01 to 100 mg L$^{-1}$ between 2 and xx
288 h. It also qualitatively predicted Zn kinetics as measured by a thin disk flow method with flow interruptions varying from 0.5 min to 30 d. Modelling and experimental results suggest that equilibrium heavy metal-Ca competition governs the retention at high heavy metal concentrations above 0.1 mM, whereas slow noncompetitive sorption processes dominate the low concentrations below 0.1 mM. The removal of organic matter and iron oxides doubled and quadrupled the Zn sorption at low concentrations, respectively and decreased the rate of reaction.
1.1. Introduction

The distribution of ionic elements in the environment is of vital interest to the researchers in various fields. Not only is nutrient cycling of importance but intensive industrial activity during the last century has caused pollution to be an important factor in the environment. Environmental problems such as toxic waste landfills, air pollution, and surface and groundwater contamination threaten terrestrial ecosystems and therefore the public health. One of the most important elements in our ecosystem is the soil. The soil represents an open system, that is, matter exchange between the hydrosphere, atmosphere, and biosphere takes place. In fact, the soil acts as an interface between ground water and surface water as well as the biosphere and atmosphere. Matter transfer between these different environments becomes a central topic in understanding the dynamics of the soil system. Knowing the dynamics of such a system will help to evaluate the effects of pollution on the ecosystem as a whole.

One of the very essential ingredients of life are reactive ions. Plants and animals need mineral nutrients, which are usually present in ionic form in aqueous solutions. Micronutrients such as zinc, copper, iron, manganese are essential to life; however, when available in excess they become toxic. The distribution of these ionic elements in the soil environment affects the plant health and therefore the overall soil
ecosystem. Assessing micronutrient and trace elements present in soil yields the following areas of research:

(i) biological effects of soil trace elements on the biosphere,
(ii) the chemical distribution of soil trace elements within the solid phase and the liquid phase and their bioavailability, and
(iii) the mass transfer of trace elements within the soil and from soil to plants and animals.

The review, presented here, will deal with (ii) and (iii) limited to the soil processes alone, for example, the chemistry and the mass transfer of trace elements in soils, soil minerals, and organic matter. First, a review of chemical processes and reactions will be followed by methods and modelling approaches; second, a review of kinetic processes will be given and followed by a description of reactive transport phenomena.

In order to emphasize the uniqueness of soils one has to define soil as an open system which consists of complex mixtures of interacting organic and inorganic solids and fluids serving as a sink and source of trace elements. Even though many of the chemical components making up the soil occur in other environments such as rivers, lakes, and sediments, the soil has its own dynamics such as the formation of horizons and accumulation of soil solids such as oxides and clay minerals in the Bt horizon. In that respect, the soil processes are somewhat related to the diagenesis of young sediments. Keeping in mind the complexity of biological, chemical and physical processes taking place in soils, one certainly can learn from the chemistry of pure soil
components. But one cannot easily take such results and apply them to soils. For example, if a certain process on a surface of a mineral has been proven to exist, one can assume that such a process will occur most likely in a soil. However, this process may contribute very little to the overall sorption behavior. Therefore, it is not surprising that empirical methods for describing soil/solute interaction remain popular. One of the advantages of empirical approaches is the simplicity of application and the ease of use. The review presented here emphasizes the behavior of metal retention in soils. General reviews of metals in the aquatic environment as well as in soils with aspects of chemical processes, occurrences, and contamination as well as remediation and reclamation are given by Honeyman and Santschi (1988), Salomons and Förstner (1986), Nriagu (1980), Dowdy and Volk (1983), Assink and van den Brink (1986), and Cairney (1987).

1.2. Processes and Modelling

1.2.1. Sorption

Since soils are 'ill-defined' systems, the mechanisms of heavy metal retention are unknown or very difficult to verify. Therefore, sorption refers to processes which associate a solute with a solid independent of the reaction mechanisms. In contrast, adsorption is defined by the association of a solute with a surface. Furthermore, outersphere and innersphere complexation are equivalent to nonspecific and specific adsorption (Sposito, 1984). Electrostatic adsorption includes the ions bound through
outersphere complexation as well as the diffuse ion swarm caused by charged surfaces. In contrast chemisorption refers to ions forming covalent or ionic bonds.

The chemical properties of soil particles often determines the nature of observed sorption processes. Electrostatic forces due to isomorphous substitutions in layer silicates may cause outersphere complexation of divalent transition and heavy metals. Spectroscopic methods such as ultraviolet-visible and electron resonance spectroscopy have been used to confirm this bonding mechanism (McBride, 1989). Since soil contains considerable amounts of Ca and Mg (exchangeable bases), the heavy metals adsorbed by electrostatic forces compete with alkaline earth elements. In fact, at low pH's some of the heavy metals and Ca exhibit the same sorption affinity (el-Sayed et al., 1970). However, the incomplete recovery or apparent hysteresis of heavy metal sorption and desorption at low surface coverage suggests other than electrostatic forces as the retention mechanism (Garcia-Miragaya and Page, 1977). Specific sorption may occur at the -SiOH and -AlOH groups of clay mineral edges. Furthermore, the formation of hydrolysis products such as hydroxy polymers may exhibit very strong affinity towards silicate surfaces (Tiller et al., 1984b).

In contrast to electrostatic adsorption, chemisorption dominates the sorption at low surface coverage of minerals such as oxyhydroxides of Fe and Al. McBride (1989) reviewed indirect evidences for chemisorption as follows: (i) divalent metal ions M$^{2+}$ exchange with up to two H$^+$, (ii) oxides exhibit highly specific sorption preference towards particular heavy metals, and (iii) metal adsorption causes surface charge changes of oxides. Furthermore, the extraction of different 'pools' of heavy
metals by extreme treatments such as the dissolution of minerals indicate specific interactions between heavy metals and minerals such as oxides of Fe, Mn, and Al. Specifically adsorbed heavy metals occur at isolated surface sites and are bound rigidly as shown by electron spin resonance spectroscopy as opposed to ions bound nonspecifically to layer silicate clays (McBride, 1989). Since inner sphere complex formation takes place at silanol and aluminol groups, the mineralogy is of great importance. Moreover, chemisorption is highly dependent on the degree of crystallinity and surface morphology of the minerals.

In addition to specific interaction of ions with mineral, surface precipitation may take place. According to Stumm and Morgan (1981), heterogeneous nucleation is a significant process contributing to crystal formation in natural aquatic environments. This nucleation is catalyzed by mineral surfaces and, therefore, homogeneous nucleation is unlikely to occur in soils. In fact, surface precipitation may take place at a concentration far below that of the solubility product (Brümmer et al., 1983; Dzombak and Morel, 1986). In addition to surface precipitation, solid solution formation can contribute to the retention of heavy metals. In contrast to precipitation solid solutions do not have constant solubility products. Solid solutions are mixtures of two solutes in the solid phase where the composition of the solid phase is dependent on the composition of the aqueous phase. Solid solution formation is supported by the fact that some heavy metal ions are of the same size as Mg and, therefore, may form mixed hydroxide interlayers in layer silicate clays (McBride,
1989). Further evidence has been advanced by Davis et al. (1987) who attributed slow sorption of Cd on calcite to recrystallization of Ca and Cd carbonate.

Soil organic matter plays an important role in sorption of heavy metals on surface soils. Due to the complex chemical structure of organics such as soil organic matter and humic substances (Oades, 1989), the bonding nature of heavy metal sorption includes inner- and outersphere complexation as well as chelation. Heavy metal affinity depends on the ratio of ions adsorbed to the total amount of available sorption sites. As shown by Hendrickson and Corey (1981), the affinity of Cd is much greater as compared to Ca at low Cd concentrations than at high ones. McBride (1989) discusses this phenomenon in terms of the Lewis acid and base concept. At low Cd loadings the affinity of the soft base Cd towards soft acidic surface functional groups is very high and therefore Cd is preferentially adsorbed. In contrast, at high Cd loadings, Ca can compete with Cd for harder bases such as carboxylate ligands. The bonding mechanism can also depend to some extent on the experimental conditions (McBride, 1989). In contrast to soil minerals, organic matter is characterized by its structural complexity and heterogeneity, which manifests itself in the diversity of possible reaction sites.

In addition to the chemical processes reviewed above, changes of the soil solid may be caused by redox reactions. Usually many reactions in the anoxic regime are catalyzed by microorganisms and hence biological processes may be significant in controlling heavy metal solubility and mobility (Domsch, 1989).
The numerous different surface functional groups of the organic and inorganic substances in soil as well as the various bonding mechanisms suggest that no single theoretical model can describe the sorption processes of heavy metals in soil. Nevertheless, predicting the fate of metals in the soil environment requires quantitative description and models of sorption and desorption processes.

The description of retention may be based on (i) well defined chemical reactions of several species in solution with different sorption sites, e.g. precipitation of a pure mineral or innersphere complexation at the solution/mineral interface; (ii) sorption of two or more competing ions regardless of the nature of the reaction; or (iii) sorption of a single solute on one (or more) reaction site(s) without any assumption of the reaction mechanism. Further details on each description of retention follows.

(i) Well defined reactions may be described by either chemical models based on molecular hypotheses or models based on thermodynamic data of the formation of pure solids and of the complex formation in the aqueous solution. The first modelling technique refers to surface complexation models, whereas the second refers to the ion-association model. In both cases, extra thermodynamic assumptions are invoked. The activity coefficients of the solid surface are predicted by surface complexation models. The ion-association model utilizes generally the Debey-Hückel theory to obtain single species activity coefficients (Sposito, 1986). The thermodynamic data base of the ion association model includes equilibrium reactions such as dissolution/precipitation, redox reactions, complex formation, and surface complexation. In general, such
thermodynamic data bases consist of equilibrium constants determined for pure minerals such as goethite, hematite, calcite, aragonite and others. The equilibrium chemistry approach for dissolution/precipitation reactions has been utilized for several years. Traditionally, activity ratios diagrams for a system of solids and solutes have been used to predict precipitation and dissolution. This approach has been described in detail by Lindsay (1979).

Computer programs for solving chemical speciation problems in aquatic environments such as rivers, lakes, aquifers, and soils have been in use for several years. Two general methods are used to determine the equilibrium concentration of the species of interest. The first is to solve a system of nonlinear equations derived from mass and/or charge balance expressions and is applied in programs such as SOILCHEM, MINTEQA2, WATEQ2, and PHREEQE (Sposito and Coves, 1988; Allison et al., 1990; Ball et al., 1979; Parkhurst et al., 1980). The other method is to minimize the change of Gibbs free energy of the overall reaction and is applied in CHARON (Bril et al., 1986). For a review of the use of current chemical computer codes the reader is referred to Basset and Melchior (1990). Also, programs such as SOILCHEM and MINTEQA2 have the option to use one or more surface complexation models. Reviews of surface complexation models are given by James and Parks (1982), Sposito (1983a), Barrow (1987), Leckie (1988), Davis and Kent (1990), and Dzombak and Morel (1990) and applications to soils are published by Goldberg and Sposito (1984), Charlet and Sposito (1987) and Zachara et al. (1989).
Since soils are complex mixtures of solids and fluids and contain numerous chemical components such as clay minerals, oxides/hydroxides of iron and aluminum, possibly carbonates, organics (such as humic and fulvic acids) and others, their interaction as well as the effect of microbiological activity may influence heavy metal sorption (Huang and Schnitzer, 1986; Stone, 1988; Domsch; 1989, Clapp et al., 1991). In addition, colloidal interaction of reactive soil particles alters the chemical behavior as predicted by using data from pure substances. In fact, the concept of sorptive additivity of systems of binary oxyhydroxides, clay minerals, and humic acids is generally not valid (Honeyman, 1984; Altmann and Leckie, 1987; Honeyman and Santschi, 1988). Furthermore, the comparison of sorption behavior of heavy metals in soils and soil minerals with the above mentioned approach resulted in several discrepancies which call into question the practical applicability of these models to predict the heavy metal fate in soils (Brümmer et al., 1983; Herms and Brümmer, 1984). Thus, the equilibrium reaction approach may not yield satisfactory results in predicting retention of heavy metals in soils. However, the advantage of this method is its universal applicability and its ability to obtain information without actually measuring the retention.

(ii) The second approach used to describe and model competitive sorption requires the measurement of at least two competing ions in the soil of interest. In general the sorption behavior can be described by ion exchange selectivity coefficients. Common expressions for exchange selectivity coefficients include Vanselow, Gaines-Thomas, Gapon, and their respective empirical selectivity
coefficients (Gaines and Thomas, 1953; Sposito, 1981). Furthermore, multiple ion exchange sites can be used to describe ion exchange in heterogeneous soil systems (Garrel and Christ, 1956; Harmsen, 1977). In contrast to the first approach, this one does not involve any assumption concerning the sorption mechanism and does not utilize equilibrium constants as determined for pure systems. Instead the equilibrium constant is computed using binary exchange data (Sposito, 1981). The thermodynamic equilibrium constant is likely to be unique to each soil so that results from such data may not be generalized to other soils.

The empirical selectivity coefficient has been applied to heavy metal/calcium exchange by Harmsen (1977) and Abd-Elfattah and Wada (1981). They found an increased sorption affinity for heavy metals with decreasing heavy metal/calcium ratio on the exchanger phase. For example, zinc/calcium selectivity coefficients varied from 10 to 100 in calcium saturated montmorillonitic soil (Abd-Elfattah and Wada, 1981). Hendrickson and Corey (1981) reviewed ion exchange equilibria studies of some heavy metals in soils. They concluded that more than one reaction site must be present in order to explain the high affinity of heavy metals at low concentration. In general, it is assumed that specific sorption at the oxide/hydroxide surfaces and broken edges of clay minerals causes this high affinity for heavy metals in soils, and under certain circumstances so do the formation of organic complexes and precipitation reactions.

(iii) The simplest approach for describing solution-solid phase distribution is the use of sorption isotherms. In this case, only the total concentration in solution and
solid phase is considered. White and Zelazny (1986) and Sposito (1984) reviewed the
general classification for adsorption isotherms given by Giles et al. (1960). The most
common curve in soils is the L curve (L = Langmuir type), which exhibits a concave
shape with respect to the solution concentration axis. Such isotherms may be
described by the following equation (Sposito, 1983b; Sposito, 1985):

\[
S = \sum_{i=1}^{n} \frac{b_i K_i^{\beta_i} c^{\beta_i}}{1 + K_i^{\beta_i} c^{\beta_i}}
\]  

[1.1]

where \( S \) is the amount sorbed per unit mass, \( c \) the amount in solution per unit volume
and \( b_i, K_i, \) and \( \beta_i \) are empirical parameters. Widely used special cases of this
equation are the Langmuir equation with \( n = 1, \beta_i = 1 \), the two-surface Langmuir
equation with \( n = 2, \beta_1 = \beta_2 = 1 \), and the Freundlich equation with \( n = 1, 0 < \beta_i < 1 \), and
\( K_i^{\beta_i} c^{\beta_i} < < 1 \) (Sposito, 1985). The sorption of ionic solutes in soils has been
described by such isotherms for the last decades.

The Langmuir and Freundlich isotherms were originally developed for
describing gas adsorption on metal surfaces. The Langmuir equation was derived on
the basis of the kinetics of monolayer adsorption. The two-surface Langmuir equation
implies that two different surfaces are present. In general, Langmuir isotherms are
characterized by the existence of an adsorption maximum, which occurs with complete
monolayer surface coverage. However, deviation from this ideal behavior is often
observed (Benjamin and Leckie, 1981). The Freundlich equation is used where the
adsorption enthalpy exhibits a logarithmic change with increasing sorption due to
surface heterogeneity. Therefore, the exponent $\beta$ in equation [1.1] can be viewed as a heterogeneity parameter. Sposito (1980) and Elprince and Sposito (1981) showed that the Freundlich and the Langmuir equations can represent ion exchange if the concentration of the ions of interest is very low in comparison to the other ions present in solution. However, soils and most of the soil minerals cannot be treated as pure ion exchangers or uniform surfaces. The use of such equations implies that the parameters obtained by curve fitting should be viewed as pure empirical constants. For example, Veith and Sposito (1977) demonstrated that sorption isotherms cannot be used to distinguish adsorption from surface precipitation.

Single site isotherms such as the Langmuir and Freundlich equations have been used to describe heavy metal retention in soils (Garcia-Miragaya and Page, 1976; Sidle et al., 1977; Levi-Minzi et al., 1976; Korte et al., 1976; Buchter et al., 1989). In contrast, Kinniburgh (1986), Kinniburgh et al. (1983), and Altmann and Leckie (1987) used other isotherms to describe heavy metal sorption in soil, iron oxides, and humic acids. In fact, the study by Kinniburgh (1986) clearly revealed that the Langmuir equation does not seem to be appropriate for describing sorption. Also, the Freundlich equation was suitable to sorption description in only one case. Instead, the Tóth isotherm (Tóth et al., 1974) was generally best for describing the data. A more general approach, the local isotherm approximation, was discussed and evaluated by Nederlof et al. (1990). This approach has been used to derive isotherm for gas adsorption on heterogeneous surfaces as far back as the 1940s (Sips, 1950). Furthermore, models describing heterogeneity are very important for soil materials
which are not very well understood. In particular, organic substances such as humic and fulvic acids are described by multiple site approaches. The distribution of the affinity coefficients of different sites can either be discrete (such as the two-surface Langmuir) or continuous (Perdue and Lytle, 1983; Sposito, 1986). Moreover, when a heavy metal occurs at high concentrations in an alkaline soil, precipitation may take place. This may be described by a simple isotherm such as the Brunauer-Emmett-Teller (BET) or the Farley-Dzombak-Morel (FDM) equations (Brunauer et al., 1938; Farley et al., 1985).

1.2.2. Kinetics

The kinetics of metal retention can be classified into physical and chemical nonequilibrium processes. The first one refers generally to diffusion and mass transfer limitations of sorption processes, whereas the second one involves the pathway of chemical reactions. The particle geometry and the spatial arrangement of reactive surfaces determine to what extent physical nonequilibrium controls the overall kinetics. The reactions taking place on a molecular level (elementary reactions) are the base for formulating chemical rate laws (Lasaga, 1981). Hence, chemical kinetics always require the knowledge of molecular mechanisms. As discussed in the previous section the heterogeneity of natural soils prevents the direct determination of molecular mechanisms. Therefore, the limitations of chemical equilibrium models to predict the fate of heavy metals in the soil environment apply equally well to chemical kinetics. However, the kinetics of particular processes are restricted to a certain range
of time. In particular nonspecific ion exchange is most commonly controlled by film diffusion with half lives in the order of 10 sec (Sposito, 1989). In fact, ion exchange occurs so fast that the kinetics may not be detectable by flow methods as shown by Seyfried et al. (1989). Also, innersphere complex formation on oxyhydroxide of iron and aluminum take place quickly such that the rate coefficients were determined by relaxation methods (Sparks and Zhang, 1991). The slow processes include recrystallization of surfaces, diffusion into micropores, surface diffusion, and solid phase diffusion (Aharoni and Sparks, 1991). For more detailed reviews of kinetic processes, the reader is referred to Lasaga and Kirkpatrick (1981) for geochemical systems, to Pankow and Morgan (1981) for aquatic environments, Sparks (1989) and Sparks and Suarez (1991) for soil environments. Since soil is a complex system of reactive solids and fluids, empirical and semi-empirical approaches are still applied to heavy metal kinetics in soil.

Empirical models have often been applied to transport studies of inorganic and organic solutes in soils (Skopp, 1986). In order to account for the lack of equilibrium, two-site models were developed. In these models a slow sorption process is assumed to occur at one type of site whereas a fast equilibrium sorption occurs at the other type site (Selim et al. 1976; Cameron and Klute, 1977; Jardine et al., 1984). In order to clarify the term 'site', a review on the use of this expression is necessary.

According to Brusseau and Rao (1989), there are four different definitions used in the literature: (1) reaction site defined on a molecular basis; (2) different sites due to different accessibility; (3) different sites due to different sorbents; and (4) different
sites due to different reaction mechanisms. The above definitions require knowledge of the actual mechanisms controlling the lack of equilibrium. However, chemical equilibrium models can be viewed as multisite models. For example, surface complexation can be defined as in (1), but when combined with other reactions, such as complexation of metals with humic acids, it would be defined as (3). This suggests at least a two site model and implies that site (1) and (3) do not necessarily represent slow kinetics.

Additionally, it is necessary to determine which of the four definitions is most suitable for nonequilibrium description of heavy metal retention in soils. The choice of the definition is highly dependent on the time frame and reactants involved in the process. Most of the sorption processes of metals in soils appear to reach equilibrium in a matter of hours, days, or weeks. In contrast to fast sorption reactions, e.g. calcium, magnesium, and sodium, heavy metals reach quasi equilibrium at a later time. In order to explain this behavior, one has to consider the structure of the soil as a whole and the microstructure of the soil particles. The soil consists of particles made up of several types of minerals and organic matter, which exists discretely or clustered into aggregates. When the solute enters the soil, it diffuses through the pores into aggregates and particles to the available sorption sites. Therefore, the soil structure dominates to a large extent the accessibility of the sorption sites so that diffusion controlled processes are often rate limiting in soils. Hence, physical nonequilibrium plays an important role in soils systems.
Generally, there are four consecutive steps in the overall diffusion process of solutes in soils (Rubin, 1983; Weber, 1984). First, the solute rapidly diffuses through the bulk solution. Second, the solute passes from the bulk solution through a film surrounding the soil particles or aggregates (film diffusion). This is followed by the third step, diffusion within the particle or aggregate (particle diffusion). The last step is the sorption process on the surface itself. Either the film or the particle diffusion is rate limiting. The particle diffusion can be further classified into diffusion within the solution of the aggregate (pore diffusion) and diffusion on the surface of the solid material (surface diffusion). In the latter case sorption takes place before the diffusional process. Surface diffusion may be of importance during ion exchange as shown by Jackman and Ng (1986). In addition, diffusion into the solid phase may take place as suggested by Brümmer et al. (1988) for Zn in goethite. In fact, only White and Yee (1986) experimentally proved that solid state diffusion plays an important role in glassy silicates. Other mechanisms involve the diffusion of a solute in micropores as shown by Smit et al. (1978). The last three processes can also be viewed as chemical nonequilibrium because ions may form chemical bonds on surfaces and may be transported on a surface or within a solid. All processes involve the breakup and creation of these bonds (Aharoni and Sparks, 1991). Other slow mechanisms are surface controlled reactions such as weathering of primary soil minerals as reviewed by Stumm and Wollast (1990).

There are two general approaches to modelling diffusional processes in soils. The first one is based on a complete description of the solid phase geometry and uses
partial differential equations (diffusion equations) to describe the temporal and spatial
distribution of the solute. The second approach utilizes a mass transfer coefficient in
order to describe the kinetics with ordinary differential equations as a function of time
only (Hines and Maddox, 1985). The mass transfer coefficient can be derived through
spatial averaging and 'parameter lumping' of the first approach and uses an average
concentration gradient as the driving force. The lack of knowledge of the spatial
arrangement of reactive soil surfaces and particles makes the use of the mass transfer
approach favorable over the first one.

For example, mass transfer of heavy metal ion exchange for some soil
constituents such as peat was controlled by film diffusion (Bunzl et al., 1976; Bunzl
and Schimmack, 1991). A more rigorous description of diffusion controlled ion
exchange is given by the Nernst-Planck equation which considers the electrical field
caused by differences of ion mobility (Helfferich, 1962; Helfferich, 1983; Hwang and
Helfferich, 1987; Nicoud and Schweich, 1989). The use of such modelling
approaches has not been utilized for heavy metal sorption in soils.

Modelling both the accessibility and the reaction mechanism seems difficult.
In fact, very few studies have been conducted to experimentally determine the
diffusional contribution to the overall kinetics (Ogwada and Sparks, 1986). In
addition, the assumptions concerning the geometry and/or the reaction mechanism
must be valid. Both criteria are based on microscopic phenomena, which are not
easily measured. In contrast, kinetic retention is generally observed on a
macroscopic scale. Relaxing all assumptions of the actual mechanisms of kinetic
retention one can use empirical approaches to distinguish different sites. For example, applying the two-surface Langmuir equation can be viewed as such an approach. Parameter optimization replaces experimental determination of the actual processes. In addition, the measurement of the solute sorption can be restricted to the monitoring of solute concentration in solution with time. Before introducing multisite models of this type, a brief review of the phenomena involved in heavy metal sorption in soils and soil constituents such as oxides, clay minerals, and organic matter is presented.

Fast, first-order kinetics were observed for K-Ca exchange on clay minerals (Jardine and Sparks, 1984; Sparks and Jardine, 1984; Parker and Jardine, 1986). Similarly, Bunzl et al. (1976) showed that first-order kinetics due to film diffusion was the time limiting step governing Pb, Cu, Cd, Zn, and Ca exchange with protons on peat. Equilibrium was reached during a period of time ranging from a few minutes to several hours in both studies so that the rate of reaction was fast as compared to slow processes such as weathering. Sorption processes of zinc on oxide minerals, such as goethite or hematite, were modelled recently with second order kinetics (Barrow et al., 1989). However, continued sorption was observed, after fast initial sorption, on oxides for more then 2 weeks (Brümmer et al., 1988). Brümmer et al. (1988) suggested that diffusion of zinc into the solid phase was occurring.

The kinetic reactions of heavy metals in soils were studied by Amacher et al. (1986), Aringhieri et al. (1985), Kuo and Mikkelsen (1979), and Christensen (1984). They found a fast initial reaction during the first hours, then slow retention the following days and weeks. Since single site models have a limited capability to
describe sorption kinetics in soils (Aringhieri et al., 1985), multisite models were
developed (Amacher et al., 1988; Selim and Amacher, 1988; Harter, 1989). Therefore, Amacher et al. (1988) and Selim and Amacher (1988) extended the two site models to multi-site models to explain the kinetic behavior of some selected heavy metals. Overall, fast kinetics in the magnitudes of minutes to few hours and slow kinetics, in the magnitude of weeks, occur in soils and different soil materials. The overall kinetic reaction of heavy metals in soils is influenced by all reaction mechanisms, through which retention on different minerals and organic matter takes place. In order to account for apparent equilibrium or quasi equilibrium sorption behavior, it can be assumed that the sorption may be described best by either (i) a Freundlich isotherm or (ii) a Langmuir-type isotherm. Modelling the kinetic behavior of heavy metal sorption in soils, utilizing the information of pure soil materials, is based on the assumptions that (i) at least one fast reversible reaction will occur, (ii) at least one slow reversible reaction will occur, and (iii) one irreversible reaction may also occur. These assumptions lead to the development of two different multi-site models. One is known as the n-th order multireaction model (Amacher et al., 1988) whereas the other is known as the second-order model by Selim and Amacher (1988). However, the shortcomings of these models lie in the dependency of the rate coefficients on the initial concentrations.
1.2.3. Transport

Transport phenomena in soil systems are reviewed by Nielsen et al. (1986) and Jury and Roth (1990). Solute transport in soils has been described traditionally by the convective-dispersive equation (CDE). The careful analysis of field solute transport experiments has revealed that the CDE is often not valid. Therefore, probabilistic modelling approaches have been developed in order to account for spatially variable physical properties of natural media (Dagan, 1986; Gelhar, 1986). Since the material presented in this work emphasizes the effect of chemical heterogeneity on the sorption, kinetics, and transport on a laboratory scale, the review focuses on the reactive solute transport using the classical CDE.

Asymmetric tracer breakthrough curves (BTCs) were observed in aggregated soil on a laboratory scale which could not be described by the conventional CDE (van Genuchten and Wierenga, 1976). In order to adequately describe this behavior, aggregation of the soil was explicitly incorporated into the CDE. These models, commonly referred to as the two-region or mobile-immobile approach (Coats and Smith, 1964; van Genuchten and Wierenga, 1976), are either based on mass transfer expressions, usually first order kinetics, or discrete geometrical description of the soil aggregates. The mass transfer approach requires the measurement of a mass transfer coefficient. This approach has been widely used for transport studies (Rao et al., 1980; Rasmuson and Neretnieks, 1980, Tang et al., 1981; van Genuchten et al., 1984; Rasmuson, 1985) and has been reviewed by van Genuchten and Dalton (1986). Obviously, both approaches represent physical nonequilibrium transport.
Reactive transport is usually modelled using a system of algebraic and partial differential equations, where the algebraic equations describe equilibrium reactions. Kinetic reactions are represented by additional first-order differential equations. Rubin (1983) classified the chemical reactions and related this classification to the mathematical formulations of reactive transport (Table 1.1). First he distinguished between homogeneous and heterogeneous reaction where the former refers to reactions in a single phase (here aqueous phase, complex formation) and the latter reactions involve at least two phases (here solid and aqueous phases). Then the heterogenous reactions are subdivided into surface reactions (ion exchange and surface complexation) and classical reactions (dissolution and precipitation). In addition, the reaction speed is used to further classify the reactions into fast and slow. The fast reactions are assumed to occur quickly such that the local equilibrium assumption (LEA) is valid. The LEA holds when the reactions take place instantaneously at all points in the system.

In order to review the reactive transport of inorganics we refer to the classification of the sorption models as described above. The combination of ion association models with the CDE yields multicomponent transport models such as CHEMTRAN, TRANQL, DYNAMICS, and EQTRAN (Miller and Benson, 1983; Cederberg, 1985; Liu and Narasimhan, 1989; Förster, 1986). For a review of multicomponent transport models the reader may refer to Mangold and Tsang (1991). Most of the multicomponent models do not account for nonequilibrium processes and hence the models usually describe reactions grouped into classes I, II, and III (Table
Table 1.1. Classification of reactions in aqueous environments by Rubin (1983).

<table>
<thead>
<tr>
<th>RATE OF REACTION</th>
<th>TYPE OF REACTION</th>
<th>HOMOGENEOUS</th>
<th>HETEROGENEOUS</th>
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<tr>
<td></td>
<td></td>
<td>SURFACE</td>
<td>CLASSICAL</td>
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<tr>
<td>FAST</td>
<td>I</td>
<td>II</td>
<td>II</td>
</tr>
<tr>
<td>SLOW</td>
<td>IV</td>
<td>V</td>
<td>VI</td>
</tr>
</tbody>
</table>

1.1). Also, the limitations of equilibrium speciation models to describe sorption processes in soil apply to the transport codes equally well. Hence, the use of such models in heterogeneous soil systems seems to be very limited. In fact, experimental data sets for validating such complex models are almost nonexistent.

The transport of exchangeable ions in soil columns has been predicted adequately with the local equilibrium approach which belongs to the class II reactions (Table 1.1) (Lai and Jurinak, 1971; Valocchi et al., 1981; Persaud et al., 1983; Gaston and Selim, 1990a). Furthermore, the kinetics of ion exchange during transport have been modelled with the Two-Region model where the rate limiting step is diffusion through soil aggregates (Selim et al., 1987; Mansell et al., 1988; Gaston and Selim, 1990b). Hence, the nonequilibrium is explicitly formulated and is independent of the reactions involved. Alternatively, the ion exchange kinetics has been modelled with a simple mass transfer coefficient which was not determined independently (Parker and Jardine, 1986). The latter approach is simpler to use; however, the mass transfer coefficient is less meaningful than that of the Mobile-Immobile model. Most of these studies dealt with two or at the most three different ions such as Ca, Mg, Na,
and/or K. The ion exchange approach for heavy metal transport has rarely been used with the exception of Dudley et al. (1991), who described the Cd and Cu transport with the Gapon selectivity coefficient.

The simplest approach for modelling heavy metal transport is using single solute approach and describing the sorption as either an equilibrium or a kinetic process. The equilibrium formulation falls into reaction class II whereas the kinetic approach falls into reaction class V (Table 1.1). Sidle et al. (1977), Poelstra et al. (1979), Swartjes et al. (1992), and Stollenwerk and Kipp (1990) used the Freundlich isotherm to model transport of heavy metals in soils, whereas Mayer (1978) applied the Langmuir equation. A modified Langmuir equation was developed and used by Schmidt and Sticher (1986) for predicting solute transfer in some Swiss soils. Clearly, the most popular isotherms used for describing solute sorption and transport are the Langmuir and Freundlich equations (Travis and Etnier, 1981). With the exception of Stollenwerk and Kipp (1990) who tested different physical nonequilibrium models, the above mentioned researchers treated the sorption as an equilibrium process. Other researchers used two site models where the kinetics was described by a mass transfer coefficient and the chemistry by either two Langmuir equations or two ion exchange sites (Flühler and Jury, 1983; Parker and Jardine, 1986). Besides mass transfer approaches, nonequilibrium has been described with first-order, nth-order, and second-order rate laws combined with the CDE (class V) (Selim et al., 1976; Mansell et al., 1977; Amoozegar-Fard et al., 1983; Murali and Aylmore, 1983), and applied to solutes like K, P, and pesticides. Selim and Amacher (1988) and Selim et
al. (1989) applied the second-order and the multireaction model to Cr transport in soil columns. However, the model did not describe the data well when independently determined parameters were used. Overall, the data of the transport of heavy metals in soil is scarce, and additional research is needed. Also, the reader may refer to Khondaker et al. (1990) for a state-of-the-art inventory of transport models in groundwater and soil physics research.

1.3. Zinc and Cadmium in Soil

The existing definition of the term 'heavy metal' is based on its density which should be greater than 6 g cm\(^{-3}\) for these metals (Alloway, 1990a). Hence almost all the transition metals are heavy metals. Also, the term 'trace metal' is used when the solution concentration of the metal of interest is below 1 mM (Sposito, 1983b). Zn and Cd belong to the IIb group of periodic table of elements with atomic numbers of 30 and 48, respectively. Both elements are closely related in their geochemical occurrence and have similar ionic structures and electronegativity. The sources of Zn and Cd in soils are the parent material and anthropogenic accumulations such as pollution. Acid magmatic rock contains approximately 40 mg kg\(^{-1}\) Zn whereas basaltic rocks have 100 mg kg\(^{-1}\) (Kiekens, 1990). Shales and clayey sediments contain amounts from 80 to 120 mg kg\(^{-1}\), whereas limestones and sandstones have lower amounts ranging from 10 to 30 mg kg\(^{-1}\). In contrast, Cd is always present in lesser quantities. In fact, the Zn:Cd ratio is on average 500:1 for all rocks. Igneous and metamorphic rocks contain from 0.1 to 1 mg kg\(^{-1}\) Cd. In contrast sedimentary rocks
may have up to 11 mg kg\(^{-1}\) Cd (Alloway, 1990b). The corresponding average Zn and Cd concentrations in soil range from 1 to 900 and 0.01 to 2 mg kg\(^{-1}\), respectively (Kabata-Pendias and Pendias, 1984). Anthropogenic sources of Zn and Cd in soil are primarily sewage sludge, composted refuse, and phosphate fertilizer (Alloway, 1990a). The highest amounts can be found in sewage sludge where the Zn and Cd contents ranges from 91 to 49,000 and 1 to 3,410 mg kg\(^{-1}\), respectively (Kabata-Pendias and Pendias, 1984). Also, mine tailings can contribute significantly to heavy metal pollution of soils (Levy et al., 1992). In contrast to Zn, Cd is not an essential micronutrient and therefore toxicity may occur at critical soil total concentrations as low as 3 mg kg\(^{-1}\) for Cd and 70 to 400 mg kg\(^{-1}\) for Zn (Kabata-Pendias and Pendias, 1984).

Zn occurs in primary soil minerals as isomorphous substitutions for Mg and Fe in olivines, pyroxenes, amphiboles, and for Fe or Mn in oxides. In contrast, Cd forms isomorphous substitutions in sulphides for Cu, Zn, Hg, and Pb. Both Zn and Cd may occur as sulphide inclusions in silicates (Sposito, 1983b). Zn is present in secondary soil minerals such as Fe and Mn oxides, illites, and smectites, whereas Cd may be found in Ca carbonates (Sposito, 1983b). If the average total amount of Zn and Cd were present in the solution of a soil with 10% moisture content, the concentration would be \(10^{-2.12}\) \(M\) for Zn and \(10^{5.27}\) \(M\) for Cd (Lindsay, 1979). It is obvious that the actual concentration in soil solution is orders of magnitude less than that mentioned by Lindsay.
Table 1.2. Predicted affinity sequences of divalent metals for oxides based on several metal properties (from McBride, 1989).

<table>
<thead>
<tr>
<th>Property</th>
<th>Predicted order of affinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic potential ($Z^2/r$)</td>
<td>Ni &gt; Mg &gt; Cu &gt; Co &gt; Zn &gt; Cd &gt; Sr &gt; Pb</td>
</tr>
<tr>
<td>First hydrolysis const. ($K^*$)</td>
<td>Cu &gt; Pb &gt; Ni &gt; Co &gt; Zn &gt; Mg &gt; Cd &gt; Sr</td>
</tr>
<tr>
<td>Electronegativity (Pauling)</td>
<td>Cu &gt; Ni &gt; Co &gt; Pb &gt; Cd &gt; Zn &gt; Mg &gt; Sr</td>
</tr>
<tr>
<td>Softness</td>
<td>Pb &gt; Cd &gt; Co &gt; Cu &gt; Ni &gt; Zn &gt; Sr &gt; Mg</td>
</tr>
<tr>
<td>Irving-Williams series</td>
<td>Cu &gt; Ni &gt; Zn &gt; Co &gt; Mg &gt; Sr</td>
</tr>
</tbody>
</table>

The affinity of soils to adsorb Zn and Cd depends on the likelihood of the metals to be bound by inner- or outersphere complexation, or by the diffuse ion swarm. In order to compare the affinity of different metals towards soils, one can first draw upon theoretical considerations. The properties of metals that can be used are the ionic potential, the first hydrolysis constant, the electronegativity, the softness, and the Irving-Williams series (McBride, 1989). Table 1.2 list the affinity sequences of most common divalent metals for oxides. The ionic potential describes the likelihood of a metal ion to be adsorbed by electrostatic forces. In addition, the electron configuration determines the ability of the metal to form ionic or covalent bonding. The electronegativity and the 'softness' parameter are a measure of covalent contributions in a chemical bond. Furthermore, a general complex stability sequence is the Irving-Williams series, which has been derived from the observation that the relative sequence of complex stability of transition elements with different organic ligands seems to be the same (Morel, 1983; Stumm and Morgan, 1981).
Table 1.3. Observed sorption affinity of heavy metals on soil and soil minerals (modified after Basta and Tabatabai (1992) and McBride (1989)).

<table>
<thead>
<tr>
<th>Material</th>
<th>Order of Affinity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous Fe hydroxides</td>
<td>Pb &gt; Cu &gt; Zn &gt; Ni &gt; Cd &gt; Co &gt; Sr &gt; Mg</td>
<td>Kinniburgh et al. (1976)</td>
</tr>
<tr>
<td>Goethite and hematite</td>
<td>Cu &gt; Pb &gt; Zn &gt; Cd &gt; Co &gt; Ni &gt; Mn</td>
<td>Schwertmann (1989)</td>
</tr>
<tr>
<td>Al hydroxides</td>
<td>Cu &gt; Pb &gt; Zn &gt; Ni &gt; Co &gt; Cd &gt; Mg &gt; Sr</td>
<td>Kinniburgh et al. (1976)</td>
</tr>
<tr>
<td>Mn oxides and hydroxides</td>
<td>Pb &gt; Cu &gt; Co &gt; Zn &gt; Ni</td>
<td>McKenzie (1980)</td>
</tr>
<tr>
<td>Silanol groups of silica</td>
<td>Pb &gt; Cu &gt; Co &gt; Zn &gt; Ni &gt; Cd &gt; Sr &gt; Mg</td>
<td>Dugger et al. (1964)</td>
</tr>
<tr>
<td>Silicate clays</td>
<td>Pb &gt; Cd = Ca</td>
<td>Bittel and Miller (1974)</td>
</tr>
<tr>
<td>Peat</td>
<td>Pb &gt; Cu &gt; Zn &gt; Ca</td>
<td>Bunzl et al. (1976)</td>
</tr>
<tr>
<td>Humic acid (pH = 4-6)</td>
<td>Cu &gt; Pb &gt; Cd &gt; Zn</td>
<td>Stevenson (1977)</td>
</tr>
<tr>
<td>Soil Fe oxide clays</td>
<td>Zn &gt; Ni &gt; Cd</td>
<td>Tiller et al. (1984b)</td>
</tr>
<tr>
<td>Soil silicate clays</td>
<td>Zn &gt; Ni = Cd</td>
<td>Tiller et al. (1984b)</td>
</tr>
<tr>
<td>Soil fulvic acid (pH = 3.5)</td>
<td>Cu &gt; Fe &gt; Ni &gt; Pb &gt; Co &gt; Ca &gt; Zn &gt; Mn &gt; Mg</td>
<td>Stevenson and Ardakani (1972)</td>
</tr>
<tr>
<td>Soil fulvic acid (pH = 5.0)</td>
<td>Cu &gt; Pb &gt; Fe &gt; Ni &gt; Mn &gt; Co &gt; Ca &gt; Zn &gt; Mg</td>
<td>Stevenson and Ardakani (1972)</td>
</tr>
<tr>
<td>Soil CEC material</td>
<td>Pb = Cu &gt; Zn &gt; Cd &gt; Ca &gt; Mg</td>
<td>Abd-Elfattah and Wada (1981)</td>
</tr>
<tr>
<td>Soil</td>
<td>Pb &gt; Cu &gt; Zn &gt; Cd</td>
<td>Elliott et al. (1986)</td>
</tr>
<tr>
<td>Soil</td>
<td>Cu &gt; &gt; Zn ≥ Ni ≥ Cd</td>
<td>Tyler and McBride (1982)</td>
</tr>
<tr>
<td>Soil</td>
<td>Pb &gt; Cu &gt; Ni ≥ Cd = Zn</td>
<td>Basta and Tabatabai (1992)</td>
</tr>
</tbody>
</table>
Furthermore, the first hydrolysis constant has been related to the affinity of heavy metals to Fe oxyhydroxide (Gerth and Brümmer, 1983). However, when comparing the affinity sequences of Table 1.2 with the observed sequences of oxides, organic matter and soils some discrepancies are obvious (Table 1.3). Especially the ionic potential does not agree with the observed sequences of oxides. Clearly, electrostatic forces cannot explain the adsorption. The electronegativity and the softness parameter are slightly better in predicting the affinity sequence; however, covalent bonding alone cannot explain the observed sequence (McBride, 1989). Hence, a combination of both electrostatic and electron-sharing properties are significant for the sorption sequence. In general, the affinity of Zn is fairly high and follows that of Pb and Cu. The affinity of Cd is always lower or equal to that of Zn. It seems that organic matter does not prefer Zn over Cd as much as oxides do. In fact, in soil fulvic acid Zn belongs to the least preferred ions and in humic acid Cd has a higher affinity than Zn (Table 1.3).

1.4. Scope of this Study

In order to present the objectives of this study in context with the literature review, a brief summary of the limitations and lack of previous research should be presented. The fundamental basis for this research is that soil must be viewed as a heterogeneous system which cannot be described by simple chemical mechanisms and models for pure substances. In particular this has been shown for the ion association model and more so for surface complexation models. Also, the kinetics of heavy
metals are not well understood especially for systems where colloidal interactions strongly affect the sorption behavior as well as mass transfer processes. Based on our knowledge of the chemical processes, the description of heavy metal transport will always be limited by those shortcomings. Nevertheless, the sorption mechanisms proven to exist on soil minerals and organic matter do occur in soil but cannot easily be quantified. Empirical models should therefore be related to processes through either 'parameter lumping' or at least qualitative reasoning.

In addition to the fundamental problems involved with heavy metal sorption, the results of soil chemical experiments such as heavy metal fractionation and extraction have not been incorporated into transport studies. Also, the studies dealing with many aspects of sorption outnumber the ones emphasizing sorption kinetics and transport. In fact experimental breakthrough curves of heavy metal are rare. In this study an attempt is made to overcome at least a number of the limitations listed above.

In Chapter 2, the relationship between isotherms and actual reactions describing the sorption as well as the heterogeneity as described by isotherms are reviewed. The effects of heterogeneity, maximum sorption capacity, affinity coefficients of seven isotherm expressions on transport behavior of heavy metals in soil is examined using a qualitative sensitivity analysis. The appearance of the breakthrough curves are related to the presented parameters. Also, a general relationship between chemical heterogeneity and transport behavior is derived and illustrated based on several examples. In Chapter 3, a general isotherm expression based on the equations used in Chapter 2 is applied to single and binary solute
systems. In particular, Zn and Cd sorption data as measured with batch experiments in a Ca background are evaluated with special cases of the general isotherm equation. Measured breakthrough curves of Zn and Cd competing with Ca at nearly constant and variable ionic strength in two acidic soils are predicted with the CDE combined with the general isotherm equation.

The subsequent three chapters (4-6) deal with the kinetics of Zn sorption in an acid soil. First, two different multisite models were evaluated in terms of their performance to describe and predict the sorption of Zn in a batch reactor at initial concentrations varying from 0.01 to 100 mg L\(^{-1}\) (Chapter 4). A new kinetic model was introduced in Chapter 5 which is explicitly related to possible reactions taking place on soil minerals and organic matter. More specifically, the model incorporates Zn/Ca competition as well as specific interaction of Zn with the soil. This model was then applied to Zn kinetics with various initial concentrations as measured with batch and thin disk flow experiments. Also, the effects of high and low Zn concentrations on the kinetics of sorption were evaluated. Chapter 6 deals with the effects of organic matter and iron oxide removal on the sorption kinetics as measured with the thin disk flow method. The final chapter presents an overall summary and conclusion of this study.
CHAPTER 2

THE EFFECTS OF CHEMICAL HETEROGENEITY DESCRIBED BY ISOTHERMS ON ONE-DIMENSIONAL REACTIVE SOLUTE TRANSPORT IN SATURATED SOILS

2.1. Introduction

The description of solute sorption in soils and sediments has gained importance over the past decades due to increased awareness of environmental problems. In order to predict the movement of solutes in the soil environment and the groundwater, it is necessary to partition the solute between the solid phase and the solution.

Solute sorption in soils has been described utilizing different approaches. Assuming certain chemical reactions between the solute in solution and the solid phase, equilibrium models can be used. Possible reactions taking place include precipitation/dissolution, redox reactions, and surface complexation, which includes ion exchange. The equilibrium approach requires knowledge of reactions actually taking place and the associated thermodynamic equilibrium constants. Due to the heterogeneous make up of a soil, this knowledge may not be available and extensive laboratory studies may need to be carried out to determine the reactions involved. In addition, aquatic speciation programs such as SOILCHEM, MINTEQA2, or PHREEQ (Sposito and Coves, 1988; Allison et al., 1990; Parkhurst et al., 1980) utilize thermodynamic databases which were developed for highly idealized environmental systems (for a review see Basset and Melchior, 1990). Furthermore, transport models based on such speciation programs have been developed (Mangold and Tsang, 1991).
However, equilibrium constants determined under idealized conditions may not apply to a complex soil system (Honeyman, 1984). Therefore, measuring sorption behavior of solutes in soils becomes unavoidable. The more information about the chemistry of sorption needed the more elaborate are the experiments necessary to solve the problem. A convenient method to minimize laboratory work, is to simply determine the solution/solid phase partitioning of the solute using simple batch experiments. In fact, most data are available in the form of simple isotherms. Furthermore, the importance of the isotherm approach has led to the incorporation of isotherm equations into chemical speciation programs such as MINTEQA2.

The sorption of several heavy metals in several soils was described by the Freundlich isotherm by Buchter et al. (1989). Other examples can be found in pertinent literature on heavy metals in the environment, such as Nriagu (1980). Since sorption data are most likely available in the form of isotherms, one may use those to predict the transport behavior of solutes which react sufficiently fast. Sidle et al. (1977), Poelstra et al. (1979), Swartjes et al. (1992), and Stollenwerk and Kipp (1990) used the Freundlich isotherm to model transport of heavy metals in soils, whereas Mayer (1978) applied the Langmuir equation. A modified Langmuir equation was developed and used by Schmidt and Sticher (1986) for predicting solute transfer in some Swiss soils. Clearly, the most popular isotherms used for describing solute sorption and transport are the Langmuir and Freundlich equations (Travis and Etnier, 1981).
Recently, Kinniburgh (1986) tested a number of isotherm equations for solute sorption on minerals and soils. He concluded that other equations provided better description of sorption phenomena in soils and soil minerals in comparison to the single site Langmuir and Freundlich approach. Even though the Freundlich and Langmuir equations are easy to use, they may not be adequate for a wide range of concentrations. In fact, solute concentrations in the soil profile may vary considerably depending on the application of the solute. Often high concentrations of fertilizer, pesticide, or heavy metals are applied to the soil surface. After several precipitation events the solute may be diluted and the transport process continues to spread the solute within the soil profile. The choice of the appropriate isotherm becomes critical when predicting the solute transport in soils. To the best knowledge of the author a systematic comparison of various isotherms in terms of their transport behavior has not been presented in the literature. The objectives of this paper are (i) the presentation of several isotherms and their relationship to actual reaction of the solute with the solid phase, (ii) the evaluation of the effects of isotherm parameters on the one-dimensional steady state transport of solutes in soils using sensitivity analyses, and (iii) a comparison of the different isotherms with respect to their transport behavior.

2.2. Theoretical

2.2.1. Isotherm Development

Most of the isotherms used to describe solute sorption were derived for gas adsorption on solid surfaces. The parameter of the isotherm equations are based on
certain assumptions such as the presence of a homogeneous surface or a functionality between surface coverage and the Gibbs free energy of adsorption. In contrast to pure metal surfaces, soils cannot be viewed as a homogeneous surface. Since the actual reactions involved in the sorption process are unknown or cannot be quantified, the parameters of sorption isotherms need to be redefined.

Altmann and Leckie (1987) reduced the reactions for the metal sorption on hydrous ferric oxides into one isotherm expression. Here, their approach is briefly reviewed in order to demonstrate the relationship between isotherms and chemical reactions. In order to derive an isotherm one can assume, for example, surface reactions taking place at the oxide/solution interface (Altmann and Leckie, 1987):

\[
\begin{align*}
XOH + H & \rightleftharpoons XO + H \rightleftharpoons XOH \\
XOH + M & \rightleftharpoons XOM + H \\
XOH + M + H_2O & \rightleftharpoons XOMOH + 2H
\end{align*}
\]

where XO denotes the surface functional group which reacts with either hydrogen ions (H) or a metal ion (M), K the equilibrium constant for the reaction, and the subscripts a and m denote surface protonation and complexation, respectively. The equations [2.1] to [2.4] represent only an example of possible reactions at the oxide/solution interface. In fact one can write similar reactions for ligands. For a more complete list of possible reactions we refer to Leckie (1988). The overall
reaction can be written by adding equations [2.1] through [2.4] and introducing stoichiometric coefficients a, b, c, (1-c) for equations [2.1], [2.2], [2.3], and [2.4], respectively (Altmann and Leckie, 1987):

\[
\begin{align*}
M + aXH_2 + bX + (1-a-b)XH + (1-c)H_2O & \rightleftharpoons \\
cM + (1-c)XMOH + (2+a-b-c)H & \quad K_O
\end{align*}
\]

where the subscript O denotes the equilibrium constant for the overall reaction. Sposito (1984) presented a reaction accounting for most possible reactions on oxide surfaces including ligand adsorption. Reaction [2.5] is only a special case of the most general form, however, it is widely used for metal surface complexation (Davis and Leckie, 1978; Dzombak and Morel, 1990). In a heterogeneous system such as soils and sediments one can expect that reactions [2.1] through [2.4] take place at different surfaces. For example, a soil may contain iron and manganese oxides. These oxides may be physically separated, such that reaction [2.1] through [2.4] may take place at each mineral surface, however, with different equilibrium constants. Therefore, one cannot expect that a single equilibrium constant can describe all possible reactions. Furthermore, describing sorption processes by such reactions implies that these reactions truly exist. Only spectroscopic measurements could confirm the exact nature of the reactions (Sposito, 1984). At this time such measurements have been carried out only for pure systems such as goethite and humic acids among others (McBride, 1989). Complex adsorbents such as soils, in contrast, pose a problem in determining concrete sorption reactions. To overcome this problem empirical approaches, such
as isotherms, represent alternatives for describing sorption phenomena. For example, to describe the sorption reactions [2.1] through [2.4] by isotherm equations one needs to measure the total amount of solute adsorbed ($s_M$) and that in solution ($M$), as well as the surface acidity ($s_H$). These macroscopic parameters are defined by:

\[ s_M = [XM] + [XMOH] \quad [2.6] \]

\[ s_H = [XH_2] + [XH] + [X] \quad [2.7] \]

\[ s_T = s_M + s_H \quad [2.8] \]

where $s_T$ is the total number of surface sites. The units for $s$ are usually mass or molarity of solute per mass of solids in soil systems, whereas for colloidal suspensions the units are expressed in terms of concentration (mol L$^{-1}$). Based on equations [2.6] to [2.8] Altmann and Leckie (1987) then derive an isotherm of the form:

\[ \Gamma = \frac{s_M}{s_T} = \frac{K_0^* [M] [H]^{-\nu}}{1 + K_0^* [M] [H]^{-\nu}} \quad [2.9] \]

where $\Gamma$ denotes the relative surface concentration of the solute, $\nu$ is the overall stoichiometric coefficient for metal/proton exchange, and $K_0^*$ is related to the overall equilibrium constant $K_O$ of equation [2.5] by:
Clearly, the overall affinity coefficient $K_0^*$ is not a constant, rather it is a lumped parameter depending on the equilibrium constant of all reactions involved. In soil systems the pH is often controlled by surface or precipitation/dissolution reactions, which may not be influenced by the solute sorption. Therefore, we may assume the simplest scenario; that is constant pH conditions which reduces equation [2.9] to:

$$\Gamma = \frac{\xi c}{1 + \xi c}$$ \hspace{1cm} [2.11]$$

where $\xi$ is the empirical affinity coefficient (M$^{-1}$ L$^3$), and $c$ is simply the solute concentration (M L$^{-3}$). This equation is known as the Langmuir equation. This isotherm expression can be viewed as the 'local' isotherm, since only one or very few reactions may be considered.

The fact that many different binding sites exist in even pure systems such as goethite suspensions or gas adsorption on solid surfaces, led surface chemists (Sips, 1950; Nederlof et al., 1991) to express sorption isotherms in the form:

$$\frac{s}{s_T} = \int_0^\infty w(\xi) \Gamma(\xi,c) \, d\xi = f(c)$$ \hspace{1cm} [2.12]$$

where $s$ is the amount of solute sorbed (M M$^{-1}$ soil), $f(c)$ a closed form isotherm expression, $w(\xi)$ is a weighting function (Sposito, 1984) or a site affinity distribution function (SADF) (Kinniburgh et al., 1983), or can be viewed as a frequency
distribution (Altmann and Leckie, 1987; Perdue and Lytle, 1983) of the 'local affinity' coefficient \( \xi \). Perdue and Lytle (1983) used a normal distribution for \( w(\xi) \) and the Langmuir equation for the 'local' isotherm \( \Gamma(\xi, c) \) to model ionic sorption on soils and humic substances, respectively. The integral of equation [2.12] does not have a closed form analytical solution when the Gaussian distribution is applied, rather numerical techniques must be used. However, Sips (1950) used the Stieltjes transformation to obtain a closed form solution of equation [2.12] for gas adsorption on solid surfaces.

The following section will present isotherms based on equation [2.12]. This includes the Langmuir, two-surface Langmuir, general Freundlich, general Langmuir-Freundlich, and Tóth isotherms (Kinniburgh et al, 1983). The Langmuir equation can be obtained by using the following weighting function:

\[
\begin{align*}
  w(\xi) &= \delta(\xi - k) \quad \text{[2.13]} \\
  \frac{S}{S_T} &= \frac{k c}{1 + k c} \quad \text{[2.14]}
\end{align*}
\]

where \( \delta \) is the Dirac delta function and \( k \) is the 'overall' affinity coefficient. The delta function is defined as follows:

\[
\int_{-\infty}^{+\infty} f(t) \delta(t - t_0) \, dt = f(t_0) \quad \text{[2.15]}
\]

and
The two-surface Langmuir (TSL) isotherm can be derived in a similar fashion. The weighting function becomes:

\[ w(\xi) = F_1 \delta(\xi - k_1) + F_2 \delta(\xi - k_2) \]  \[2.17\]

yielding the isotherm equation:

\[ \frac{s}{s_T} = \frac{F_1 k_1 c}{1 + k_1 c} + \frac{F_2 k_2 c}{1 + k_2 c} \]  \[2.18\]

where \( F \) denotes the fraction of site one and two, and the subscripts 1 and 2 the site one and two, respectively. It is obvious that all sum of Langmuir equations will yield a weighting function which consists of a sum of Dirac delta functions. The sum of the fractions of all sites must be equal to one, such that \( F_1 = 1 - F_2 \) for the TSL isotherm. The numerical value of the 'local' and 'overall' affinity coefficient are identical for all Langmuir expressions.

The general Freundlich (GF) isotherm is based on a hyperbolic weighting function (Kinniburgh et al., 1983):

\[ w(\xi) = \frac{\xi^\alpha \sin(\pi\alpha)}{\pi \xi(\xi - k)} \]  \[2.19\]

yielding an isotherm of the form:
\[ \frac{s}{s_T} = \left[ \frac{k \cdot c}{1 + k \cdot c} \right]^\alpha \]  

[2.20]

where \( \alpha \) is a dimensionless heterogeneity factor constrained by:

\[ 0 < \alpha < 1 \]  

[2.21]

This coefficient determines the spread of the distribution function \( w(\xi) \) as shown in Figure 2.1. Obviously the 'overall' affinity coefficient \( k \) represents the minimum of the 'local' affinity coefficient \( \xi \). The weighting function consists of a high affinity tail only.

The general Langmuir-Freundlich (GLF) isotherm was derived by Sips (1950). The significance of this isotherm for ion exchange was elucidated by Sposito (1981). The shape of the weighting function resembles closely that of the normal distribution (Sposito, 1981; Kinniburgh et al., 1983):

\[ w(\xi) = \frac{\sin(\pi \alpha)}{\pi \left(k^{-\alpha} \cdot \xi^\alpha + 2 \cos(\pi \alpha) + k^\alpha \cdot \xi^{-\alpha}\right)} \]  

[2.22]

yielding the GLF isotherm:

\[ \frac{s}{s_T} = \frac{(k \cdot c)^\alpha}{1 + (k \cdot c)^\alpha} \]  

[2.23]

where \( \alpha \) is subject to constraint [2.21]. Here the 'overall' affinity coefficient represents the mean of the distribution function as shown in Figure 2.2.

It should be noted that for the general Langmuir-Freundlich a limiting case for low sorption concentrations can be derived. Assume that:
Figure 2.1. Weighting function of the general Freundlich (GF) isotherm for three different values of the heterogeneity factor $\alpha$. 
Figure 2.2. Weighting function of the general Langmuir-Freundlich (GLF) isotherm for three different values of the heterogeneity factor $\alpha$. 

\[ a = 0.5, \quad a = 0.9, \quad 0.8 - 1.0 \]
\[
\frac{1}{k} \gg c
\]  

then the denominator of equation [2.23] approaches 1 such that this isotherm equation can be expressed as:

\[
\frac{s}{s_T} = (k \ c)^\alpha \tag{2.25a}
\]

and introducing \( k_F = s_T k^\alpha \) yields:

\[
\frac{s}{s_T} = k_F \ c^\alpha \tag{2.25b}
\]

which is commonly referred to as the Freundlich isotherm.

Another isotherm, the Tóth isotherm, was derived by Tóth et al. (1974) for describing gas adsorption on activated carbon. The weighting function is a bell shape distribution skewed towards the low affinity side (shown in Figure 2.3):

\[
w(\xi) = \frac{k \sin \left( \frac{1}{\alpha} \arctan \left( \frac{\xi^\alpha \sin(\pi \alpha)}{k^\alpha + \xi^\alpha \cos(\pi \alpha)} \right) \right)}{\pi \xi \left[ k^{2\alpha} + 2k^\alpha \xi^\alpha \cos(\pi \alpha) + \xi^{2\alpha} \right]^{3\alpha}} \tag{2.26}
\]

yielding the Tóth isotherm:

\[
\frac{s}{s_T} = \frac{k \ c}{ \left[ 1 + (k \ c)^\alpha \right]^{1/\alpha}} \tag{2.27}
\]

where \( \alpha \) is subjected to the constraint [2.21].
Figure 2.3. Weighting function of the Tóth isotherm for three different values of the heterogeneity factor $\alpha$. 
2.2.2. The Farley-Dzombak-Morel (FDM) Surface Precipitation Isotherm

So far, all isotherms presented exhibit a sorption maximum. When surface precipitation takes place one should expect that the solution concentration will be controlled by the solubility product of the precipitate formed. That implies that the isotherm may exhibit a change from convex to concave and finally reaches a point when precipitation will dominate the sorption process. In such a case the soil will sorb any additional solute and the concentration in solution remains constant. Farley et al. (1985) developed a surface precipitation model for oxide minerals, such as iron and aluminium oxides and oxyhydroxide. In their model the surface precipitation and complexation reactions take place simultaneously at all concentrations. At low concentrations the surface complexation reaction dominates the overall solute retention whereas the precipitation reaction controls the sorption process at high concentrations. At constant pH the model can be reduced to an isotherm expression. The basic assumption are (i) the solute of interest forms a surface complex, (ii) the solute of interest forms a solid solution with the sorbate, and (iii) the solid solution behaves like an ideal solution, e.g., the activity is proportional to the mole fraction. This isotherm can be derived from three independent reactions (Farley et al., 1985):

\[ \equiv YOH^0 + M^{2+} + 2H_2O \rightleftharpoons Y(OH)_3(s) + =MOH_2^+ + H^+ \quad K_{AM} \quad [2.28] \]

\[ =MOH_2^+ + M^{2+} + 2H_2O \rightleftharpoons M(OH)_2(s) + =MOH_2^+ + 2H^+ \quad K_{PM} \quad [2.29] \]
\[ \equiv YOH^0 + Y^{3+} + 3H_2O \rightleftharpoons Y(OH)_3(s) + \equiv YOH^0 + 3H^+ \quad K_{PY} \quad [2.30] \]

where \( Y \) denotes a metal forming a hydroxide (e.g. Fe or Al), \( M \) the solute of interest, \( s \) is the solid phase, and \( = \) and \( \equiv \) are divalent and trivalent bondings of the metal ions to the surface, respectively. The equilibrium constant \( K_{AM}, K_{PM}, \) and \( K_{PY} \) stand for the adsorption and the solid solution formation (precipitation) of the metal of interest (\( M \)), and the solid solution formation of the hydroxide (\( Y \)), respectively. Equation [2.28] describes the adsorption reaction of solute \( M \) onto the solid surface of \( YOH \), whereas reactions [2.29] and [2.30] represent the surface precipitation described as a solid solution formation of \( M \) and \( Y \). In order to develop an isotherm from these reactions one has to assume that the concentration of \( Y \) and the pH remain constant. Furthermore, the activity coefficient for the solution species should be treated as constant so that they can be lumped with the equilibrium constant to form a conditional equilibrium constant unique for each pH, total concentration of \( M \), and ionic strength. The activity of the surface species is assumed to be unity and the solid solution activity equals the mole fractions so that the mass action laws can be written as:

\[ k_1 = \frac{s_M}{c s_Y} \quad [2.31] \]

\[ k_2 = \frac{p_M}{(p_M + p_Y)c} \quad [2.32] \]
where $k_1$, $k_2$, and $k_3$ denote the conditional equilibrium constants derived from reactions [2.28], [2.29], and [2.30], respectively, $s_M$ and $s_Y$ are the amounts of solute M and Y adsorbed to the surface, $p_M$ and $p_Y$ are the amounts of solute M and Y which form the solid solution (surface precipitate), and $c$ is the amount of solute M in aqueous solution. Furthermore, additional mass balance equations can be formulated:

\[
s_T = s_M + s_Y \tag{2.34}
\]

\[
M_T = c + s_M + p_M \tag{2.35}
\]

\[
Y_T = Y + s_Y + p_Y \tag{2.36}
\]

where $s_T$ denotes the total amount of metals M and Y adsorbed to the surface, $M_T$ is the total amount of metal M in the system, and $Y_T$ is the total amount of metal Y in the system which can either form a solid solution with M or a surface site. Given that $Y$ remains constant, equations [2.31] to [2.36] form a system of algebraic equations with 6 unknowns. The goal is to derive a simple isotherm expression which relates the total amount of solute M associated with the solid phase ($s_M + p_M$) as a function of the total amount of M in solution denoted as $c$ in the isotherm expression. Such an expression can be written as:

\[
k_3 = \frac{p_Y}{(p_M + p_Y)c} \tag{2.33}
\]
\[ s = \frac{s_T k_1 c}{1 + k_1 c} + \left( \frac{p_T - s_T + s_T k_1 c}{1 + k_1 c} \right) \left( \frac{k_2 c}{1 - k_2 c} \right) - \frac{k_2}{k_3} c \]  

[2.37]

where \( s \) denotes the sum of \( s_M \) and \( s_Y \), and \( p_T \) denotes the total amount of solutes forming the precipitate (solid solution). The expression derived here, appears slightly different than the equation derived by Farley et al. (1985). Here, it is easily shown that the FDM isotherm consist of a Langmuir equation (the first term of equation [2.37]) and a second term governed by the surface precipitation (the remainder). If \( k_2 \) equals 0, then equation [2.37] becomes identical to the single site Langmuir equation.

It should be noted that all isotherms presented here can be reduced to a single site Langmuir equation. If the heterogeneity coefficient \( \alpha \) equals 1, then the GF, GLF, and Tóth isotherms are identical to the Langmuir equation. The two-surface Langmuir equation reduces to the single site Langmuir equation when \( F_1 \) or \( F_2 \) equals 0 or 1.

2.2.3. One-Dimensional Reactive Solute Transport in Water-Saturated Soil

The one-dimensional reactive solute transport can be described by the transport equation based on a solute mass balance. For a single solute one can write (Nielsen et al., 1986):
\[
\frac{\partial c}{\partial t} + \left( \frac{\rho}{\theta} \right) \frac{\partial s}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z}
\]  \hspace{1cm} [2.38]

where \( t \) denotes time (T), \( z \) distance (L), \( D \) is the dispersion coefficient \((L^2 T^{-1})\), \( v \) is the pore water velocity \((L T^{-1})\), \( \theta \) is the volumetric water content \((L^3 L^{-3})\), and \( \rho \) is the bulk density of the porous medium \((M L^{-3})\). Since equation [2.38] should be expressed in terms of \( c \) only, the solute amount sorbed \( s \) needs to be expressed in terms of the amount of solute in solution \( c \) using the isotherm expression discussed above. One can rewrite [2.38] to yield:

\[
R(c) \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z}
\]  \hspace{1cm} [2.39]

where the retardation factor \( R \) can be derived:

\[
R(c) = 1 + \left( \frac{\rho}{\theta} \right) \frac{\partial s}{\partial c}
\]  \hspace{1cm} [2.40]

In order to solve equation [2.39] the boundary and initial conditions have to be specified. Here the following conditions are applied:

\[
-D \frac{\partial c}{\partial z} + vc = vc_0(t) \quad \text{for} \quad z = 0, \quad t > 0 \]  \hspace{1cm} [2.41a]

\[
\frac{\partial c}{\partial z} = 0 \quad \text{for} \quad z = L, \quad t > 0 \]  \hspace{1cm} [2.41b]
where \( L \) denotes the length of the column (\( L \)), \( c_0 \) and \( c_i \) the inlet and initial concentration, respectively. The inlet boundary condition used here is a pulse of duration \( t_p \) and concentration \( c_p \) which can be expressed as follows:

\[
\begin{align*}
c_0(t) &= c_p, & 0 < t < t_p \quad [2.43a] \\
c_0(t) &= 0, & t_p < t < \infty \quad [2.43b]
\end{align*}
\]

Furthermore, the initial concentration within the soil profile is often assumed to be constant and is zero for pollutants which are not native to soils.

2.2.4. Dimensional Analysis

Our objective is to investigate the effects of the isotherm parameters on the solute behavior in soils during transport when different isotherms are used. For simplicity the isotherm equations [2.16], [2.18], [2.20], [2.23], [2.27], and [2.37], as well as the transport equation with its boundary and initial conditions were rewritten in dimensionless form. This was achieved using the following dimensionless notation:

\[
Z = \frac{z}{L} \quad [2.44a]
\]

\[
T = \frac{t}{L} \frac{V}{V_0} = \frac{V}{V_0} \quad [2.44b]
\]
\[ S = \frac{s}{s_T} \quad [2.44c] \]
\[ C = \frac{c}{c_p} \quad [2.44d] \]
\[ Pe = \frac{L \nu}{D} \quad [2.44e] \]
\[ \Phi = \left( \frac{\theta}{\rho} \right) \frac{c_p}{s_T} \quad [2.44f] \]
\[ \kappa_j = c_p k_j \quad [2.44g] \]

where \( Z, T, C, \) and \( S \) denote dimensionless distance, time, solution concentration, and the amount sorbed, respectively, \( Pe \) is the Peclet number, \( \Phi \) is a dimensionless solute saturation coefficient, \( \kappa \) is the dimensionless affinity coefficient of the isotherms, and the subscript \( j \) refers to the coefficient where applicable. \( V \) denotes the volume of solution \( (L^3) \) entering the column, and \( V_0 \) is the solution filled pore space \( (L^3) \). Obviously the dimensionless time and the amount of pore volume which leached from the column are numerically identical (Equation [2.44b]).

Using dimensionless notation the transport equation then reduces to:

\[ \frac{\partial C}{\partial T} + \frac{1}{\Phi} \frac{\partial S}{\partial T} = \frac{1}{Pe} \frac{\partial^2 C}{\partial Z^2} - \frac{\partial C}{\partial Z} \quad [2.45] \]

and the retardation factor becomes:
\[ R(C) = 1 + \frac{1}{\Phi} \frac{\partial S}{\partial C} \]  

The boundary and initial conditions become:

\[ -\frac{1}{\text{Pe}} \frac{\partial C}{\partial Z} + C = C_0(T) \quad Z = 0, \quad T > 0 \]  

\[ \frac{\partial C}{\partial Z} = 0 \quad Z = 1, \quad T > 0 \]  

\[ C = C_i(Z) \quad 0 < Z < 1, \quad T = 0 \]  

with

\[ C_i(Z) = \frac{c_i(z)}{c_p} \]  

In addition, the upper boundary condition was chosen to be a pulse which can be written as follows:

\[ C_0(T) = 1, \quad 0 < T < T_p \]  

\[ C_0(T) = 0, \quad T_p < T < \infty \]  

with the following dimensionless notations:

\[ C_0(T) = \frac{c_0(t)}{c_p} \]
Table 2.1. Retardation factors (R(C)) of all isotherms used in this study (Langmuir - L, two-surface Langmuir - TSL, general Freundlich - GF, general Langmuir-Freundlich - GLF, Freundlich - FRD, Farley-Dzombak-Morel - FDM).

<table>
<thead>
<tr>
<th>ISOThERm</th>
<th>R(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>$1 + 1/\Phi (\kappa {1 + \kappa C}^{-2})$</td>
</tr>
<tr>
<td>TSL</td>
<td>$1 + 1/\Phi (F_1 \kappa_1 {1 + \kappa_1 C}^{-2} + F_2 \kappa_2 {1 + \kappa_2 C}^{-2})$</td>
</tr>
<tr>
<td>GF</td>
<td>$1 + 1/\Phi (\alpha \kappa {\kappa C}^{\alpha-1} {1 + \kappa C}^{1-\alpha})$</td>
</tr>
<tr>
<td>GLF</td>
<td>$1 + 1/\Phi (\alpha \kappa {\kappa C}^{\alpha-1} {1 + {\kappa C}^{\alpha-1}}^{-2})$</td>
</tr>
<tr>
<td>FRD</td>
<td>$1 + \alpha C^{\alpha-1}$</td>
</tr>
<tr>
<td>TÓTH</td>
<td>$1 + 1/\Phi (\kappa {1 - (\kappa C)\alpha [1 + (\kappa C)\alpha^{-1}] {1 + (\kappa C)\alpha^{-2}})$</td>
</tr>
<tr>
<td>FDM</td>
<td>$1 + 1/\Phi (\kappa_1 {1 + \kappa_1 C}^{-2} + \Psi \kappa_2 (1 - \kappa_2 C)^{-2} + \kappa_2 (\kappa_1 + \kappa_2)^{-1}$</td>
</tr>
</tbody>
</table>

$$T_p = \frac{t_p \nu}{L} \quad [2.51b]$$

The retardation factors of all isotherms presented here are listed in Table 2.1. Here we choose the dimensionless representation of the isotherms.

All isotherms, but the FDM equation, can be generalized and reduced to:

$$\frac{s}{s_T} = \sum_{j=1}^{n} F_j \left[ \frac{(k_j c)^{\lambda_j}}{1 + (k_j c)^{\lambda_j}} \right]^{\beta_j} \quad [2.52]$$
where the Langmuir and two-surface Langmuir isotherms are obtained for \( n = 1, \ F_j = 1, \ \lambda_j = 1, \ \beta_j = 1 \) and for \( n = 2, \ 0 < F_j < 1, \ \lambda_j = 1, \ \beta_j = 1 \), respectively. Before identifying the isotherm equations with an exponent, it should be noted that \( \alpha \) denotes a number between zero and one. The general Freundlich equation can be derived when \( n = 1, \ F_j = 1, \ \lambda_j = 1, \) and \( \beta_j = \alpha \). The general Langmuir-Freundlich equation is obtained for \( n = 1, \ F_j = 1, \ \beta_j = 1, \) and \( \lambda_j = \alpha \). The Tóth isotherm equation is given when \( n = 1, \ F_j = 1, \ \lambda_j = \alpha, \) and \( \beta_j = 1/\alpha \). Finally, the Freundlich equation is obtained for \( n = F_j = 1, \ 1/\kappa_j > C, \) and \( \lambda_j \beta_j = \alpha (0 < \alpha < 1) \).

Applying the dimensionless groups to the FDM isotherm yields the following equation:

\[
S = \frac{\kappa_1 C}{1 + \kappa_1 C} + \left( \frac{\Psi - 1 + \kappa_1 C}{1 + \kappa_1 C} \right) \left[ \frac{\kappa_2 C}{1 - \kappa_2 C} \right] - \frac{\kappa_2}{\kappa_3} C \tag{2.53}
\]

where an additional dimensionless parameter has to be defined:

\[
\Psi = \frac{P_T}{S_T} \tag{2.54}
\]

which is the ratio of the amount of the mixed solid solution and the amount of surface sites. For example, the amount of iron oxide, which forms the solid solution with the solute of interest and the total amount of surface sites forming the surface complex are considered here. In other words the parameter \( \Psi \) is the ratio of how much of the solute retained is bond as a surface complex or as a surface precipitate (solid
solution). However, for an 'ill defined' systems, such as a soil, this parameter should be viewed as an empirical parameter.

Since the Freundlich isotherm does not approach a maximum value \( s_F \) one has to choose a different nondimensional parameter for the affinity coefficient \( k \) and the amount sorbed \( s \). Here we obtain the dimensionless notation:

\[
S_F = \left( \frac{\rho}{\theta} \right) \frac{s}{c_p} \quad [2.55a]
\]

\[
\kappa_F = \left( \frac{\rho}{\theta} \right) \frac{c_p^{\alpha-1}}{k_F} \quad [2.55b]
\]

where the subscript \( F \) denotes dimensionless parameters associated with the Freundlich isotherm only. The transport equation can be rewritten in the dimensionless form:

\[
\frac{\partial C}{\partial T} + \frac{\partial S}{\partial T} = \frac{1}{\text{Pe}} \frac{\partial^2 C}{\partial Z^2} - \frac{\partial C}{\partial Z} \quad [2.56]
\]

Equations [2.45], [2.46], and the special cases of the retardation factor listed in Table 2.1 were solved using implicit-explicit finite difference techniques using an IBM 3090 mainframe computer of Louisiana State University.

### 2.3. Results and Discussion

#### 2.3.1. Isotherm Behavior

Before interpreting the isotherm behavior in detail, it should be noted that the work by Altmann and Leckie (1987) demonstrates that an isotherm is a lumped parameter representation of actual chemical reactions taking place. An isotherm,
therefore, should be viewed as a valid tool in describing solute retention in systems which are not well defined. The use of an isotherm may be advantageous especially for soil or other 'ill defined' systems, since chemical reactions are difficult to prove. One should, however, not forget that an isotherm represents a very specific case of a sum of chemical reactions, valid only at a constant pH, and ionic strength, and for a given background solution composition.

Isotherms can be characterized by their behavior at low and high concentrations as demonstrated by Kinniburgh (1986). At high concentrations Langmuir type isotherms approach a constant value, usually denoted as the maximum sorption capacity. This term may relate to the specific surface area in pure substances. However, sorption maxima are rarely observed for ion sorption on soils and soil minerals and organic matter. At low concentrations the Langmuir type isotherms can be represented by a linear isotherm. More precisely, the first derivative of \( s \) with respect to \( c \) (\( \frac{\partial s}{\partial c} \)) is finite at the origin. This is not the case for the Freundlich isotherm with \( \alpha < 1 \), where the first derivative approaches infinity when \( c \) goes to zero. In order to demonstrate these asymptotic behaviors we present two Figures (2.4 and 2.5), in which \( s \) is plotted against \( c \) and the distribution coefficient (\( K_D = s/c \)) versus \( s \). Both plots are on a logarithmic scale. The first is sometimes referred to as the Freundlich plot, since the Freundlich equation yields a straight line. When \( K_D \) vs. \( s \) is plotted on a linear scale, it is often referred to as the Scatchard plot. This plot yields a straight line when the single Langmuir equation is plotted. Since we present this plot on a logarithmic scale, we refer to it as the logarithmic Scatchard
Figure 2.4. Freundlich plot of all isotherms (Langmuir, general Freundlich (GF), general Langmuir-Freundlich (GLF), Freundlich (F), Tóth, two-surface Langmuir (TSL), and Farley-Dzombak-Morel (FDM)) using the bold values of Table 2.2.
Figure 2.5. Logarithmic Scatchard plot of all isotherms (Langmuir, general Freundlich (GF), general Langmuir-Freundlich (GLF), Freundlich (F), Tóth, two-surface Langmuir (TSL), and Farley-Dzombak-Morel (FDM)) using the bold values of Table 2.2.
plot. The Freundlich plot is most useful for showing the existence of a sorption maximum, whereas the logarithmic Scatchard plot will demonstrate sorption linearity at low concentrations due to a constant $K_D$. In addition, the logarithmic Scatchard plot will display a minimum $K_D$ for isotherms with an inflection point such as the FDM and the Brunauer-Emmett-Teller (BET) isotherm (Brunauer et al., 1938). Whenever surface precipitation will take place in considerable amounts one should observe a minimum $K_D$ on the Scatchard plot, both on a linear and logarithmic scale.

The TSL and Tóth isotherms exhibit both asymptotic behaviors at low and high concentrations (Figures 2.4 and 2.5). The GF and GLF isotherms approach a maximum sorption at high concentration, whereas nonlinearity prevails at low concentrations. The FDM isotherm reaches a constant $k_D$ at low concentrations and is bounded by a solution concentration maximum ($1/k_2$ in equation [2.37]), where the amount sorbed goes to infinity. Clearly, this isotherm shows a similar behavior to the BET isotherm (Farley et al., 1985; Brunauer et al., 1938). The Freundlich isotherm does not show any asymptotic limits and is represented by a straight line in both the Freundlich and logarithmic Scatchard plots.

In the literature on solute sorption, the Freundlich and Langmuir isotherms are the most popular equations used for the description of the sorption of organics (such as pesticides), heavy metals, and other solutes to soils and soil components such as clay minerals, oxides and hydroxides of Fe and Al, and humic substances (Nriagu, 1980; Dowdy and Volk, 1983; Mortvedt et al., 1972). Since a sorption maximum is rarely observed, the Freundlich equation seems to be more applicable than the
Langmuir. However, for some sorbate/sorbent systems, such as goethite and Zn, different slopes on a Freundlich plot for large concentration ranges were found (Kinniburgh, 1976). In addition some authors found sorption linearity at low concentrations of some heavy metals/oxide systems (Davis and Leckie, 1978). These findings supported the use of other isotherms which are capable of describing such phenomena.

The Tóth isotherm proved to be useful in describing the sorption of P and K in soils, Cu on Na-montmorillonite, and Zn on ferrihydrite (Kinniburgh, 1986). Later, Altmann and Leckie (1987) applied successfully the Tóth isotherm to Cu sorption on goethite, humic acids, and mixtures of both. Kinniburgh et al. (1983) used the Langmuir, TSL, GF, GLF, and Tóth isotherm to describe the sorption of Zn and Ca on ferrihydrite. They found that the ability to fit the data over various pH's decreased in the following order:

\[ TSL = \text{Tóth} > \text{GF} = \text{GLF} > \text{Langmuir}. \]

In order to compare the isotherms one can assume the same values for the parameters or use parameter estimates of the different equations for the same data set.

First we used the same parameters to obtain isotherms. The parameter values are the bold face values in Table 2.2 and the results are presented Figures 2.4 and 2.5. Due to the fact that the GF, GLF, and Freundlich isotherms exhibit increasing affinity of the solute with decreasing concentrations, the retention described by these isotherms will always be greater than that of the other equations. Figures 2.4 and 2.5 clearly show that the GF, GLF, and Freundlich show higher sorption at low
Table 2.2. Parameter values used for sensitivity analysis of one-dimensional saturated transport for all isotherms used in this study.

<table>
<thead>
<tr>
<th>PARAMETER 1</th>
<th>VALUES 2</th>
<th>ISOTHERMS 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi$</td>
<td>0.05, 0.1, 0.5, 1.0</td>
<td>L, TSL, GF, GLF, TÓTH, FDM</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>0.1, 0.5, 1.0, 5.0</td>
<td>L, GF, GLF, TÓTH</td>
</tr>
<tr>
<td>$\kappa_F$</td>
<td>3.16, 7.07, 10.0, 22.4</td>
<td>F</td>
</tr>
<tr>
<td>$\kappa_1$</td>
<td>0.1, 0.5, 1.0, 5.0*</td>
<td>TSL, FDM</td>
</tr>
<tr>
<td>$\kappa_2$</td>
<td>0.01, 0.05@, 0.1, 0.5, 1.0#, 5.0f</td>
<td>TSL, FDM</td>
</tr>
<tr>
<td>$\kappa_3$</td>
<td>100</td>
<td>FDM</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.1, 0.2&amp;, 0.5, 0.9</td>
<td>GF, GLF, TÓTH, F</td>
</tr>
<tr>
<td>$P_c$</td>
<td>0.2, 0.5, 0.8, 0.95</td>
<td>TSL</td>
</tr>
<tr>
<td></td>
<td>5, 20, 60</td>
<td>ALL</td>
</tr>
</tbody>
</table>

1 Parameters are defined in equations [41] through [50];
2 Values in bold are used for the reference breakthrough curve;
* Value used for FDM only;
@ Value used for reference breakthrough curve of FDM;
# Values used only for TSL,
& Value used for Freundlich equation only

concentrations for the same parameter values. At high solute concentration the FDM and Freundlich equation will always exhibit a higher retention as compared to the other isotherms. This is simply caused by the lack of a sorption maximum. Overall the Tóth isotherm exhibits the lowest sorption at all concentrations.

Figures 2.6 and 2.7 show the Langmuir, TSL, GF, GLF, and Tóth isotherms for simulated Zn adsorption on ferrihydrite at a pH of 5.5 as determined by Kinniburgh et al. (1983). Table 2.3 shows the numerical values of the parameters used to generate these isotherms as corrected for constant pH. In order to fit the same
Table 2.3. Parameter estimation of Zn adsorption on ferrihydrite at pH 5.5 according to Kinniburgh et al. (1983) for the Langmuir, general Freundlich (GF), the general Langmuir-Freundlich (GLF), the Tóth, and two-surface Langmuir (TSL) isotherms.

<table>
<thead>
<tr>
<th>ISOTHERM</th>
<th>$s_T$</th>
<th>$k$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mol Zn/mol Fe)</td>
<td>(mol$^{-1}$ L)</td>
<td></td>
</tr>
<tr>
<td>LANGMUIR</td>
<td>$3.750 \times 10^{-2}$</td>
<td>$1.048 \times 10^{3}$</td>
<td>-</td>
</tr>
<tr>
<td>GF</td>
<td>$8.128 \times 10^{-2}$</td>
<td>$6.738 \times 10^{1}$</td>
<td>0.798</td>
</tr>
<tr>
<td>GLF</td>
<td>$8.750 \times 10^{-2}$</td>
<td>$6.792 \times 10^{1}$</td>
<td>0.804</td>
</tr>
<tr>
<td>TÓTH</td>
<td>$6.776 \times 10^{-1}$</td>
<td>$1.679 \times 10^{2}$</td>
<td>0.203</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ISOTHERM</th>
<th>$s_T$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$F_1$</th>
<th>$F_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mol Zn/mol Fe)</td>
<td>(mol$^{-1}$ L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSL</td>
<td>$1.008 \times 10^{-1}$</td>
<td>$2.688 \times 10^{4}$</td>
<td>$4.330 \times 10^{1}$</td>
<td>0.0235</td>
<td>0.9765</td>
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</tbody>
</table>

data set the Tóth isotherm parameter exhibits a low value for $\alpha$ and higher values for $k$ and $s_T$. The values for the GF and GLF isotherms are very similar and the isotherms are almost identical. The differences of the goodness of fit for the same data are due to the inability of the GF and GLF equations to describe the constant $K_D$ sorption at low concentrations. The data from Kinniburgh et al. (1983) show indeed
Figure 2.6. Freundlich plot of the isotherms tested by Kinniburgh et al. (1983) for Zn adsorption on ferrihydrite at pH of 5.5 (Langmuir, general Freundlich (GF), general Langmuir-Freundlich (GLF), Tóth, two-surface Langmuir (TSL)) with the isotherm parameters from Table 2.4.
Figure 2.7. Logarithmic Scatchard plot of the isotherms tested by Kinniburgh et al. (1983) for Zn adsorption on ferrihydrite at pH of 5.5 (Langmuir, general Freundlich (GF), general Langmuir-Freundlich (GLF), Tóth, two-surface Langmuir (TSL) with the isotherm parameters from Table 2.4.
this behavior and, hence, the Tóth and two-surface Langmuir equation are more successful in describing the data.

The choice of the right isotherm equation depends obviously on the data. If the data approach a constant $K_D$ at low concentrations the equations which may fit the data best are the Langmuir, two-surface Langmuir, and the Tóth isotherms. In the case of increasing $K_D$ at low concentrations the GF, GLF, and Freundlich may describe the data best. Using the Freundlich and logarithmic Scatchard plots one can qualitatively eliminate the equations which do not agree with the observed phenomena. Choosing the appropriate isotherm equation is essential in order to describe and predict the transport of solutes in soil.

2.3.2. Comparison of Transport Behavior

Reactive transport has long been simulated using the Langmuir and Freundlich isotherms. The effect of the chemistry or solute retention on the transport behavior is emphasized here. Breakthrough curves (BTCs) are the usual means of describing one-dimensional solute transport and are measured by miscible displacement techniques in soil columns. The BTCs can be characterized in a solute front, a peak, and a tail. Helfferich (1962) classified breakthroughs into self-sharpening and self-widened fronts and tails depending on the solute retention behavior. For soils, this classification has been reviewed by Schweich and Sardin (1981). According to the classification of Giles et al. (1960), solute sorption isotherms of the L type ($L$=Langmuir), exhibit convex shape with respect to solution concentration. Such
isotherms produce a self-sharpening front with an extensive tailing. All isotherms but the FDM isotherm fall in this category. In contrast, linear isotherms produce a nearly symmetrical BTC. Isotherms with a concave shape do not exhibit tailing; rather, the front shows a slow increase with time as shown by Schweich and Sardine (1981). If an isotherm displays both convex and concave behavior at low and high concentrations, the shape of the BTC will show initially a steep front which will flatten at a later point in time when the solute concentration is within the concave region of the isotherm. Accordingly, the desorption side displays an initial steep drop followed by extensive tailing at low concentrations. The FDM isotherm falls in this category. Overall, one can expect an increasing deviation from BTC symmetry with an increasing deviation from sorption linearity. Nonlinearity is not the only cause of tailing. Rather, physical and chemical nonequilibrium can produce significant deviations from breakthrough symmetry as was pointed out by Schweich and Sardin (1981) and Brusseau and Rao (1989). In order to differentiate between the tailing caused by nonequilibrium and sorption nonlinearity one has to know the equilibrium and/or the kinetics of the sorption process. The effects of nonlinearity of the sorption isotherm can be examined by varying parameters.

In order to compare the isotherms in terms of their effect on transport behavior we use the bold numbers of Table 2.2, which were also used for the isotherm plots of Figures 2.4 and 2.5, as the reference values. The corresponding BTCs are presented in Figures 2.8 and 2.9. Since we need to compare the different BTCs, the Langmuir based BTC is plotted in both Figures 2.8 and 2.9. The Tóth BTC is the
least retarded with a steep front and pronounced tailing (Figure 2.8). Second, the GLF and TSL based BTCs reach their maxima at almost the same time, but the GLF based BTC exhibits much more tailing and a slightly steeper front. The Langmuir based BTC displays similarities to the TSL and, to a lesser extent to the GLF based BTCs, but the tailing is not as prolonged. The BTCs, based on the GF and FDM isotherms, are more retarded than that for FDM. In contrast to the GF based BTC, the FDM based BTC does not show a steep front. Instead it exhibits the most front-spread of all isotherms tested here. The most retarded BTC is obtained by using the Freundlich isotherm (Figure 2.9). The shape of this BTC is very similar to that of the GF based BTC.

Since the weighting function of the Tóth isotherm has a skewed low-affinity tail (Figure 2.3), it should come as no surprise that this BTC is less retarded than the Langmuir based BTC. The prolonged tailing of the Tóth based BTC is due to the high affinity side of the weighting function. The GLF based BTC shows more retardation with a sharp front and more tailing than the Tóth based BTC. This is due to the pseudo normal-distributed weighting function (Figure 2.2). The high retardation and prolonged tailing of the GF based BTC is caused by the hyperbolic high affinity weighting function (Figure 2.1). The BTC obtained by using the TSL isotherm shows more tailing than the Langmuir based BTC due to the additional high affinity site \( \kappa_2 > \kappa_1 \). In contrast, the highly retarded BTC of the FDM isotherm can be explained by the solid solution formation or surface precipitation. The higher the solution concentration is the higher will be the sorption and therefore the retardation.
Figure 2.8. Breakthrough curves using the Langmuir, general Freundlich (GF), general Langmuir-Freundlich (GLF), and Tóth isotherms for the same values of the dimensionless saturation index $\Phi$, the affinity coefficient $\kappa$, and $\alpha$ (see Table 2.2).
Figure 2.9. Breakthrough curves using the Langmuir, two-surface Langmuir (TSL), Freundlich, and Farley-Dzombak-Morel (FDM) isotherms with the parameter values of Table 2.2 (bolded values).
Due to the concave and convex shape of the isotherm the BTC front is not as steep as that of the Langmuir based isotherm.

Generally, one can intuitively predict the general breakthrough behavior provided the weighting function of a particular isotherm is known. If the weighting function displays a large number of sites in the high affinity range, such as the GF weighting function, one can expect excessive tailing. Conversely, if low affinity sites dominate the weighting function, one can expect early breakthroughs, such as the Tóth based BTC. In fact the relationship between the SADF and the retardation factor can be quantified by combining equations [2.12] and [2.40] and applying Leibniz's rule in order to obtain:

$$R(c) = 1 + \frac{\rho}{\theta} s_T \int_0^\infty w(\xi) \frac{\partial \Gamma(\xi, c) \partial c}{c} \, d\xi$$  \hspace{1cm} [2.57]

Clearly, the weighting function remains unchanged and therefore, it is directly related to the retardation factor. Furthermore, the most common local isotherm is the Langmuir equation [2.11]. Combining equations [2.11] and [2.57] yields:

$$R(c) = 1 + \frac{\rho}{\theta} s_T \int_0^\infty w(\xi) \frac{\xi}{(1 + \xi c)^2} \, d\xi$$  \hspace{1cm} [2.58]

Hence, a generalized relationship between the weighting function and the retardation factor has been established which can be applied to any arbitrary weighting functions.

Alternatively, one can use isotherm parameters fitted to the same data and compare the corresponding BTCs. Here, we used the isotherm parameters from
Kinniburgh et al. (1983). The Zn concentrations at a pH of 5.5 used in their study ranged from approximately $10^{-6}$ to $10^{-2} \text{ M}$. In order to show the transport behavior at high and low concentrations, we choose two pulse concentrations, $10^{-2}$ and $10^{-4} \text{ M}$, to obtain BTCs for a pulse duration of 5 pore volumes (T). The bulk density and the volumetric water content were chosen to be $1.325 \text{ g cm}^{-3}$ and $0.50 \text{ cm}^3 \text{ cm}^{-3}$, respectively. The dimensionless parameters $\Phi$ and $\kappa$ are presented in Table 2.4. Figures 2.10 and 2.11 show that the TSL and Tóth based BTCs are least retarded at the high pulse concentration. Both BTCs reach a peak at a similar time, however, the BTC based on the Tóth isotherm exhibits more tailing. At low pulse concentration the BTCs deviate dramatically from a highly retarded Tóth based BTC and an early BTC of the TSL isotherm. The Tóth BTC exhibits even more retardation than the GLF and GF based BTCs. The isotherms with the second best fit, the GF and GLF, show very similar BTCs for both the high and low pulse concentrations. Both display somewhat similar tailing, whereas the BTC fronts are slightly different. The Langmuir based BTC shows most retardation compared to the other isotherms for both high and low pulse concentrations.

The deviation of the TSL and Tóth based BTCs at low input pulse concentration can be explained by the different shape of the isotherms in Figures 2.6 and 2.7. Although, both isotherms do fit the data equally well, according to Kinniburgh et al. (1983), the observed deviation may lead to erroneous conclusions. For example, if the Tóth isotherm is the appropriate representation of the equilibrium batch data and the TSL isotherm was used instead, the TSL based BTC may display
Table 2.4. Dimensionless parameter for breakthrough curves using data from Table 2.3 (according to Kinniburgh et al., 1983) assuming a bulk density ($\rho$) of 1.325 g cm$^{-3}$ and a volumetric water content ($\theta$) of 0.5 cm$^3$ cm$^{-3}$.

<table>
<thead>
<tr>
<th>ISOTHERM</th>
<th>$\Phi$</th>
<th>$\kappa$</th>
<th>$c_p$</th>
<th>FIGURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>LANGMUIR</td>
<td>1.006 $10^1$</td>
<td>1.048 $10^1$</td>
<td>$10^{-2}$</td>
<td>2.6</td>
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<td></td>
<td>1.006 $10^3$</td>
<td>1.048 $10^1$</td>
<td>$10^{-4}$</td>
<td>2.7</td>
</tr>
<tr>
<td>GF</td>
<td>4.643 $10^2$</td>
<td>6.738 $10^1$</td>
<td>$10^{-2}$</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>4.643 $10^4$</td>
<td>6.738 $10^3$</td>
<td>$10^{-4}$</td>
<td>2.7</td>
</tr>
<tr>
<td>GLF</td>
<td>4.313 $10^2$</td>
<td>6.792 $10^1$</td>
<td>$10^{-2}$</td>
<td>2.6</td>
</tr>
<tr>
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<td>4.313 $10^4$</td>
<td>6.792 $10^3$</td>
<td>$10^{-4}$</td>
<td>2.7</td>
</tr>
<tr>
<td>TÓTH</td>
<td>5.569 $10^5$</td>
<td>1.679 $10^0$</td>
<td>$10^{-2}$</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>5.569 $10^7$</td>
<td>1.679 $10^2$</td>
<td>$10^{-4}$</td>
<td>2.7</td>
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<table>
<thead>
<tr>
<th>ISOTHERM</th>
<th>$\Phi$</th>
<th>$\kappa_1$</th>
<th>$\kappa_2$</th>
<th>$c_p$</th>
<th>FIGURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSL</td>
<td>3.745 $10^{-2}$</td>
<td>2.688 $10^{-1}$</td>
<td>4.330 $10^1$</td>
<td>$10^{-2}$</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>3.745 $10^{-4}$</td>
<td>2.688 $10^3$</td>
<td>4.330 $10^3$</td>
<td>$10^{-4}$</td>
<td>2.7</td>
</tr>
</tbody>
</table>

an early breakthrough which perhaps does not agree with observed transport data. Hence, one may possibly conclude that the discrepancy between the predicted and observed BTC is caused by chemical or physical nonequilibrium. This example leads to the reevaluation of the criteria used to determine the goodness of fit of the sorption isotherms. Kinniburgh et al. (1983) use the residual root mean square error (RSME) as a measure for comparing the goodness of fit between different isotherms. They
Figure 2.10. Breakthrough curves using the best fit isotherm parameter (see Table 2.4) from Kinniburgh et al. (1983) for Zn adsorption on ferrihydrite at a pulse concentration of 0.01 mol/L for 5 pore volume (T).
Figure 2.11. Breakthrough curves using the best fit isotherm parameter (see Table 2.4) from Kinniburgh et al. (1983) for Zn adsorption on ferrihydrite at a pulse concentration of 0.0001 mol/L for 5 pore volume (T).
also mention that the residuals of the fitted Tóth isotherm displayed a trend, which indicates that some portions of the data are under- or overestimated by the isotherm equation. This trend, however, has no influence of the RSME value. Ideally, no trend of the residuals should be observed. Specifically, the best fit would be an isotherm equation with the lowest RSME and with random residuals.

2.3.3. Parameter Sensitivity

(i) Effect of $\alpha$: As shown by equations [2.57] and [2.58] the retardation factor and, therefore, the BTCs are directly related to the weighting function. In particular, the heterogeneity factor $\alpha$ is a measure of the width of the weighting function. The lower the value of $\alpha$, the wider is the distribution of the local affinity coefficient $\xi$ (Figures 2.1 through 2.3). Thus the effect of $\alpha$ on the BTCs should be interpreted in terms of the weighting functions. Based on the different weighting functions the corresponding BTCs appear very dissimilar. The GLF based BTC shows at $\alpha=0.1$ an early breakthrough with extended tailing (Figure 2.12). At $\alpha=0.9$, the breakthrough is the latest with the least tailing. The BTC at $\alpha=0.5$ lies in between the others. The GLF weighting function is close to a normal distribution which implies that with decreasing $\alpha$ the amount of low and high affinity sites increase. This leads to the observed early breakthrough with prolonged tailing at low $\alpha$ and later breakthrough with less tailing at high $\alpha$ (Figure 2.13). The effect of $\alpha$ on the BTC of the GF isotherm is prolonged tailing (Figure 2.12). The BTC with $\alpha=0.1$ has a maximum peak height of approximately $C=0.1$ at $T=11$. The higher $\alpha$ the
greater the peak height and the lesser the tailing (Figure 2.1). Since the GF weighting function consists only of a high affinity side such breakthrough behavior should be expected. The Tóth based BTCs show somewhat similar behavior as the GLF isotherms with respect to $\alpha$ (Figure 2.14). The earlier breakthrough at a low $\alpha$ ($=0.1$) is due to the skewed low affinity side of the weighting function (Figure 2.3). This behavior is more pronounced for the Tóth BTCs than for the GLF BTCs. The BTCs obtained from the Freundlich isotherm exhibits similar behavior as the GF based BTCs, that is that the BTCs are highly sensitive to a change in $\alpha$. However, the Freundlich equation is not associated with a weighting function and thus the interpretation of the BTCs cannot be based on equations [2.57] and [2.58].

(ii) Effect of $\Phi$: The dimensionless parameter $\Phi$ may be viewed as the ratio of the pulse concentration to the maximum sorption capacity or as an empirical isotherm coefficient. For a given input pulse duration this dimensionless parameter relates the amount of solute given into the column to the total amount of available sorption sites. Hence, this parameter can be viewed as a mass balance coefficient. All but the Freundlich isotherm are described using this parameter. Figure 2.16 shows the effect of changing $\Phi$ for the Langmuir BTC. For low $\Phi$, the BTCs are highly retarded with an increased tailing and decreasing peak maximum. For high $\Phi$, the BTCs approach the shape of a conservative tracer breakthrough. Once the value of $\Phi$ is below 0.5 the effect of the BTC spreading seems to become more severe. Also, the nonlinearity seems to dominate the BTC shape at low $\Phi$, since maximum sorption capacity $s_T$ exceeds the input pulse concentration $c_p$. The results for the TSL, GF, GLF, and
Figure 2.12. Breakthrough curves for the sensitivity of the dimensionless heterogeneity coefficient $\alpha$ for the general Langmuir-Freundlich isotherm (GLF).
Figure 2.13. Breakthrough curves for the sensitivity of the dimensionless heterogeneity coefficient $\alpha$ for the general Freundlich isotherm (GF).
Figure 2.14. Breakthrough curves for the sensitivity of the dimensionless heterogeneity coefficient $\alpha$ for the Tóth isotherm.
Figure 2.15. Breakthrough curves for the sensitivity of the dimensionless heterogeneity coefficient $\alpha$ for the Freundlich isotherm.
Toth isotherms are in Figures 2.17, 2.18, 2.19, and 2.20, respectively. All Figures show the same phenomenon as described for the Langmuir based BTC. Thus, the conclusions can be extended to all isotherms used here. The meaning of $\Phi$ for FDM isotherm is slightly different; only the amount of surface sites are considered. However, the same conclusions can be drawn from Figure 2.21 for the other BTCs.

(iii) Effect of $\kappa$: The dimensionless affinity coefficient for all isotherms was varied from 0.1 to 5. As expected, increasing $\kappa$ will yield a more retarded BTC for all isotherms as shown in Figures 2.22 through 2.29. At a value of 0.1 most BTCs reach a maximum of the pulse concentration within the first five pore volumes (T). With increasing $\kappa$ the BTCs exhibit prolonged tailing especially for the GF and GLF based BTCs. For the TSL based BTCs, the tailing depends highly on both, $\kappa_1$ and $\kappa_2$ (Figure 2.23). A more detailed discussion will be given when describing the effects of the fractions $F_1$ and $F_2$ of site one and two, respectively, of equation [2.18]. The FDM BTCs depend on $\kappa_1$ and $\kappa_2$ in a different way. Increasing $\kappa_1$ resulted in an increasing retardation and tailing of the BTCs (Figure 2.28), whereas, the shape of the BTC front was not affected. This is different for $\kappa_2$ which is a measure for the maximum value of the solute concentration in solution (Figure 2.29). When $\kappa_2$ is increased, the breakthrough is not only more retarded but also the slope of the BTC front decreases which is consistent with the findings of Schweich and Sardin (1981).

(iv) Effect of $F$: Varying the fraction of site 1 and 2 of the TSL isotherm reflects the effect of a relative increase or decrease of the high affinity sites. Figure
Figure 2.16. Breakthrough curves for the sensitivity of $\Phi$ for the Langmuir isotherm at values of 0.05, 0.1, 0.5, 1.0.
Figure 2.17. Breakthrough curves for the sensitivity of $\Phi$ for the two-surface Langmuir isotherm (TSL) at values of 0.05, 0.1, 0.5, 1.0.
Figure 2.18. Breakthrough curves for the sensitivity of $\Phi$ for the general Freundlich isotherm (GF) at values of 0.05, 0.1, 0.5, 1.0.
Figure 2.19. Breakthrough curves for the sensitivity of $\phi$ for the general Langmuir-Freundlich isotherm (GLF) at values of 0.05, 0.1, 0.5, 1.0.
Figure 2.20. Breakthrough curves for the sensitivity of $\Phi$ for the Tóth isotherm at values of 0.05, 0.1, 0.5, 1.0.
Figure 2.21. Breakthrough curves for the sensitivity of $\Phi$ for the Farley-Dzombak-Morel isotherm (FDM) at values of 0.05, 0.1, 0.5, 1.0.
Figure 2.22. Breakthrough curves for the sensitivity of the dimensionless affinity coefficient $\kappa$ for the Langmuir isotherm.
Figure 2.23. Breakthrough curves for the sensitivity of the dimensionless affinity coefficient $\kappa_1$ and $\kappa_2$ for the two-surface Langmuir isotherm (TSL).
Figure 2.24. Breakthrough curves for the sensitivity of the dimensionless affinity coefficient $\kappa$ for the general Freundlich isotherm (GF).
Figure 2.25. Breakthrough curves for the sensitivity of the dimensionless affinity coefficient $\kappa$ for the general Langmuir-Freundlich isotherm (GLF).
Figure 2.26. Breakthrough curves for the sensitivity of the dimensionless affinity coefficient $\kappa_F$ for the Freundlich isotherm.
Figure 2.27. Breakthrough curves for the sensitivity of the dimensionless affinity coefficient $\kappa$ for the T6th isotherm.
Figure 2.28. Breakthrough curves for the sensitivity of the dimensionless affinity coefficient \( \kappa_1 \) for the Farley-Dzombak-Morel isotherm (FDM).
Figure 2.29. Breakthrough curves for the sensitivity of the dimensionless affinity coefficient $\kappa_2$ for the Farley-Dzombak-Morel isotherm (FDM).
2.30 shows that the BTCs display an increase of tailing and to a lesser extent, retardation with an increase of $F_1$.

(v) Effect of $\Psi$: $\Psi$ is a dimensionless parameter describing the ratio of the amount of the salt (forming the solid solution or coprecipitate $p_T$) to the amount of surface sites $s_T$. The larger $\Psi$ becomes the greater the amount of solute is involved in the surface precipitation. The effect is obvious: the BTCs are more retarded with slight increase in tailing (Figure 2.31).

(vi) Effect of $Pe$: The dimensionless Peclet number describes the ratio of the column length, the pore water velocity, and the dispersion coefficient. Here, we chose the values 5, 20, and 60, which are similar to the Peclet numbers used by van Genuchten and Alves (1982). The effect of the Peclet number on the BTCs of all isotherms used here is very similar. Figures 2.32 through 2.38 show that increasing the Peclet number yields later breakthrough with less prolonged tailing. The maximum peak arrival time is usually not influenced. The isotherms which exhibit the most (highest) retardation seem to be least affected by a change of the Peclet number, e.g. the GF based BTC in Figure 2.34 show very similar tailing and slightly shifted BTC fronts. Conversely, the least retarded BTCs, such as the Tóth based BTCs show more pronounced effects (Figure 2.37).

In addition to the effects of isotherm parameter changes on transport, the sensitivities of different parameters with respect to each other have to be examined. For this purpose the BTCs which are determined using the data from Kinniburgh et al. (1983) will be compared. Since the parameters $\Phi$ and $\kappa$ are nondimensionalized
Figure 2.30. Breakthrough curves for the sensitivity of the dimensionless site fraction coefficient $F$ for the two-surface Langmuir isotherm (TSL).
Figure 2.31. Breakthrough curves for the sensitivity of the dimensionless coefficient $\Psi$ describing the ratio of amount of solids involved in the solid solution formation and surface sites for the Farley-Dzombak-Morel isotherm (FDM).
Figure 2.32. Breakthrough curves for the sensitivity of the dimensionless Peclet number Pe for the Langmuir isotherm.
Figure 2.33. Breakthrough curves for the sensitivity of the dimensionless Peclet number $Pe$ for the two-surface Langmuir isotherm (TSL).
Figure 2.34. Breakthrough curves for the sensitivity of the dimensionless Peclet number $Pe$ for the general Freundlich isotherm (GF).
Figure 2.35. Breakthrough curves for the sensitivity of the dimensionless Peclet number Pe for the general Langmuir-Freundlich isotherm (GLF).
Figure 2.36. Breakthrough curves for the sensitivity of the dimensionless Peclet number $Pe$ for the Freundlich isotherm.
Figure 2.37. Breakthrough curves for the sensitivity of the dimensionless Peclet number Pe for the Tóth isotherm.
Figure 2.38. Breakthrough curves for the sensitivity of the dimensionless Peclet number Pe for the Farley-Dzombak-Morel isotherm (FDM).
using the pulse concentration $c_p$, a change in $c_p$ results in a change of both parameters (Equations [2.44f] and [2.44g]). When the pulse concentration changes from $10^{-2}$ to $10^{-4} M$ the dimensionless parameters $\Phi$ and $\kappa$ both decrease two orders of magnitude (Table 2.4). Decreasing $\Phi$ will yield a more retarded BTC, whereas a decrease of $\kappa$ will produce an earlier BTC. If both parameters have the same effect on the transport, the simulated BTCs using the different parameters should exhibit similar shape. However, as shown in Figures 2.10 and 2.11 the BTCs with the lower pulse concentration are significantly more retarded. This shows clearly, that the transport is much more sensitive to a change in $\Phi$ than a change in $\kappa$. In fact, one can view $\Phi$ as a mass balance parameter since it is the ratio of input concentration and maximum sorption capacity, whereas $\kappa$ determines the shape of the isotherm. Since $\alpha$ and $F$ are dimensionless, the effect of these parameters are independent of the pulse concentration. Comparing the effects of $\Phi$ and $\kappa$ on the transport with those of $\alpha$ and $F$ leads to the conclusion that the former parameters are much more sensitive towards the transport than the latter.

2.4. Summary and Conclusion

Sorption isotherms are limited in their application towards describing solute retention. However, their application towards systems which are not well defined or simply not understood is a valid tool which is simple to use. The isotherm parameter should be viewed generally as purely empirical coefficients, although they can be related to actual chemical reactions. The goodness of fit of isotherm equations to
measured sorption data should be determined in terms of the patternless distribution of the residuals. If simple equations, such as the Freundlich or Langmuir isotherm, are not adequate to describe the data, more complicated models should be used until no pattern of the residuals occur. Furthermore, the asymptotic behavior of isotherms can be used in selecting the appropriate isotherm equation. Using the Freundlich plot (log s vs. log c), the linear Scatchard plot (s/c vs. s), and the logarithmic Scatchard plot (log s/c vs. log s) illustrated here one should be able to determine whether or not the data show some kind of asymptotic behavior at low and/or at high concentrations.

Most of the commonly used isotherms equations may be viewed as a variation of a generalized isotherm equation [2.52]. All isotherms with a high affinity weighting function exhibit excessive tailing, whereas the Langmuir, TSL, and FDM isotherms show the least tailing. The weighting function can, therefore, be viewed as a tool to predict qualitatively the breakthrough behavior. In fact, equations [2.56] and [2.57] relate the weighting function to the transport behavior through the retardation factor.

The isotherm and transport parameter effect on the BTCs in terms of the retardation decreases in the following order:

$$\Phi > \kappa > \alpha > Pe$$

However, the dimensionless parameter $\kappa$ has the most influence on the tailing. The effect of heterogeneity parameter $\alpha$ reflects the shape of the weighting function.
CHAPTER 3
THE TRANSPORT OF SELECTED HEAVY METALS IN SOIL COLUMNS
AT CONSTANT AND VARIABLE IONIC STRENGTH: EXPERIMENTAL
EVIDENCE AND MODELLING APPROACHES

3.1. Introduction

Environmental problems associated with heavy metal pollution have increased
during the last decades. Since the soil is a key element in controlling the fate of
heavy metals in the environment, it is of great importance to understand the transport
behavior of heavy metals.

First, the chemical reactions associated with the retention of heavy metals need
to be addressed. McBride (1989) reviewed the reactions controlling heavy metal
solubility in soils. The surface reactions on mineral and organic matter surfaces are
often innersphere complexations with considerable high binding energies. This is
often referred to as specific sorption (Sposito, 1984). In addition, surface
precipitation on oxide or hydroxide, and carbonate surfaces may occur for Zn and Cd
(Dzombak and Morel, 1990). For example, Farley et al. (1986) presented a surface
precipitation model with changing composition of the surface precipitate.
Furthermore, heavy metal ions may penetrate the lattice of minerals (Brümmer et al.,
1988; White and Yee, 1986). In addition organic matter binds heavy metal ions with
varying adsorption energies. The nature of most soils prevents the identification of
particular reactions on soil minerals or organic matter. The reaction occurring on
these soil components have been examined for pure systems such as goethite or humic
acids. Since soils can be viewed as mixtures of pure substances, they form a chemically heterogeneous system which is not well defined. Therefore, the description of heavy metal sorption remains often empirical in nature and chemically meaningful models are difficult to employ.

Because of the shortcomings of chemical models such as surface complexation models, empirical approaches are commonly in use to obtain sorption and mobility information of heavy metals. These methods include (i) the measurement of isotherms for single and binary solute systems and (ii) the chemical fractionation of heavy metals by extracting the soil with various chemicals. The first method is employed when the sorption behavior of a heavy metal on uncontaminated soil will be examined. Once a soil is polluted, the second method is commonly used. In fact, most of the practical soil characterization is based on extraction methods, such as the determination of exchangeable cations. Even though isotherms, determined by heavy metal addition to uncontaminated soil, have been applied to transport studies, extraction methods are rarely used.

In this study, we applied Zn and Cd to two different soils in a Ca background solution. The sorption was treated as a single solute system as well as a binary solute (ion exchange). The transport of both heavy metals as affected by ionic strength were examined. Previous research revealed that heavy metals are highly retarded (Buchter et al., 1989; Harmsen, 1977; Abd-Elfattah and Wada, 1981). Furthermore, the transport has been modelled with isotherms such as the Freundlich (Sidle et al., 1977; Poelstra et al., 1979; Swartjes et al., 1990; and Stollenwerk and Kipp, 1990) and
Langmuir (Mayer, 1978), even though Kinniburgh (1986) showed that often other isotherm equations are more suitable to describe solute sorption in soils. Furthermore, ion exchange equilibria have been employed to describe sorption of heavy metals (Abd-Elfattah and Wada, 1981; Harmsen, 1977; Bittel and Miller, 1974). They revealed that the affinity of heavy metals increases with decreasing heavy metal percentage on the exchanger. Using an empirical selectivity coefficient, they showed for example that the affinity of Zn increased up to two order of magnitude with low surface coverage in a Ca background solution. Variable selectivity coefficients have been applied to the transport of Ca, Mg, and Na systems (Mansell et al., 1988). However, this approach has not been applied to model the transport of heavy metals in soil columns.

The objectives of this work are (i) to measure the sorption of Zn and Cd in two acid soils using batch experiments; (ii) to describe the sorption using single and binary (ion exchange) solute isotherm equations; and (iii) to apply ion exchange and single solute isotherms to modelling the transport of Zn and Cd in soil columns under conditions of constant and variable ionic strengths. Furthermore, the suitability of extraction methods for determining Zn and Cd sorption when competing with Ca and its applicability to transport modelling is examined.
3.2. Theoretical

3.2.1. Sorption Isotherms

Since soils are complex mixtures of solids such as clay minerals, oxides/hydroxides, and organic matter, they are often referred to as 'ill defined' systems (Leckie, 1988). Due to the fact that chemical models such as surface complexation models are limited to well defined systems, simpler and usually empirical approaches are used. As yet, no theoretical framework has been developed to explain and predict the sorption of single and binary solute sorption in 'ill defined' systems. More specific, the activity of the surface or sorbed phase cannot be predicted. However, using ion exchange techniques the activity of the exchanger can be determined experimentally by measuring ion exchange isotherms (Gaines and Thomas, 1953). Hence, the measurement of sorption is unavoidable and the description remains largely empirical.

Sposito (1986b) classified the models of ion exchange reaction into activity, adsorption, and kinetic models. The first category includes models based on theoretical assumptions concerning the activity of the surface species. For example, the Vanselow selectivity coefficient is based on the assumption that the surface species behave like an ideal solid solution; that is, the activity is proportional to the mole fraction of the sorbed phase. Empirical relationships such as the Rothmund-Kornfeld expression for ion exchange or the Freundlich equation for single solute sorption represent the second category. Here no mechanistic hypothesis concerning the surface activity is employed, rather a pure macroscopic approach is preferred. Considering
the chemical heterogeneity of soils the second approach seems to be preferable over the first. In spite of this assumption, Altmann and Leckie (1988) showed that isotherm expressions are lumped parameter representations of actual surface chemical reactions. They employed the Tóth isotherm to Cu sorption on binary mixtures of humic acids and goethite. Even though the formulation of surface reactions for their systems did not involve noninteger stoichiometric exchange of protons and trace metals, the overall isotherm exhibits noninteger stoichiometric exchange. In order to develop a general isotherm expression for single and binary solute systems the following equation can be given (Sips, 1950; Nederlof et al., 1990):

\[
\frac{s}{s_T} = \int_0^\infty w(K_i, k_i, \alpha_i) \Gamma(K_i, \xi) \, dK_i = f(k_i, \alpha_i, \xi) \quad [3.1]
\]

where \( s \) denotes the amount of solute sorbed (M M\(^{-1}\) soil), \( s_T \) is the maximum sorption capacity (M M\(^{-1}\)), \( w \) is a weighting function (Sposito, 1984) or site affinity distribution function (Kinniburgh et al., 1983; Nederlof et al., 1990), or a frequency distribution (Altmann and Leckie, 1987; Perdue and Lytle, 1983), \( K \) is the local affinity coefficient (dimensionless), \( k \) is the overall or global affinity coefficient (dimensionless), \( \alpha \) is an empirical exponent often referred to as the heterogeneity factor, which is constrained to \( 0 < \alpha < 1 \) (Sposito, 1983), \( \Gamma \) is the local isotherm equation, \( \xi \) is an activity or concentration term, and \( f \) the overall or global isotherm equation. The activity or concentration term \( \xi \) is either the solution concentration of
a single solute or the ratio of the solution concentrations of two competing ions 
\( \frac{c_1}{c_2} \). The local isotherm equation is often assumed to be the Langmuir equation:

\[
\Gamma(K, \xi) = \frac{K \xi}{1 + K \xi} \tag{3.2}
\]

Nederlof et al. (1990) gave a review and new insights into the use of equation [3.1] to model solute sorption in heterogeneous systems. Here, only the weighting functions which yield analytical solutions of equations [3.1] are considered for the description of single and binary solute systems. The closed-form isotherm equations derived from equation [3.1] and [3.2] were presented by Kinniburgh et al. (1983) and can be summarized by the following equations:

\[
\frac{s_i}{s_T} = \sum_{i=1}^{n} F_i \left[ \frac{(k_i \xi_i)^{\lambda_i}}{1 + \varepsilon_i (k_i \xi_i)^{\lambda_i}} \right]^{\beta_i} \tag{3.3}
\]

where \( F_i \) denotes the fraction of site \( i \), \( n \) the number of sites, \( k \) the overall or global affinity coefficient, \( \lambda \) and \( \beta \) are empirical exponents usually determining the width of the site affinity distribution function, and \( \varepsilon_i \) is an integer which is zero only for the Freundlich equation and one for all other equations. Equation [3.3] has been applied to soil minerals and mixtures of ferric hydrite and humic acids for varying pH's (Altmann and Leckie, 1987). In this case the concentration term \( \xi \) equals \( c/[H^+]^\nu \), where \( \nu \) is the noninteger stoichiometric exchange coefficient between the metal and
Table 3.1. Special cases of the general isotherm equation as given by equation [3.3].

<table>
<thead>
<tr>
<th>ISO THERM†</th>
<th>$\xi_i$ ‡</th>
<th>n</th>
<th>$\lambda_i$</th>
<th>$\beta_i$</th>
<th>$\epsilon_i$</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>LANG</td>
<td>$c$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>Kinniburgh et al.(1983), Kinniburgh (1986), Harter (1983)</td>
</tr>
<tr>
<td></td>
<td>$c/[H^+]$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSL</td>
<td>$c$</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>Kinniburgh et al.(1983), Kinniburgh (1986), Selim and Amacher (1988)</td>
</tr>
<tr>
<td></td>
<td>$c/[H^+]$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF</td>
<td>$c$</td>
<td>1</td>
<td>1</td>
<td>$\alpha$</td>
<td>1</td>
<td>Kinniburgh et al.(1983), Kinniburgh (1986)</td>
</tr>
<tr>
<td></td>
<td>$c/[H^+]$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GLF</td>
<td>$c$</td>
<td>1</td>
<td>$\alpha$</td>
<td>1</td>
<td>1</td>
<td>Kinniburgh et al.(1983), Kinniburgh (1986)</td>
</tr>
<tr>
<td></td>
<td>$c/[H^+]$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TÓTH</td>
<td>$c$</td>
<td>1</td>
<td>$\alpha$</td>
<td>$1/\alpha$</td>
<td>1</td>
<td>Kinniburgh et al.(1983), Kinniburgh (1986), Altmann and Leckie (1987)</td>
</tr>
<tr>
<td></td>
<td>$c/[H^+]$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FRD</td>
<td>$c$</td>
<td>1</td>
<td>$\alpha$</td>
<td>1</td>
<td>0</td>
<td>Buchter et al. (1990), Sidle et al. (1977)</td>
</tr>
<tr>
<td>S</td>
<td>$c_1/c_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>Abd-Elfattah and Wada (1981), Harmsen (1977), Bittel and Miller (1974)</td>
</tr>
<tr>
<td>RK</td>
<td>$c_1/c_2$</td>
<td>1</td>
<td>$\alpha$</td>
<td>1</td>
<td>1</td>
<td>Harmsen (1977), Bond and Phillips (1990)</td>
</tr>
</tbody>
</table>

† LANG - Langmuir, TSL - two-site Langmuir, GF - general Freundlich, GLF - general Langmuir-Freundlich, FRD - Freundlich, S - empirical selectivity coefficient for homovalent ion exchange, RK - Rothmund-Kornfeld equations; ‡ $c$ - solution concentration, $c/[H^+]$ - ratio of heavy metal and proton concentrations in solution with noninteger stoichiometric exchange coefficient
proton. Also, equation [3.3] is easily adapted to ion exchange equilibria. In fact, Kinniburgh (1986) applied a special case of equation [3.3] to the exchange of K with Ca and Mg in soils. The special cases of equation [3.3] is summarized in Table 3.1.

The Langmuir equation is not only the simplest special case of equation [3.3], but also one of the most commonly used equation for describing solute sorption in soils. In addition to the Langmuir approach, the Freundlich equation is perhaps the most popular isotherm equation used for heavy metal sorption. At low solution concentrations the Freundlich equation can be derived from the general Freundlich-Langmuir equation (Sposito, 1980). However, the usage of the Freundlich equation in practice is not restricted to low concentrations alone. Furthermore, at low concentrations heavy metal may exhibit a constant affinity towards the sorbent and hence this behavior is better described by the Langmuir, the two-site Langmuir, or Tóth equations than the Freundlich equation. Therefore, the Freundlich equation may best describe sorption at intermediate concentration ranges. In fact, this was pointed out by Farley et al. (1985) who derived a surface precipitation model in which the heavy metal sorption exhibited 'Freundlich' behavior at intermediate concentrations. The general Freundlich and the general Freundlich-Langmuir have been applied to Zn sorption on ferrihydrite by Kinniburgh et al. (1983) with limited success. The former isotherm is based on a hyperbolic weighting function, whereas the latter is based on a quasi normal distribution. The weighting function of the Tóth isotherm differs from that of the general Langmuir-Freundlich such that the distribution is skewed towards the low affinity side (Tóth et al, 1974). This isotherm has been the most successful
equation for describing various isotherm data (Kinniburgh, 1986; Altmann and Leckie, 1987).

3.2.2. Steady State Transport

The transport of solutes in porous media can be described by the convective-dispersive equation (CDE), sometimes referred to as the transport equation:

$$\frac{\partial c_j}{\partial t} + \frac{\rho}{\theta} \frac{\partial s_j}{\partial t} = D \frac{\partial^2 c_j}{\partial z^2} - v \frac{\partial c_j}{\partial z}$$

where $\rho$ is the bulk density ($\text{M} \text{L}^{-3}$), $\theta$ the volumetric water content ($\text{L}^3 \text{L}^{-3}$), $t$ time ($\text{T}$), $D$ the dispersion coefficient ($\text{L}^2 \text{T}^{-1}$), $v$ the pore water velocity ($\text{L} \text{T}^{-1}$), $z$ the length coordinate ($\text{L}$), and $j$ the solute 1 or 2. Here we consider either single solute or binary solute systems. For the latter we consider two CDE's for each solute. In order to solve equation [5] we introduce the retardation factor $R$ for solute $j$:

$$R_j = 1 + \frac{\rho}{\theta} \frac{\partial s_j}{\partial c_j}$$

In particular we consider single and binary solute systems. Assuming that the concentration term $\xi$ in equation [3.3] equals the concentration $c$ the retardation factor becomes:
\[ R(c) = 1 + \frac{\rho}{\theta} s_T \sum_{i=1}^{n} F_i \frac{\beta_i \lambda_i}{c(1 + \epsilon_i(k_i c)^{\lambda_i})} \left[ \frac{(k_i c)^{\lambda_i}}{1 + \epsilon_i(k_i c)^{\lambda_i}} \right] \beta_i \]  

For homovalent ion exchange the concentration term \( \xi \) equals \( c_1/c_2 \) and assuming that the total concentration \( c_T \) equals \( c_1 + c_2 \) and remains constant the retardation factor becomes:

\[ R(c_j) = 1 + \]

\[ \frac{\rho}{\theta} s_T \sum_{i=1}^{n} F_i \frac{\lambda_i \beta_i c_T (c_T - c_1)^{\lambda_i}}{c_1 (c_T - c_1) \left[ (c_T - c_1)^{\lambda_i} + (k_i c_1)^{\lambda_i} \right]} \left[ \frac{(k_i c_1)^{\lambda_i}}{(c_T - c_1)^{\lambda_i} + (k_i c_1)^{\lambda_i}} \right] \beta_i \]  

Combining equations [3.4] and [3.5] we obtain:

\[ R_j \frac{\partial c_j}{\partial t} = D \frac{\partial^2 c_j}{\partial z^2} - \nu \frac{\partial c_j}{\partial z} \]  

Equation [3.7] was solved using implicit-explicit finite difference scheme carried out on the LSU mainframe computer.

Since local equilibrium may not be valid in soils with considerable structure, we relax this assumption as follows. We assumed diffusion controlled reactions may in fact dominate such soils. In order to account for diffusion of the solute to the sorption site we may introduce a mass transfer coefficient according to Flühler and Jury (1983):
\[
\frac{\partial s_j^*}{\partial t} = k_m(s_j^* - s_j) \tag{3.9}
\]
where \(k_m\) denotes the mass transfer coefficient (T\(^{-1}\)) and \(s_j^*\) denotes the equilibrium sorption amount. This expression is based on the assumption that the kinetics can be described with a steady state diffusion process, where the right hand side of equation [3.9] represents the average concentration gradient. The mass transfer coefficient \(k_m\) may be related to the effective diffusion coefficient as shown by Hines and Maddox (1985). Equation [3.9] is combined with equation [3.4] and the equilibrium sorption term \(s^*\) is calculated using equation [3.3].

### 3.3. Materials and Methods

#### 3.3.1. Soils

The soils used in this case study are listed in Table 3.2 along with their taxonomic classification and selected chemical properties. These soils were air-dried and passed through a 2-mm sieve before use. The soils were analyzed for pH by the 1:1 soil/water paste method (McLean, 1982), for organic matter by the acid-dichromate oxidation method (Nelson and Sommers, 1982), for free iron oxides by the dithionite-citrate-bicarbonate method (Mehra and Jackson, 1960), and for the cation exchange capacity (CEC) of the acid soils by the method of Gillman (1979).
Table 3.2. Taxonomic classification and selected soil properties.

<table>
<thead>
<tr>
<th>Soil§</th>
<th>Horizon</th>
<th>Taxonomic Classification</th>
<th>pH</th>
<th>TOC %</th>
<th>sum of cations</th>
<th>exch.</th>
<th>MnO₂</th>
<th>Fe₂O₃</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>sand %</th>
<th>silt %</th>
<th>clay %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivier</td>
<td>Ap</td>
<td>fine-silty, mixed, thermic Aquic Fragiaudalf</td>
<td>6.6</td>
<td>0.83</td>
<td>8.6</td>
<td>1.9</td>
<td>0.27</td>
<td>0.30</td>
<td>0.71</td>
<td>0.071</td>
<td>4.4</td>
<td>89.4</td>
<td>6.2</td>
</tr>
<tr>
<td>Windsor</td>
<td>Ap</td>
<td>mixed, mesic Typic Udipsamment</td>
<td>5.3</td>
<td>2.03</td>
<td>2.0</td>
<td>10.2</td>
<td>0.041</td>
<td>0.42</td>
<td>1.23</td>
<td>0.56</td>
<td>76.8</td>
<td>20.5</td>
<td>2.8</td>
</tr>
</tbody>
</table>

§ The states from which the soil samples originated are Louisiana (Olivier soils) and New Hampshire (Windsor soil).
3.3.2. Sorption Experiments

The first type of sorption experiment consisted of monitoring only the heavy metal of interest (Zn and Cd) in solution. Solutions of 0.01, 0.05, 0.1, 0.5, 1.0, 2.0, 5.0, 10.0, 50.0, 100.0 mg L\(^{-1}\) of Zn(NO\(_3\))\(_2\) and Cd(NO\(_3\))\(_2\) in 0.005 \(M\) Ca(NO\(_3\))\(_2\) were prepared. These solutions were then spiked with radio isotopes, specifically \(^{65}\)Zn and \(^{119}\)Cd at an activity of approximately 9.25 \(\times\) 10\(^{12}\) Bq kg\(^{-1}\). Then 3 g of air-dried soil was added to a 40 ml centrifuge tube, which was followed by the addition of 30 ml of the solutions. The amount of isotope disappearance in the solution was measured with time as described elsewhere (Amacher et al., 1986). The activity of the radio isotopes where monitored using liquid scintillation counting.

The second type of experiment consisted of measuring binary systems of Zn/Ca and Cd/Ca. First, solutions of metal/Ca ratios of 0.1, 0.7, 0.5, 0.3, 0.1 were prepared at 0.5 \(M\) concentration. For each solution three replicates of 10 g of air-dried soil added to 40 ml centrifuge tubes were prepared. In order to achieve saturation of the soil with the different solutions, 30 ml of the metal/Ca solutions were added to the soil twice and after each addition the supernatant was discarded. Then the stock solutions were diluted to 0.005 \(M\). The soil was washed six times with these solutions, in order to reduce the ionic strength of the soil solution and to ensure complete saturation of the soil with the appropriate metal/Ca ratio. The tubes were then centrifuged at 2000 rpm and the supernatants were kept for inductively coupled plasma spectroscopic (ICP) analysis. The last step involved the extraction of the soil with 1 \(M\) NH\(_4\)OAc at pH’s of 7.0 and 5.5. The extraction was initially started with
three washings of 30 ml each at a pH of 7. Each time the supernatant solutions were collected after centrifuging in 100 ml volumetric flasks and analyzed using ICP analysis. This procedure was repeated using the pH 5.5 solution.

3.3.3. Transport Experiments

Transport experiments were carried out using plexiglas columns of 10 cm length and 6.4 cm diameter. Soil which had been previously passed through a 2 mm sieve was packed into the columns using a funnel with an tube extension such that the outlet was kept on the surface of the soil at all times of the packing. Then the column were wetted from the bottom with 0.005 \( M \) \( \text{Ca(NO}_3\text{)}_2 \). At least 10 pore volumes of the Ca solution were pumped at a slow flow rate using a piston pump (Fluid Metering, Inc. Lab Pump, Model RP-G6) through the column in order to remove the entrapped air and to ensure Ca saturation of the exchange sites of the soil. After this procedure a pulse of either \( \text{Zn(NO}_3\text{)}_2 \) or \( \text{Cd(NO}_3\text{)}_2 \) were introduced to the column. Two different pulses were applied: one in a \( \text{Ca(NO}_3\text{)}_2 \) background solution and one without. The first column run exhibited nearly constant ionic strength whereas the second type of experiment demonstrated the effects of variable ionic strength. Table 3.3 summarizes all experimental data of the transport experiments. In order to perform simulations of the reactive transport of Zn and Cd, the dispersion coefficient was fitted using tritium breakthrough curves. The results are presented in Table 3.4. In order to demonstrate the reproducibility of the column experiments the measured
and fitted breakthrough curves for tritium from two different data sets are presented in Figure 3.1.

3.4. Results and Discussions

3.4.1. Sorption

The special cases of equation [3.3] as presented in Table 3.1 were fitted to the Zn and Cd sorption data sets of Windsor and Olivier soils at equilibration times of 24 and 288 h. More specifically, parameter estimates of the general Freundlich, the general Langmuir-Freundlich, the Tóth, and the Freundlich equations are presented in Tables 3.5 and 3.6, whereas the Langmuir, two-site Langmuir parameter are presented in Table 3.7. All parameters were obtained using a nonlinear least square minimization program.

Isotherms can be characterized by their behavior at low and high concentrations as demonstrated by Kinniburgh (1986). Two limiting criteria can be expressed as follows:

$$\lim_{c \to 0} \left( \frac{\partial s}{\partial c} \right) = \infty \quad \text{or} \quad \frac{\partial s}{\partial c} |_{c=0} = \text{const.} \quad [3.10]$$

at the low concentration and

$$\lim_{c \to \infty} s(c) = \infty \quad \text{or} \quad \lim_{c \to \infty} s(c) = s_T \quad [3.11]$$

At high concentrations Langmuir type isotherms approach a constant value, usually denoted as the maximum sorption capacity which may be related to the specific
Table 3.3. Experimental data for the miscible displacement of Zn and Cd in Windsor and Olivier soils at variable and nearly constant ionic strength.

<table>
<thead>
<tr>
<th>CASE(1)</th>
<th>SOIL(2)</th>
<th>EL(3)</th>
<th>( \rho(4) )</th>
<th>( V_0(5) )</th>
<th>( \theta(6) )</th>
<th>( V/V_0(7) )</th>
<th>TIME(8)</th>
<th>Me(8)</th>
<th>Ca(9)</th>
<th>Vel.(10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPF</td>
<td>WI</td>
<td>Zn</td>
<td>1.58</td>
<td>127.6</td>
<td>0.404</td>
<td>10.43</td>
<td>3.145</td>
<td>1.72</td>
<td>0.00</td>
<td>79.03</td>
</tr>
<tr>
<td>SPF</td>
<td>WI</td>
<td>Cd</td>
<td>1.56</td>
<td>130.0</td>
<td>0.411</td>
<td>10.20</td>
<td>3.331</td>
<td>1.91</td>
<td>0.00</td>
<td>76.10</td>
</tr>
<tr>
<td>SPS</td>
<td>WI</td>
<td>Zn</td>
<td>1.56</td>
<td>130.0</td>
<td>0.411</td>
<td>9.72</td>
<td>3.597</td>
<td>1.72</td>
<td>0.00</td>
<td>27.23</td>
</tr>
<tr>
<td>SPS</td>
<td>WI</td>
<td>Cd</td>
<td>1.56</td>
<td>130.0</td>
<td>0.411</td>
<td>9.94</td>
<td>3.944</td>
<td>1.91</td>
<td>0.00</td>
<td>27.46</td>
</tr>
<tr>
<td>CT</td>
<td>WI</td>
<td>Zn</td>
<td>1.56</td>
<td>130.0</td>
<td>0.411</td>
<td>8.06</td>
<td>2.917</td>
<td>1.02</td>
<td>5.20</td>
<td>28.58</td>
</tr>
<tr>
<td>CT</td>
<td>WI</td>
<td>Cd</td>
<td>1.56</td>
<td>130.0</td>
<td>0.411</td>
<td>8.16</td>
<td>2.917</td>
<td>1.00</td>
<td>5.20</td>
<td>28.77</td>
</tr>
<tr>
<td>CT</td>
<td>OL</td>
<td>Zn</td>
<td>1.16</td>
<td>177.9</td>
<td>0.562</td>
<td>26.80</td>
<td>4.875</td>
<td>1.02</td>
<td>5.20</td>
<td>54.66</td>
</tr>
<tr>
<td>CT</td>
<td>OL</td>
<td>Cd</td>
<td>1.16</td>
<td>177.9</td>
<td>0.562</td>
<td>27.07</td>
<td>4.875</td>
<td>1.00</td>
<td>5.20</td>
<td>54.51</td>
</tr>
</tbody>
</table>

(1) SPF - snowplow fast, SPS - snowplow slow, CT - constant concentration; (2) WI - Windsor soil, OL - Olivier soil, EU - Eustis soil; (3) Element; (4) bulk density; (5) pore volume; (6) volumetric water content; (7) relative pore volume; (8) metal concentration of pulse; (9) calcium concentration of pulse(s); (10) pore water velocity
Table 3.4. Parameter optimization of the dispersion coefficient (D), the retardation factor (R) with the standard error of estimate (SE) along with the coefficient of determination ($r^2$) using the tritium miscible displacement experiments for the different soil columns as reported in Table 3.3.

<table>
<thead>
<tr>
<th>CASE</th>
<th>SOIL</th>
<th>EL</th>
<th>$r^2$</th>
<th>RMS</th>
<th>D</th>
<th>SE</th>
<th>R</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPF</td>
<td>WI</td>
<td>Zn</td>
<td>0.9933</td>
<td>0.02902</td>
<td>90.40</td>
<td>6.066</td>
<td>1.047</td>
<td>0.01391</td>
</tr>
<tr>
<td>SPF</td>
<td>WI</td>
<td>Cd</td>
<td>0.9979</td>
<td>0.02196</td>
<td>17.95</td>
<td>1.221</td>
<td>1.060</td>
<td>0.007385</td>
</tr>
<tr>
<td>SPS</td>
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<td>Zn</td>
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Figure 3.1. Tritium breakthrough curves (BTCs) in Windsor and Olivier soil columns (case CT) for Zn and Cd runs presented as relative concentration ($C/C_0$) as function of pore volumes ($V/V_0$).
surface area in pure substances. At low concentrations the Langmuir type isotherms can be represented by a linear isotherm. The first derivative (equation [3.10]) at $c = 0$ of the Langmuir, the two-site Langmuir, and the Tóth equations approaches a constant value. In contrast, the slope of the general Freundlich, the general Langmuir-Freundlich, and the Freundlich equations approach infinity when $c$ goes to zero. In other words, the sorption affinity of a solute reaches a constant in the former case or increases with decreasing concentration in the latter case. At high concentrations all isotherms approach the maximum sorption capacity $s_T$ except the Freundlich equation.

In order to demonstrate these asymptotic behaviors we present Figures 3.2 through 3.5, which show Zn and Cd isotherms in Windsor and Olivier soil on a logarithmic scale (sometimes this plot is referred to as the Freundlich plot). At low concentrations, the Langmuir-type isotherms show a slope of one. Hence, simple observation of the slope of the data points allows an educated guess which isotherm may best fit isotherm results. The lines in Figures 3.2 through 3.5 represent the best fits of the isotherm equations. At low concentrations, the general Langmuir-Freundlich equation shows a good fit to the data. Since parameter estimation is based on a nonlinear least-square procedure the high concentrations are emphasized. Careful observation of the data reveal that the data do not reach a slope of one at low concentrations, and therefore the Langmuir-type equations underestimate the data at low concentrations. Hence the results are deviating from the work by Kinniburgh et al. (1983) on ferrihydrite, by Kinniburgh (1986) on soils and soil minerals, and by
Table 3.5. Results of the parameter optimization of the general Freundlich (GF), the general Langmuir-Freundlich (GLF), the Tóth, and Freundlich (FRD) isotherms of Zn in Windsor and Olivier soil.

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Table 3.6. Results of the parameter optimization of the general Freundlich (GF), the general Langmuir-Freundlich (GLF), the Tóth, and Freundlich (FRD) isotherms of Cd in Windsor and Olivier soil.

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Table 3.7. Parameter estimation of Zn and Cd sorption of Olivier and Windsor soil of the Langmuir (LANG) and two-site Langmuir (TSL) equations.

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<td>0.06061</td>
<td>49.46</td>
<td>6.306</td>
<td>0.1304</td>
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<tr>
<td>WI</td>
<td>Zn</td>
<td>24</td>
<td>LANG</td>
<td>0.9936</td>
<td>0.04346</td>
<td>2.126</td>
<td>0.07755</td>
<td>3.148</td>
<td>0.3082</td>
<td>0.1978</td>
<td>0.1155</td>
<td>0.6268</td>
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<td>TSL</td>
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<td>3.218</td>
<td>0.7915</td>
<td>12.40</td>
<td>7.625</td>
<td>0.1978</td>
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<td></td>
<td>288</td>
<td>LANG</td>
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Figure 3.2. Isotherm data of Zn in Windsor soil at 24 and 288 h equilibration times with fitted isotherm equations (LANG - Langmuir, TSL - two-site Langmuir, GF - general Freundlich, GLF - general Langmuir-Freundlich, and FRD - Freundlich equations).
Figure 3.3. Isotherm data of Cd in Windsor soil at 24 and 288 h equilibration times with fitted isotherm equations (LANG - Langmuir, TSL - two-site Langmuir, GF - general Freundlich, GLF - general Langmuir-Freundlich, and FRD - Freundlich equations).
Figure 3.4. Isotherm data of Zn in Olivier soil at 24 and 288 h equilibration times with fitted isotherm equations (LANG - Langmuir, TSL - two-site Langmuir, GF - general Freundlich, GLF - general Langmuir-Freundlich, and FRD - Freundlich equations).
Figure 3.5. Isotherm data of Cd in Olivier soil at 24 and 288 h equilibration times with fitted isotherm equations (LANG - Langmuir, TSL - two-site Langmuir, GF - general Freundlich, GLF - general Langmuir-Freundlich, and FRD - Freundlich equations).
Altmann and Leckie (1987) on humic acid and goethite and their mixtures. They found that the Tóth equation was most successful in describing sorption of a variety of inorganic ions onto soils and minerals. Here, we see that there is no particular equation which guarantees successful description of the data. The results from parameter estimation reveal that parameter values should be treated as purely empirical. This becomes apparent when comparing the parameter fit of the Tóth isotherm with the general Langmuir-Freundlich and general Freundlich. For example, the maximum sorption capacity \( s_T \) was always larger for the Tóth isotherm than for the other isotherm equations. This clearly reflects the nature of the different approaches.

In order to obtain ion exchange parameters from the sorption data we assumed that the soil is Ca-saturated. Knowing the amount of Zn or Cd sorbed, the maximum sorption capacity (CEC/2), and the total concentration the amount of sorbed Ca was calculated. Then the concentration term \( \xi \) of equation (3.3) which was set equal to the concentration ratio of the heavy metal \( c_1 \) and Ca \( c_2 \) \( (c_1/c_2 \text{ in Table 3.1}) \) was computed. The results of the parameter optimization of the selectivity coefficient and the Rothmund-Kornfeld equation is presented in Table 3.8. It is obvious that Zn and Cd is preferred over Ca especially at low heavy metal concentrations which is demonstrate by the fact that the selectivity coefficient is greater than unity for Cd sorption on Olivier and Windsor soils at an equilibration time of 288 h. Nevertheless, the data are best described by the Rothmund-Kornfeld equation which is indicated by the high value of the correlation coefficient \( r^2 \) and the lower value of the standard
Table 3.8. Parameter optimization of the empirical selectivity coefficient (S) and the Rothmund-Kornfeld (RK) equation of Zn and Cd sorption in Windsor and Olivier soil.

<table>
<thead>
<tr>
<th>SOIL</th>
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<th>RSM</th>
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<th>$k_1$</th>
<th>SE</th>
<th>$\alpha$</th>
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<td>0.1436</td>
<td>0.888</td>
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error of estimate (SE) of the affinity coefficient \( (k_1) \) as presented in Table 3.8. Since the heterogeneity factor \( (\alpha) \) of the Rothmund-Kornfeld equation is less than one, the affinity of the heavy metal increases with decreasing solution concentration. In other words the selectivity is a function of the exchanger composition.

In contrast to the sorption experiment, the ion exchange experiments are based on the extractibility of the heavy metal after the soil has been saturated with the heavy metal. Some arbitrariness in selecting an extraction method is unavoidable. Since the \( \text{NH}_4\text{OAc} \) extraction is the most commonly used method in determining the cation exchange capacity, it is of interest whether or not the obtained values are applicable to transport studies of heavy metals. The results of the parameter optimization of the selectivity coefficient and the Rothmund-Kornfeld equation are presented in Table 3.9 and Figure 3.6. In contrast to the sorption experiment the affinity coefficients of the Rothmund-Kornfeld equation are greater than one with the exception of Zn sorption in Windsor soil. The ion exchange isotherms in Figure 3.6 show the relative amount of heavy metal sorbed as a function of the relative solution concentration. The diagonal line represents the nonpreference isotherm \( (k_1 = 1, \alpha = 1) \). The sigmoidal shape of the isotherms reveals that the heavy metal sorption exhibit a higher affinity at low concentrations whereas Ca seems to have a higher affinity at high concentrations of the heavy metal.

When comparing our data with the results of Abd-Elfattah and Wada (1981) and Harmsen (1977), the observations agree in principle. Abd-Elfattah and Wada's data show very large differences of selectivity coefficients between low and high
Table 3.9. Parameter optimization of the empirical selectivity coefficient (S) and the Rothmund-Kornfeld equation (RK) of Zn and Cd sorption in Windsor and Olivier soil as measured by NH$_4$OAc extraction method.

<table>
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<td></td>
<td></td>
<td>(mmol kg$^{-1}$)</td>
<td></td>
<td>(L mmol$^{-1}$)</td>
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<tr>
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<td>0.9297</td>
<td>0.05125</td>
<td>0.569</td>
<td>0.02499</td>
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</table>
Figure 3.6. Ion exchange isotherms of Cd-Ca and Zn-Ca exchange in Olivier and Windsor soil as measured by NH$_4$OAc extraction with the best fit of the Rothmund-Kornfeld equation.
heavy metal exchanger concentrations. Such high selectivity differences were observed for neither the Windsor nor the Olivier soil. This is especially true for the extraction method employed here. Also, the method employed here is similar to that used by Bittel and Miller (1974) who did not observe high values for the selectivity coefficient as compared to the data of Abd-Elfattah and Wada (1981).

3.4.2. Transport

In Windsor soil the breakthrough curves (BTCs) at nearly constant ionic strength exhibit a steep front slope and extensive tailing indicating nonlinearity of the sorption process(Figures 3.7 and 3.8). The modelled BTCs are based on the isotherm parameters for Zn and Cd sorption on Windsor at equilibration times of 24 and 288 h as shown in Table 3.5, 3.6, and 3.7. All curves are very similar and the agreement with the experimental results is quite well for the Zn transport using the 24 h isotherm. In particular, the tailing is very well predicted by the different isotherms. Considering that all isotherm equations but the general Langmuir-Freundlich equation exhibit great deviations from the data at very low concentration, the predicted BTCs are surprisingly similar. Since the fitted isotherms describe the sorption data equally well at high concentrations (Figures 3.2 to 3.5), the isotherm behavior at low concentration does not influence the transport at high concentrations. It becomes apparent that below a solution concentration of 0.01 mM Zn, the differences of the fitted isotherm equations are simply not detectable for the experimental conditions of the miscible displacement experiments chosen in this study. Also, the time
Figure 3.7. Experimental Zn breakthrough curves in Windsor soil with predictions based on the Langmuir (LANG), two-site Langmuir (TSL), general Freundlich (GF), general Langmuir-Freundlich (GLF), Tóth, and Freundlich (FRD) equations as measured at 24 and 288 h equilibration times.
Figure 3.8. Experimental Cd breakthrough curves in Windsor soil with predictions based on the Langmuir (LANG), two-site Langmuir (TSL), general Freundlich (GF), general Langmuir-Freundlich (GLF), Tóth, and Freundlich (FRD) equations as measured at 24 and 288 h equilibration times.
dependency of heavy metal sorption is greatest at low concentrations. Hence the
difference between the simulated BTCs which are based on the 24 and 288 h
equilibration time is small. This indicates that the local equilibrium assumption may
be valid for transport of heavy metals at high input concentrations provided that
diffusion is not rate limiting. This is especially true for a pulse input similar to our
experimental conditions presented. However, when the solute is applied as an
impulse, that is, a very high concentration is applied for a very short time
(approaching the Dirac delta function), the concentration within the column will vary
from that of the input at the top of the column to very low concentration at the
bottom. In this case a much wider range of concentrations have to be modelled and,
therefore, the isotherm equation needs to describe the data equally well at all
concentrations.

In contrast to the Zn BTC shown in Figure 3.7 the Cd BTCs for Windsor soil
are considerably different (Figure 3.8). The slope of the front of Cd BTC is not as
steep as the Zn BTC. However, the predicted BTCs do not describe this phenomena
and are very similar to the modelled Zn BTCs. Considering that the isotherms of Cd
and Zn are quite similar (Figures 3.2 and 3.3), the difference can not be explained by
the sorption behavior. This may indicate that other reactions take place which are not
described adequately by the sorption approach.

The transport behavior of Cd and Zn treated as an ion exchange reaction with
constant and variable selectivity coefficients at variable ionic strength are presented
in Figures 3.9 to 3.16. Here the column effluent of both Ca and the heavy metal
were monitored. Since the ionic strength of the Zn and Cd solutions were much lower than that of the Ca solution, chromatographic peaks are observed at pore volume 13 of the Zn BTCs and pore volume 14-15 of the Cd BTCs (Figures 3.9, 3.10, 3.12, and 3.13). These peaks have higher concentrations than input concentrations and are most pronounced for the Zn BTCs. This phenomenon has also been termed the snow-plow effect (Starr and Parlange, 1979).

Figures 3.9 and 3.10 show experimental and modelled Zn and Ca BTCs in Windsor soil at variable ionic strength (case SPF and SPS in Tables 3.2 and 3.3). The short dashed line represents model prediction using a constant selectivity coefficient equals one. The breakthrough front is in excellent agreement with the data for the fast velocity run (Figure 3.9), whereas the tailing is grossly underestimated. In contrast, the prediction based on the Rothmund-Kornfeld equation (solid line) determined from the sorption data set (RK1) shows better agreement for the tailing than the breakthrough front. The prediction based on the ion exchange data set (RK2) overestimates the retardation of the front. The simulated BTCs of the slow velocity run of the Zn miscible displacement experiments at variable ionic strength are not as good as the ones of the fast run. In particular, the constant selectivity prediction (S) does not agree with the experimental data at the breakthrough front and tail. The simulated Rothmund-Kornfeld (RK1) BTC initially describes the breakthrough front well, however, at high concentrations the simulated BTC flattens and deviates considerably from the data (Figure 3.10). This may be explained by the fact that the affinity of Ca is greater than that of Zn at high concentrations as described by
Figure 3.9. Zn breakthrough curve in Windsor soil at variable ionic strength (case SPF in Tables 3.2 and 3.3) modelled using a constant selectivity coefficient (S) and the Rothmund-Kornfeld equation based on the sorption experiment (RK1) and the ion exchange experiments (RK2).
Figure 3.10. Zn breakthrough curve in Windsor soil at variable ionic strength (case SPS in Tables 3.2 and 3.3) modelled using a constant selectivity coefficient (S) and the Rothmund-Kornfeld equation based on the sorption experiment (RK1) and the ion exchange experiments (RK2).
Figure 3.11. Zn breakthrough curve in Windsor soil at nearly constant ionic strength (case CT in Tables 3.2 and 3.3) modelled using a constant selectivity coefficient ($S$) and the Rothmund-Kornfeld equation based on the sorption experiment (RK1) and the ion exchange experiments (RK2).
Rothmund-Kornfeld equation. Hence, the description of ion exchange with the Rothmund-Kornfeld equation may be limited to the lower concentration range. This is supported by the reasonably good agreement of the simulated and measured Zn BTCs of nearly constant ionic strength run (Figure 3.11). Overall, the Rothmund-Kornfeld equation seems to be adequate in describing the ion exchange of Zn with Ca under transport conditions.

The Cd BTC results at variable ionic strength are considerably different from that of the Zn BTCs. First, the chromatographic peak is not as pronounced as Zn peaks and second, the Cd BTCs exhibit a plateau right before the chromatographic peak (Figures 3.12 and 3.13). The simulation using the constant selectivity predicts the peak location accurately, however, the tailing is underestimated. In contrast the Rothmund-Kornfeld based BTC (RK1) describes the tailing fairly well but the breakthrough front is considerably steeper than the measured values. The modelled BTCs using the ion exchange data set are overestimating the extent of retardation. This is also true for the measured BTC at nearly constant ionic strength (Figure 3.14).

In contrast to the asymmetric BTCs of Zn and Cd in Windsor soil, the BTCs in Olivier soil show a steadily increasing front with tailing, such that the BTC is almost symmetrical (Figures 3.15 and 3.16). It should be noted that the soils differ with respect to their physical and chemical properties. More specifically, the Oliver soil is a silt loam, whereas the Windsor soil is a sandy soil. Hence, one can expect more structure in Olivier soil than in Windsor. This is supported by the fact that for the same packing technique the bulk density of the Olivier soil columns was 1.18 g
Figure 3.12. Cd breakthrough curve in Windsor soil at variable ionic strength (case SPF in Tables 3.2 and 3.3) modelled using a constant selectivity coefficient (S) and the Rothmund-Kornfeld equation based on the sorption experiment (RK1) and the ion exchange experiments (RK2).
Figure 3.13. Cd breakthrough curve in Windsor soil at variable ionic strength (case SPS in Tables 3.2 and 3.3) modelled using a constant selectivity coefficient (S) and the Rothmund-Kornfeld equation based on the sorption experiment (RK1) and the ion exchange experiments (RK2).
Figure 3.14. Cd breakthrough curve in Windsor soil at nearly constant ionic strength (case CT in Tables 3.2 and 3.3) modelled using a constant selectivity coefficient (S) and the Rothmund-Kornfeld equation based on the sorption experiment (RK1) and the ion exchange experiments (RK2).
cm$^3$ in contrast to 1.56 of the Windsor soil columns. In addition, the Olivier has a much larger cation exchange capacity, most likely caused by smectitic clay minerals. The Windsor soil is an A horizon whose chemical properties are most likely controlled by the amount of organic matter. In addition the pore water velocities for the Olivier soil were about twice that of the Windsor soil column run (Table 3.2). Since the Olivier soil is a much finer textured soil than the Windsor soil, differences in the transport behavior should be expected.

Applying the isotherm parameters of Table 3.8 and 3.9 to predict the BTCs no agreement between experimental data and modelled curves were observed (Figures 3.15 and 3.16). The modelled BTCs for Zn and Cd are very similar. The constant selectivity predicts an earlier breakthrough as compared to the measured data, however, the symmetry of the modelled BTC is somewhat similar. The Rothmund-Kornfeld BTC of the sorption data set grossly overestimates the retardation. In contrast, the parameters obtained from the ion exchange experiment predict the peak location well. However, the symmetry of the simulated BTCs deviate drastically from the measured data. The front is obviously too steep whereas the tailing agrees with the experimental data.

Considering the differences of the soils and the experimental conditions as pointed out above, other mechanisms which cannot be described with a single or binary isotherm approach may take place. The interpretation of the BTCs should be carried out in light of the classification of BTCs as reviewed by Schweich and Sardin (1981). A convex isotherm will have a self sharpening front with prolonged tailing.
Figure 3.15. Zn breakthrough curve in Olivier soil at nearly constant ionic strength (case CT in Tables 3.2 and 3.3) modelled using a constant selectivity coefficient (S) and the Rothmund-Kornfeld equation based on the sorption experiment (RK1) and the ion exchange experiments (RK2).
This is consistent with experimental results for the Zn BTC in Windsor soil at nearly constant ionic strength. However, the BTCs in Olivier soil do not show such a clear behavior. There are two possibilities in explaining the closely symmetric BTCs in Olivier soil: (i) the sorption isotherm obtained from the batch experiments are not adequate to model the transport, and/or (ii) nonequilibrium processes may take place in the column experiments which cannot be detected by batch experiments. Surface precipitation may take place such that the Farley-Dzombak-Morel isotherm may describe the sorption, and hence the breakthrough front may not be self-sharpening as shown in Chapter 2. Also, when surface precipitation takes place, one can expect that this process is slower than an adsorption reaction (Dzombak and Morel, 1986). In addition, considering the fast pore water velocity and the chemical properties of the Olivier soil, one cannot rule out that the accessibility of the sorption sites may be restricted. Hence, mass transfer limitation could cause nonequilibrium behavior, and thus, a kinetic approach may possibly improve the modelling results. Therefore equation [5.9] was applied to model the BTCs of Zn and Cd in Olivier soil assuming a constant selectivity coefficient. Figures 3.17 and 3.18 show the results of the simulation using mass transfer coefficients $k_m$ ranging from 1 to 5 d$^{-1}$. Clearly, the lower the mass transfer coefficient the better the agreement between the prediction and measured data. As compared to the modelling results assuming local equilibrium, the mass transfer approach represents an improvement. Nevertheless the simulated results still need further refinements.
Figure 3.17. Zn breakthrough curve in Olivier soil at nearly constant ionic strength (case CT in Tables 3.2 and 3.3) modelled using a constant selectivity coefficient and the mass transfer kinetics.
Figure 3.18. Cd breakthrough curve in Olivier soil at nearly constant ionic strength (case CT in Tables 3.2 and 3.3) modelled using a constant selectivity coefficient and the mass transfer kinetics.
3.5. Summary and Conclusions

A general equation describing single solute or binary solute sorption during transport in soils is presented. Batch experiment isotherms for single and binary solute systems were determined for an Olivier and Windsor soil. Zn and Cd sorption on Windsor soil were best described by the general Langmuir-Freundlich equation. The sorption of Zn and Cd in Olivier soil was also well described with the general Langmuir-Freundlich equation, however, the Tóth equation described the data equally well. For the ion exchange data the Rothmund-Kornfeld equation was successfully used to model the sorption data set as well as the ion exchange data set. The transport of Zn in Windsor soil was predicted using single and binary solute isotherms assuming local equilibrium. The modelled curves are in close agreement with the measured data. This agreement was not observed for Cd transport in Windsor soil. The modelling of the transport of Zn and Cd in Olivier soil was least successful using variable and constant selectivity coefficients and assuming local equilibrium. In this case the batch experiment could not be used to obtain the necessary data for the transport. When invoking mass transfer kinetics for the Zn and Cd transport in Olivier the prediction improved slightly. Overall, the general isotherm equation presented here seems to be a powerful tool in describing solute sorption and to a limited extent the solute transport.
CHAPTER 4

HEAVY METAL RETENTION IN SOILS: APPLICATION OF MULTISITE MODELS TO ZINC SORPTION

4.1. Introduction

Exposure of soil and groundwater to heavy metals increased rapidly during the 20th century due to industrial manufacturing of metal products. Huge amounts of wastes were produced and often disposed improperly. The problem of proper waste management is recognized today. Measures to clean up contaminated soil have now been developed and are being applied (Assink and van den Brink, 1986; Cairney, 1987). One source of heavy metal pollution are mining, smelting, plating, alloy production (Haines and Harris, 1987). Another source is application of contaminated sludge to agricultural land and much research has been carried out to study the effects of high loading of heavy metals in such soils (Beckett, 1989; Dowdy and Volk, 1983). Zinc is among the heavy metals of interest. Although it may occur in high concentrations in contaminated soils, it also is an essential micronutrient for plants and animals. The occurrence of zinc in soils, groundwater, and the environment, in general, has been reviewed extensively (Lindsay, 1972; Mortvedt et al., 1972; Hem, 1972; Shuman, 1980; Pickering, 1980; Nriagu, 1980).

Understanding heavy metal retention and release in soils is a vital step in developing remedial management practices. The impact assessment of heavy metal
pollution in soils requires the knowledge of how these elements react and move in soils and how they become available to plants and animals. Common remedial techniques for removal of heavy metals include chemical treatments such as acid extraction and ion exchange (USEPA, 1985; Hoogendoorn and Rulkens, 1986; Smith, 1987). Chemical extraction methods are commonly used in soil science in order to determine the bioavailability and the geochemical distribution between the soil solution and the different solid phases (Page, 1982; Salomons and Förstner, 1986). Therefore, the knowledge gained from heavy metal research in soil science is of value to the engineer who deals with soil remediation.

Modelling solute retention and release in soils require the description of the solution-solid phase partitioning and the time dependent processes during sorption/desorption and transport. This chapter focuses on the modelling of time-dependent retention using empirical approaches. Evaluation of such approaches will be illustrated using zinc sorption results for three different soils.

4.2. Describing Retention

4.2.1. Retention at Equilibrium

The description of retention may be based on (i) well defined chemical reactions of several species in solution with different sorption sites, e.g. precipitation of a pure mineral; (ii) sorption of two or more competing species disregarding the nature of the reaction; or (iii) sorption of one solute on one (or more) reaction site(s) without the description of a reaction mechanism.
(i) The first approach is based on thermodynamic data for equilibrium reactions such as dissolution/precipitation, redox reactions, complex formation, and surface complexation. In general such thermodynamic data bases consist of equilibrium constants determined for pure minerals such as goethite, hematite, calcite, aragonite and so forth. With such data one can speciate the solute of interest and determine the predominant form in solution. In addition, one can calculate the solute distribution among the different solid phases. The equilibrium chemistry approach for dissolution/precipitation reactions has been utilized for several years. Traditionally, activity ratios diagrams for a system of solids and solutes have been used to predict precipitation and dissolution. This approach has been described in detail by Lindsay (1979). However, the sorption behavior of heavy metals including zinc in soils and soil minerals cannot be fully explained by this approach (Brümmer et al., 1983).

In general, heavy metals, are present in the soil at such low concentration that precipitation is unlikely to occur. Therefore, reactions other than surface precipitation on mineral and organic surfaces play a significant role influencing sorption processes of heavy metals in soils. Recently, much progress has been made by utilizing surface complexation models applied to pure oxide/hydroxide surfaces of iron and aluminum. Reviews of these models are given by Sposito (1983a), Barrow (1987), and Leckie (1988) and applications to soils are published by Goldberg and Sposito (1984), Charlet and Sposito (1987) and Barrow (1986). These models are based on the description of the surface in terms of its electrical properties and its chemical and physical
interaction with different ionic species in solution. Several extrathermodynamic assumptions have to be valid in order to apply successfully such models.

Since soils are complex mixtures of solids and fluids and contain numerous different chemical components such as clay minerals, oxides/hydroxides of iron and aluminum, possibly carbonates, organics (such as humic and fulvic acids) and others, their interaction as well as the effect of microbiological activity may influence heavy metal sorption (Huang and Schnitzer, 1986; Stone, 1988; Domsch, 1989). Thus, the equilibrium reaction approach may not yield satisfactory results in predicting retention of heavy metals in soils. However, the advantage of this method is its universal applicability and the information obtained without actually measuring the retention.

(ii) The second approach used to describe and model competitive sorption, requires the measurement of at least two competing ions in the soil of interest. In general the sorption behavior can be described by ion exchange selectivity coefficients. Common expressions for exchange selectivity coefficients includes the Vanselow, the Gaines-Thomas, the Gapon, and the empirical selectivity coefficients (Sposito, 1981). In contrast to the first approach this one does not involve any assumption concerning the sorption mechanism and does not utilize equilibrium constants determined for pure systems. Instead the equilibrium constant is computed using binary exchange data (Sposito, 1981). The thermodynamic equilibrium constant is likely to be unique to each soil so that results from such data may not be generalized to other soils. The empirical selectivity coefficient has been applied to heavy metal/calcium exchange by Harmsen (1977) and Abd-Elfattah and Wada (1981).
They found an increased sorption affinity for the heavy metal with decreasing heavy metal/calcium ratio in the exchanger phase. For example, zinc/calcium selectivity coefficients varied from 10 to 100 in calcium saturated montmorillonitic soil (AbdElfattah and Wada, 1981). Hendrickson and Corey (1981) reviewed ion exchange equilibria studies of some heavy metals in soils. They concluded that more than one reaction site must be present in order to explain the high affinity of heavy metals at low concentration. In general, it is assumed that specific sorption at the oxide/hydroxide surfaces and broken edges of clay minerals causes this high affinity for heavy metals in soils. Under certain circumstances so does the formation of organic complexes and precipitation reactions.

(iii) The simplest approach for describing solution-solid phase distribution is the use of sorption isotherms. In this case only the total concentration in solution and solid phase is considered. White and Zelazny (1986) and Sposito (1984) reviewed the general classification for adsorption isotherms given by Giles et al. (1960). The most common curve in soils is the L curve (L=Langmuir type), which exhibits a concave shape with respect to the solution concentration axis. Such isotherm may be described by the following equation (Sposito, 1983b; Sposito, 1985):

\[
S = \sum_{i=1}^{n} \frac{b_i K_i^{\beta_i} c^{\beta_i}}{1 + K_i^{\beta_i} c^{\beta_i}} \tag{4.1}
\]

where \( S \) is the amount sorbed per unit mass, \( c \) the amount in solution per unit volume and \( b_i, K_i, \) and \( \beta_i \) are empirical parameters. Widely used special cases of this
equation are the Langmuir equation with \( n = 1, \beta_1 = 1 \), the two-surface Langmuir equation with \( n = 2, \beta_1 = \beta_2 = 1 \), and the Freundlich equation with \( n = 1, 0 < \beta_1 < 1 \), and \( K_1^\beta_1 c^{\beta_1} \ll 1 \) (Sposito, 1985). The sorption of ionic solutes in soils has been described by such isotherms for the last decades.

The Langmuir and Freundlich isotherms were originally developed for describing gas adsorption on metal surfaces. The Langmuir equation was derived on the basis of the kinetics of monolayer adsorption. The two-surface Langmuir equation implies that two different surfaces are present. In general, Langmuir isotherms are characterized by the existence of an adsorption maximum, which occurs with complete monolayer surface coverage. However, deviation from this ideal behavior is often observed (Benjamin and Leckie, 1981). The Freundlich equation is used where the adsorption enthalpy exhibits a logarithmic change with increasing sorption due to surface heterogeneity. Therefore, exponent \( \beta \) in equation [4.1] can be viewed as a heterogeneity parameter. Sposito (1980) and Elprince and Sposito (1981) showed that the Freundlich and the Langmuir equations can represent ion exchange if the concentration of the ions of interest is very low in comparison to the other ion present in solution. However, soils and most of the soil minerals cannot be treated as pure ion exchangers or uniform surfaces. The use of such equations implies that the parameters obtained by curve fitting should be viewed as pure empirical constants. For example, Veith and Sposito (1977) demonstrated that sorption isotherms cannot be used to distinguish adsorption from surface precipitation.
Single site isotherms such as the Langmuir and Freundlich equations have been used to describe heavy metal retention in soils (Garcia-Miragaya and Page, 1976; Sidle et al., 1977; Levi-Minzi et al., 1976; Korte et al., 1976; Buchter et al., 1989). Buchter et al. (1989) showed that the retention behavior of zinc is similar to that of cadmium, cobalt, and nickel in several soils.

Computer programs for solving chemical speciation problems in aquatic environments such as rivers, lakes, aquifers, and soils have been in use for several years. Two general methods are used to determine the equilibrium concentration of the species of interest. The first is to solve a system of nonlinear equations derived from mass and/or charge balance expressions and is applied in programs such as SOILCHEM, MINTEQA2, WATEQ2, and PHREEQE (Sposito and Coves, 1988; Allison et al., 1990; Ball et al., 1979; Parkhurst et al., 1980). The first two programs mentioned allow the use of all three types of modelling approaches, whereas the latter are primarily applied to the first approach. The other method is to minimize the change of Gibbs free energy of the overall reaction and is applied in CHARON (Bril et al., 1986). Programs, which simultaneously solve both chemical speciation and transport problems include CHEMTRAN, FIESTA, and EQTRN (Miller and Benson, 1983; Theis et al., 1982; Förster, 1986).

Since the measurement of sorption isotherms is convenient and easy to carry out the third modelling approach is emphasized in this chapter. The discussion of how to use this approach for modelling time dependent process in soils is elaborated in the following paragraph.
4.2.2. Retention as a Kinetic Process

Transport studies of inorganic and organic solutes in solutes have demonstrated that equilibrium reactions alone cannot explain the effluent concentration behavior during miscible displacement experiments (Skopp, 1986). In order to account for the lack of equilibrium two-site models were developed. In these models a slow sorption process is assumed to occur at one type of site whereas a fast equilibrium sorption occurs at the other type site (Selim et al. 1976; Cameron and Klute, 1977). In order to clarify the term 'site' a review on the use of this expression is necessary. According to Brusseau and Rao (1989) there are four different definitions used in the literature: (1) reaction site defined on a molecular basis; (2) different sites due to different accessibility; (3) different sites due to different sorbents; and (4) sites due to different reaction mechanisms. The above definitions require knowledge of the actual mechanisms controlling the lack of equilibrium. However, chemical equilibrium models can be viewed as multi-site models. For example, surface complexation can be defined as (1), but when combined with other reactions, such as complexation of metals with humic acids, it would be defined as (3). This suggests at least a two site model and implies that site (1) and (3) do not necessarily represent kinetically inhibited reactions.

This leads to the question, which of the four definitions is most suitable for nonequilibrium description in soils. The answer is highly dependent on the time frame and reactants involved in the process. Most of the sorption processes of metals in soils appear to reach equilibrium in a matter of hours, days, or weeks. In contrast
to fast sorption reactions, e.g. calcium, magnesium, and sodium, heavy metals reach quasi equilibrium at a later time. In order to explain this behavior one has to consider the structure of the soil as a whole and the microstructure of the soil particles. The soil consists of particles made up of several types of minerals and organic matter, which exists discretely or clustered into aggregates. When the solute enters the soil it diffuses through the pores into aggregates and particles to the available sorption sites. Therefore, the soil structure dominates to a large extent the accessibility of the sorption sites so that diffusion controlled processes are often rate limiting in soils.

Generally, there are four consecutive steps in the overall diffusion process of solutes in soils (Rubin, 1983; Weber, 1984). First, the solute rapidly diffuses through the bulk solution. Second, the solute passes from the bulk solution through a film surrounding the soil particles or aggregates (film diffusion). This is followed by the third step, diffusion within the particle or aggregate (particle diffusion). The last step is the sorption process on the surface itself. Either the film or the particle diffusion is rate limiting. The particle diffusion can be further classified into the diffusion within the solution of the aggregate (pore diffusion) and diffusion on the surface of the solid material (surface diffusion). In the latter case sorption takes place before the diffusional process. Surface diffusion may be of importance during ion exchange as shown by Jackman and Ng (1986). In addition diffusion into the solid phase may take place as suggested by Brümm er et al. (1988) for zinc in goethite. This process may be regarded as particle diffusion in the broadest sense.
There are two general approaches to modelling diffusional processes in soils. These models, commonly referred to as the two-region or mobil-immobile approach (Coats and Smith, 1964; van Genuchten and Wierenga, 1976), are either based on mass transfer expressions, usually first order kinetics, or discrete geometrical description of the soil particles. The mass transfer approach requires the measurement of a mass transfer coefficient. For example, mass transfer of heavy metal ion exchange for some soil constituents such as peat was controlled by film diffusion (Bunzl et al. 1976). The second approach requires the knowledge of the geometry of the particles. Then the diffusion equation is used to model the transfer of the solute within the particles. This approach has been widely used for transport studies (Rao et al., 1980; Rasmuson and Neretnieks, 1980, Tang et al., 1981; van Genuchten et al., 1984; Rasmuson, 1985) and has been reviewed by van Genuchten and Dalton (1986). A more rigorous description of diffusion controlled ion exchange is given by the Nernst-Planck equation which considers the electrical field caused by differences of ion mobility (Hwang and Helfferich, 1987; Nicoud and Schweich, 1989). The use of such modelling approaches has not been utilized for heavy metal sorption in soils.

An example of reaction mechanism as a criteria for sites is Ca-Al exchange on kaolinite. Jardine et al. (1985) used a two-site model to account for Ca-Al exchange as a fast reaction and Al polymerization on kaolinite surface as a slow process. Recent applications of this approach to heavy metal retention has been limited so far.

However, to model both the accessibility and the reaction mechanism seems difficult. In addition, the assumptions concerning the geometry and/or the reaction
mechanism must be valid. Both criteria are based on microscopic phenomena, which are not easily measured. In contrast, kinetic retention is generally observed on a macroscopic scale. Relaxing all assumptions of the actual mechanisms of kinetic retention one can use empirical approaches to distinguish different sites. For example, applying the two-surface Langmuir equation can be viewed as such an approach. Parameter optimization replaces experimental determination of the actual processes. In addition, the measurement of the solute sorption can be restricted to the monitoring of solute concentration in solution with time. Before introducing multisite models of this type, a brief review of the phenomena involved in heavy metal sorption in soils and soil constituents such as oxides, clay minerals, and organic matter is presented.

Fast, first-order kinetics were observed for K-Ca exchange on clay minerals (Sparks and Jardine, 1984; Parker and Jardine, 1986). Similarly, Bunzl et al. (1976) showed that first-order kinetics due to film diffusion was the time limiting step governing Pb, Cu, Cd, Zn, and Ca exchange with protons on peat. Equilibrium was reached during a period ranging from few minutes to several hours in both studies so that fast reaction could be assumed. Sorption processes of zinc on oxide minerals, such as goethite or hematite, were modelled recently with second order kinetics (Barrow et al., 1989). However, continued sorption was observed, after fast initial sorption, on oxides for more then 2 weeks (Brümmer et al., 1988). Brümmer et al. (1988) suggested, that diffusion of zinc into the solid phase was occurring.

The kinetic reactions of heavy metals in soils were studied by Amacher et al. (1986), Aringhieri et al. (1985), Kuo and Mikkelsen (1979), and Christensen (1984).
They found fast initial reaction during the first hours, then slow retention the following days and weeks. Since single site models have a limited capability to describe sorption kinetics in soils (Aringhieri et al., 1985), multisite models were developed (Amacher et al., 1988; Selim and Amacher, 1988, Harter, 1989). Therefore, Amacher et al. (1988) and Selim and Amacher (1988) extended the two site models to multi-site models to explain the kinetic behavior of some selected heavy metals. Overall, fast kinetics in the magnitudes of minutes to few hours and slow kinetics, in the magnitude of weeks, occur in soils and different soil materials. The overall kinetic reaction of heavy metals in soils is influenced by all reaction mechanisms, through which retention on different minerals and organic matter takes place. In order to account for apparent equilibrium or quasi equilibrium sorption behavior it can be assumed that the sorption may be described best by either (i) a Freundlich isotherm or (ii) a Langmuir-type isotherm. Modelling the kinetic behavior of heavy metal sorption in soils, utilizing the information of pure soil materials, is based on the assumptions that (i) at least one fast reversible reaction will occur, (ii) that at least one slow reversible reaction will occur, and (iii) that one irreversible reaction may also occur. These assumptions lead to the development of two different multi-site models.

The first model, denoted as the nonlinear multireaction model (Amacher et al., 1988) (see Figure 4.1), is based on the assumption that both types of sites, the slow and fast, can be described by two different Freundlich equations when apparent equilibrium conditions are attained. Both reactions are assumed to be reversible and
Figure 4.1. Scheme of the multireaction model, where $S$ and $C$ denotes the amount of solute sorbed and in solution, respectively, and subscripts the site.
are concurrent, yielding the following equations:

\[ \rho \frac{dS_1}{dt} = k_1 \theta C^n - k_2 \rho S_1 \] \[4.2\]

\[ \rho \frac{dS_2}{dt} = k_3 \theta C^m - k_4 \rho S_2 \] \[4.3\]

where \( S \) denotes the amount sorbed (M M\(^{-1}\) soil), \( C \) the amount of solute in solution (M L\(^{-1}\)), \( k_1, k_3, \) and \( k_2, k_4 \) the forward and backward rate coefficients (T\(^{-1}\)), respectively, subscript 1 and 2 of \( S \) the sites, and \( n \) and \( m \) the reaction order. Harter (1989) considered a special case where \( m=n=1 \) for different heavy metals. Two Freundlich equations will express the equilibrium conditions as follows:

\[ S = S_1 + S_2 = \left( \frac{\theta}{\rho} \right) \left[ \frac{k_1}{k_2} C^n + \frac{k_3}{k_4} C^m \right] \] \[4.4\]

If \( m=n \) this equation can be reduced to a traditional Freundlich equation:

\[ S = (K_1 + K_2) C^m = KC^m \] \[4.5\]

where \( K \) denotes an empirical parameter.

The second-order model (Selim and Amacher, 1988) utilizes the fact, that for increasing concentration of a heavy metal in soil solution a maximum sorption capacity can be reached. At equilibrium a simple Langmuir or a two-surface Langmuir can describe the data. Since a slow and a fast reaction have to be distinguished the two-surface Langmuir expression is used to develop a second-order model, yielding:
\[
\rho \frac{dS_1}{dt} = k_1 \theta C (S_T F - S_1) - k_2 \rho S_1
\]  
\[4.6\]

\[
\rho \frac{dS_2}{dt} = k_3 \theta C (S_T (1-F) - S_2) - k_4 \rho S_2
\]  
\[4.7\]

where \(F\) is the fraction of the maximum sorption capacity \(S_T\) available on site one.

At equilibrium the equations will yield the two-surface Langmuir equation:

\[
S = \frac{F S_T K_1 C}{1 + K_1 C} + \frac{(1-F) S_T K_2 C}{1 + K_2 C}
\]  
\[4.8\]

where the subscripts refer to the sites. If \(F=1\), then equation \[4.7\] reduces to a single site Langmuir equation. For both models, multireaction and second-order, the empirical constants \(K\) for each site at equilibrium in equations \[4.5\] and \[4.8\] are given by:

\[
K_1 = \left(\frac{\theta}{\rho} \right) \frac{k_1}{k_2} \quad \text{and} \quad K_2 = \left(\frac{\theta}{\rho} \right) \frac{k_3}{k_4}
\]  
\[4.9\]

In addition to the reversible reactions one may have to consider irreversible reactions for the time of observation. This may be expressed in terms of a first-order reaction as follows:

\[
\rho \frac{dS_{irr}}{dt} = k_{irr} \theta C
\]  
\[4.10\]

where \(k_{irr}\) denotes the forward rate coefficient. Quasi irreversible reaction may occur due to slow surface precipitation or diffusion into the solid phase.
The above equations represent an initial value problem with the initial conditions:

\[ C(0) = C_0 \quad \text{and} \quad S(0) = S_1(0) = S_2(0) = S_{irr}(0) = 0 \quad [4.11] \]

where \( C_0 \) denotes the initial concentration of the Zn solution applied to the soil. For the application described in the next paragraph both systems of equations, the multireaction and the second order, were solved numerically using finite difference approximation.

4.2.3. Measuring Retention

Modelling retention either as an equilibrium or a time dependent process requires appropriate input parameters, such as equilibrium constants and rate coefficients. Experimental techniques used to obtain such parameters as well as model validation should be chosen according to the objectives and the purpose of the model. For example, transport phenomena are involved in modelling the general behavior of heavy metals in soils. Therefore, assessment of potential remediation techniques such as in situ leaching requires experimental methods which simulate such a flow situation.

When choosing a technique to determine the rate coefficients, one has to consider the time frame of all processes involved. One of the critical parameters during transport is the dimensionless Damköhler number:
\[
D = \frac{k}{v}
\]

where \( k \, T^{-1} \) is a rate coefficient, \( v \, L \, T^{-1} \) pore water velocity, and \( l \, L \) the length of the soil column. This nondimensional rate coefficient can be derived through nondimensionalizing the transport and kinetic rate equations. Considering a fixed length of a soil column, the rate coefficient and velocity are the controlling parameters for the use of equilibrium or kinetic modelling approaches. Jennings (1987) indicated that Damköhler numbers above 100 allow use of equilibrium reactions for adsorption and ion exchange during transport. The determination of the magnitude of the leaching flux generally does not pose a problem. However, reaction rates, especially diffusion controlled reaction sites, cannot be determined in situ. Therefore, the methodology chosen for the determination of the rate coefficients should resemble as closely as possible the in situ process.

Depending on the time frame of the reaction kinetics, different techniques for diffusion controlled reactions and rapid reactions can be distinguished (Sparks, 1989). Rapid reactions (half lives less than 20 s) are usually studied with relaxation, stopped flow, or electrical field methods. These methods are reviewed by Sparks (Sparks, 1989). For environmental applications, slow reactions are often of more importance than fast reactions. Therefore, fast reactions may be treated as instantaneous equilibrium reactions and experimental techniques for diffusion controlled processes should be emphasized.
The batch technique is one of the most common methods used to measure retention at equilibrium or as a kinetic process (Helfferich, 1962). In this technique a soil suspension is either stirred or shaken in a reaction vessel. The advantage of this technique is its simplicity, however, it suffers from several disadvantages. The soil/solution ratio is usually much higher than its occurrence in situ. In addition, the soil solids and solution must be separated in order to monitor the soil solution composition. Centrifuging may alter the particle interaction due to electrokinetic effects. Depending on the mixing of the suspension, different mass transfer processes may control the reaction kinetics (Ogwada and Sparks, 1986). Too vigorous shaking will increase the surface area due to abrasion of the soil particles and, therefore, alter the chemical behavior of the soil.

Flow methods are superior, for example abrasion is prevented. Another advantage of flow methods lies in the fact that the soil/solution ratio resembles in situ conditions more closely than the other methods. Also, diffusion controlled processes are not influenced by stirring or shaking so that the estimated rate coefficients do not depend on experimental conditions. Determination of rate coefficients which are universally applicable is especially difficult, however, when dealing with diffusion controlled kinetics caused by soil structural properties. Stirred flow systems, even though they provide easy measurement and useful data they may not be appropriate for determining the rate coefficients needed for in situ situations. An extensive review and description of kinetic methods are given by Sparks (1989). However, as
yet there are no definitive methods for the determination of universally applicable kinetic rate coefficients.

4.3. A Case Study

4.3.1. Zinc Retention in Soils

The soils used in this case study are listed in Table 4.1 along with their taxonomic classification and selected chemical properties. These soils were air-dried and passed through a 2-mm sieve before use. The soils were analyzed for pH by the 1:1 soil/water paste method (McLean, 1982), for organic matter by the acid-dichromate oxidation method (Nelson and Sommers, 1982), for free iron oxides by the dithionite-citrate-bicarbonate method (Mehra and Jackson, 1960), and for the cation exchange capacity (CEC) of the acid soils by the method of Gillman (1979) or the cation exchange capacity of the alkaline soils by the sum of cations method (Thomas, 1982).

Reagent-grade zinc nitrate tetrahydrate and calcium nitrate tetrahydrate were used. Radioactive $^{65}\text{Zn}$ ($9.25 \times 10^{12}$ Bq kg$^{-1}$) was used as a tracer to monitor the extent of Zn reactivity with the soils.

The retention of Zn was studied in batch experiments as outlined by Amacher et al. (1986). Initial concentrations of Zn in the solutions reacted with the soils were 0.01, 0.05, 0.1, 0.5, 1, 2, 5, 10, 50, 100, and 200 mg/L. The background solution composition for the Zn solutions was $0.005 \, M \, \text{Ca(NO}_3\text{)}_2$. The radioactive zinc was added to the solutions in order to follow the extent of the retention reactions.
Table 4.1. Taxonomic classification and selected soil properties.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Horizon</th>
<th>Taxonomic Classification</th>
<th>pH</th>
<th>TOC</th>
<th>CEC</th>
<th>OH</th>
<th>sum of cations exch.</th>
<th>MnO₂</th>
<th>amor. free Fe₂O₃</th>
<th>free Fe₂O₃</th>
<th>Al₂O₃</th>
<th>sand</th>
<th>silt</th>
<th>clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norwood</td>
<td>Ap</td>
<td>fine-silty, mixed (calc.), thermic Typic Udifluvent</td>
<td>6.9</td>
<td>0.21</td>
<td>4.1</td>
<td>0.0</td>
<td>0.008</td>
<td>0.061</td>
<td>0.30</td>
<td>0.016</td>
<td>79.2</td>
<td>18.1</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Olivier</td>
<td>Ap</td>
<td>fine-silty, mixed, thermic Aquic Fragiudalf</td>
<td>6.6</td>
<td>0.83</td>
<td>8.6</td>
<td>1.9</td>
<td>0.27</td>
<td>0.30</td>
<td>0.71</td>
<td>0.071</td>
<td>4.4</td>
<td>89.4</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>Eustis</td>
<td>B21h</td>
<td>Spodosol</td>
<td>4.3</td>
<td>1.98</td>
<td>2.7</td>
<td>5.2</td>
<td>0.0000</td>
<td>0.009</td>
<td>0.008</td>
<td>0.22</td>
<td>90.2</td>
<td>6.0</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Windsor</td>
<td>Ap</td>
<td>mixed, mesic Typic Udipsamment</td>
<td>5.3</td>
<td>2.03</td>
<td>2.0</td>
<td>10.2</td>
<td>0.041</td>
<td>0.42</td>
<td>1.23</td>
<td>0.56</td>
<td>76.8</td>
<td>20.5</td>
<td>2.8</td>
<td></td>
</tr>
</tbody>
</table>

§ The states from which the soil samples originated are Louisiana (Norwood and Olivier soils), New Hampshire (Windsor soil), and Florida (Eustis).
The retention experiments were carried out as follows. Duplicate 4.0-g samples of each soil were added to preweighed 50-mL polypropylene centrifuge tubes. Forty mL of Zn solution were then added to the duplicate samples of each soil and the samples were vortex mixed. The centrifuge tubes were placed endwise in a box on a shaker set to shake at 120 osc/min. The Zn samples were shaken 15 min every 6 hr. After 2, 8, 24, 48, 72, 96, 144, 192, 240, and 288 hr, the samples were centrifuged for 5 min at 2500 rpm, aliquots of 250 μL of the supernatant were withdrawn for ⁶⁵ᵐZn counting by liquid scintillation spectrometry, the pH of the supernatant was measured, and the samples were reweighed, vortex mixed, and returned to the shaker.

Details of the calculations of the amounts of Zn retained by the soils are outlined elsewhere (Amacher et al., 1986). Concentrations of Zn in the sample solutions were calculated from the specific activities of the initial solutions and the measured activities of the sample aliquots. Correction for radionuclide decay was avoided by counting the initial solutions each time the samples were counted. The amounts of each metal retained by the soils were calculated from the difference between the initial concentrations in solution and the concentrations in solution at each sampling time with a correction for the amounts removed for counting.

The nonlinear, multireaction model described above was fit to the retention data using a nonlinear, least-squares, curve-fitting method by Marquardt (van Genuchten, 1981; Marquardt, 1963; Daniel and Woods, 1973). The criteria used for
estimating goodness-of-fit of the model to the data were the r-square and the root mean square statistics. The root mean square is calculated by

\[
\text{rms} = \left( \frac{\text{rss}}{m - p} \right)^{0.5} \tag{4.13}
\]

where \( \text{rms} \) is the root mean square, \( \text{rss} \) is the residual sum of squares, \( m \) is the number of data points, and \( p \) is the number of parameters.

The extra sum of squares principle was used to determine if there was any statistically significant improvement of the model by adding more parameters (i.e., a two reaction, three parameter model vs. a three reaction, five parameter model) (Kinniburgh, 1986). The F-ratio needed for this test is calculated by

\[
F(p_2 - p_1, m - p_2) = \left( \frac{\text{rss}_1 - \text{rss}_2}{p_2 - p_1} \right) \left( \frac{m - p_2}{\text{rss}_2} \right) \tag{4.14}
\]

where \( m, p, \) and \( \text{rss} \) are defined as before and the subscripts refer to the model variations. The extra sum of squares principle can only be applied provided one model is a variation of another, as is the case here.

In order to reduce the number of parameters to be estimated in the multisite models, the Freundlich \( n \) and the Langmuir \( S_T \) was obtained by fitting the data at \( t = 288 \) h using least square technique (SAS, 1985). The \( F \) and \( S_T \) parameters for the two-surface Langmuir equation were determined using the method described in Sposito (Chapter 4) (1984). The rate coefficients for both multisite models were then estimated.
4.3.2. Applications of Multisite Models

Results of time-dependent retention of Zn for five different initial concentrations varying over five orders of magnitudes in Windsor soil are given in Figure 4.2. At high initial concentrations (e.g. 100 mg/L) the sorption shows an initial sharp drop and reached by then a quasi equilibrium condition. In contrast, the sorption process at low initial concentration (e.g. 0.01 mg/L) continued to decrease, after the initial concentration drop, for 14 days. The amount of Zn, that reacted with the soil after 50 h was low, so that the changes that took place at high initial concentration were below the accuracy of measurement. Similar results were obtained for the Norwood and Olivier soils (see Figures 4.3 and 4.4). However, the kinetic behavior of sorption of Eustis soil differed in that equilibrium was reached after 8 h for all concentrations (Figure 4.5).

At the last sampling time (288 h) the data for all applied concentrations were used to determine the Freundlich and Langmuir isotherm parameters, which are shown in Tables 4.2 and 4.3. As indicated by the low standard error, the Freundlich equation provides a good fit for all soils. The single-site Langmuir equation differs from the two-surface Langmuir in the best-fit maximum sorption capacity ($S_T$). The $S_T$ value was smaller for the two-surface Langmuir than for the traditional Langmuir isotherm (see Table 4.3). Comparing the $S_T$ values with the cation exchange capacity, obvious discrepancy was observed. Windsor soil had the lowest CEC of the soils used in this study (see Table 4.1), but the $S_T$ value obtained was the highest. This indicated that the $S_T$ value should be viewed as a fitting parameter rather than a
Figure 4.2. The kinetics of zinc sorption in Windsor soil for five different initial concentrations (squares are experimental result) and multireaction and second-order model fit (solid lines), which are identical.
Figure 4.3. The kinetics of zinc sorption in Norwood and Olivier soil for three different initial concentrations (symbols are measured) and multireaction model fit (solid lines).
Figure 4.4. The kinetics of zinc sorption in Norwood and Olivier soil for three different initial concentrations (symbols are measured) and second-order model fit (solid lines).
Figure 4.5. The kinetics of zinc sorption to Eustis soil for five initial concentrations.
meaningful chemical constant. Furthermore, there remained also the question regarding the meaning of the fraction defining the distribution of the solute between sites 1 and 2 in the two-surface Langmuir equation.

The kinetic retention data were utilized for the determination of the rate coefficients for our soils. The results for the least squares fits are listed in Tables 4.4 and 4.5. In comparison of the best-fit for the three-parameter model (considering site one and the irreversible site; i.e. $k_1$, $k_2$, and $k_{irr}$), the five-parameter model fit (considering site one, two, and the irreversible site; i.e. $k_1$, $k_2$, $k_3$, $k_4$, and $k_{irr}$) indicated that latter yielded superior results. This is documented by the value of the F-test (Tables 4.4 and 4.5), which showed significant improvement by assuming three sites (five parameter) instead of two (three parameter). Additionally, the standard errors of the five parameter fit was lower than the three-parameter fit (see Figures 4.8 and 4.9). It also showed that in general the five parameter model provides a better fit of the data at low initial concentrations better than at high initial concentrations. Both the multireaction and the second-order model show similar results with respect to the number of parameter fitted (Figures 4.6 and 4.7).

In order to evaluate the validity of the above models, one can utilize the concepts of chemical kinetics. That is (i) the rate coefficients should be constant regardless of the initial concentration, (ii) the apparent equilibrium constants determined by the quotients of the rate coefficients and by the least-square fit of the equilibrium data should be equal, and (iii) the rate coefficients determined for one
Table 4.2. Freundlich parameter K and n with standard errors (SE) using nonlinear least square fit and linear regression for Windsor, Olivier, and Norwood soil.

<table>
<thead>
<tr>
<th>SOIL</th>
<th>K</th>
<th>SE</th>
<th>N</th>
<th>SE</th>
<th>log K</th>
<th>SE</th>
<th>n</th>
<th>SE</th>
<th>r²</th>
</tr>
</thead>
<tbody>
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<td>Windsor</td>
<td>203.2</td>
<td>15.1</td>
<td>0.40</td>
<td>0.02</td>
<td>1.05</td>
<td>0.04</td>
<td>0.62</td>
<td>0.02</td>
<td>0.969</td>
</tr>
<tr>
<td>Olivier</td>
<td>24.06</td>
<td>3.01</td>
<td>0.45</td>
<td>0.03</td>
<td>1.31</td>
<td>0.02</td>
<td>0.48</td>
<td>0.02</td>
<td>0.996</td>
</tr>
<tr>
<td>Norwood</td>
<td>64.53</td>
<td>1.42</td>
<td>0.45</td>
<td>0.01</td>
<td>1.81</td>
<td>0.01</td>
<td>0.45</td>
<td>0.01</td>
<td>0.999</td>
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</table>

*linear regression equations of the form logS = log k + n log C
Table 4.3. Langmuir parameter $S_T$ and $K$ for single site, and $S_T$, $FR$, $K$, and $K_2$ for two-site equations with standard error (SE) for Windsor, Olivier, and Norwood soil.

<table>
<thead>
<tr>
<th>SOIL</th>
<th>$S_T$</th>
<th>SE</th>
<th>$K$</th>
<th>SE</th>
<th>$S_T$</th>
<th>FR</th>
<th>$K_1$</th>
<th>SE</th>
<th>$K_2$</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Windsor</td>
<td>1393.0</td>
<td>64.8</td>
<td>0.064</td>
<td>0.09</td>
<td>996.0</td>
<td>0.955</td>
<td>0.148</td>
<td>0.056</td>
<td>107.7</td>
<td>920.4</td>
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<tr>
<td>Olivier</td>
<td>164.0</td>
<td>12.9</td>
<td>0.079</td>
<td>0.03</td>
<td>201.0</td>
<td>0.730</td>
<td>0.020</td>
<td>0.007</td>
<td>0.291</td>
<td>0.323</td>
</tr>
<tr>
<td>Norwood</td>
<td>758.4</td>
<td>99.6</td>
<td>0.022</td>
<td>0.01</td>
<td>552.0</td>
<td>0.900</td>
<td>0.043</td>
<td>0.014</td>
<td>4.66</td>
<td>19.15</td>
</tr>
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</table>
Table 4.4. Goodness-of-fit, model parameters, and parameter standard error of the nonlinear multireaction model for describing Zn retention by Windsors, Norwood, and Olivier soil at several initial concentrations.

<table>
<thead>
<tr>
<th>Soil</th>
<th>( C_0 )</th>
<th>( r^2 )</th>
<th>( \text{rms} )</th>
<th>( F )</th>
<th>( n )</th>
<th>( K_1 )</th>
<th>SE</th>
<th>( k_2 )</th>
<th>SE</th>
<th>( k_3 )</th>
<th>SE</th>
<th>( k_4 )</th>
<th>SE</th>
<th>( k_{\text{tr}} )</th>
<th>SE</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>mg/L</td>
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<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>h(^{-1})</td>
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<td>0.0125</td>
<td>0.341</td>
<td>0.0753</td>
<td>0.0210</td>
<td>0.00331</td>
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<td></td>
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<td></td>
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<td>0.000059</td>
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<td>0.0994</td>
<td>0.00802</td>
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<td>0.0846</td>
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<td>0.62</td>
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<td>0.0158</td>
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<td>0.996</td>
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<td>0.587</td>
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<td></td>
<td>0.701</td>
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<td>0.0 NS</td>
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<td>0.0190</td>
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<td>0.0133</td>
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<td>3.5 NS</td>
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<td>Olivier</td>
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<td>2.69</td>
<td>0.251</td>
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<td>0.979</td>
<td>0.0260</td>
<td>0.5 NS</td>
<td>0.45</td>
<td>2.93</td>
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<td>0.353</td>
<td>0.112</td>
<td>0.0772</td>
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<td>0.45</td>
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</table>

**, ** Indicate that the root mean squares are significantly different at the 0.05 and 0.01 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Table 4.5.  Goodness-of-fit model parameters, parameter values and parameter standard errors of the second order two-site model for describing Zn retention by Windsor, Norwood, and Olivier soil at several initial concentrations.

<table>
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<tr>
<th>Soil</th>
<th>Co (mg/L)</th>
<th>r²</th>
<th>rms</th>
<th>F</th>
<th>FR</th>
<th>k₁</th>
<th>SE</th>
<th>k₂</th>
<th>SE</th>
<th>k₃</th>
<th>SE</th>
<th>k₄</th>
<th>SE</th>
<th>k₅₆₇₈</th>
<th>SE</th>
<th>h²</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Windsor</td>
<td>0.01</td>
<td>0.929</td>
<td>0.000431</td>
<td></td>
<td></td>
<td>0.000034</td>
<td>0.000094</td>
<td>0.218</td>
<td>0.0716</td>
<td>0.0237</td>
<td>0.00360</td>
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</tr>
<tr>
<td></td>
<td>0.999</td>
<td>0.00062</td>
<td>164.8**</td>
<td>0.955</td>
<td>0.000054</td>
<td>0.000004</td>
<td>0.0153</td>
<td>0.00258</td>
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<td>0.00360</td>
<td>0.0135</td>
<td>0.00157</td>
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<td>0.1</td>
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<td>0.00970</td>
<td>85.1**</td>
<td>0.955</td>
<td>0.000058</td>
<td>0.000007</td>
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<td>0.00406</td>
<td>0.00909</td>
<td>0.001172</td>
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* and ** indicate that the root mean squares are significantly different at the 0.05 and 0.01 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Figure 4.6. Fit of the multireaction model using three parameter \( (k_1, k_2, k_{\text{irr}}) \) and five parameter \( (k_1, k_2, k_3, k_4, k_{\text{irr}}) \) to Windsor soil for three different initial concentrations.
Figure 4.7. Fit of the second-order model using three parameter ($k_1$, $k_2$, $k_{irr}$) and five parameter ($k_1$, $k_2$, $k_3$, $k_4$, $k_{irr}$) to Windsor soil for three different initial concentrations.
initial concentration should predict the time dependent sorption for another initial concentration.

The multireaction model showed an increase of the forward rate coefficients $k_1$ and $k_3$ with increasing initial concentration, but a decrease of the backward rate coefficients $k_2$ and $k_4$ and the irreversible coefficient $k_{irr}$. This is illustrated in Figure 4.8, where the $k_1$ is plotted as a function of the initial concentration. Both the three-parameter and the five-parameter model versions showed similar behavior in increasing values of best fit rate coefficients. The difference between the rate coefficients determined by both fits was generally small. In contrast, the second-order model showed decreasing of the forward coefficients with increasing initial concentration. In addition the three and five parameter fits exhibited considerable discrepancy (Figure 4.9). The facts that the rate coefficients show a dependency on the initial concentrations do not invalidate the models. In fact due to experimental errors one should expect some variation in the outcome of the least-square fit, which may not affect the predictions of the model greatly.

A valid model should describe the equilibrium as well as the kinetic behavior of the sorption of zinc. Since we used $n=m$ for the parameter optimization, the Freundlich parameter $K$ was obtained by summing $K_1$ and $K_2$ of equations [4.9]. The Langmuir $K$ was calculated using $K_1$ of equations [4.9], because site one always represents the larger fraction of the total sorption capacity (see Table 4.3). Comparison of the apparent equilibrium constants $K$ for the Freundlich and Langmuir equations with the quotients of the kinetic models reveals large deviations (Tables 4.2
Figure 4.8. Representation of the rate coefficient $k_1$ (error bars are standard errors from Table 4.4) of the multireaction model for three- and five-parameter fit as a function of the initial concentration in Windsor soil.
Figure 4.9. Representation of the rate coefficient $k_1$ (error bars represent standard errors of Table 4.5) of the second-order model for three- and five-parameter fit as a function of the initial concentration in Windsor soil.
and 4.3, Figures 4.10 and 4.11). For the multireaction model the kinetic parameter estimation yielded much lower values than that for the equilibrium data fit. This can be observed also for the second-order model. For both models the trend of the apparent equilibrium constants indicated similar behavior of the forward rate coefficients $k_1$. Determining the apparent equilibrium constants from the last measured samples (288 h) for all concentrations implies that the apparent equilibrium constant obtained from kinetic rate coefficients for only one concentration can vary considerably. For example the lowest initial concentration (0.01 mg/L) used in this case study represents the first experimental data point on the quasi equilibrium isotherm. Therefore, the rate coefficients determined using this lowest concentration data set was based on only a very narrow concentration range. Similarly, at high initial concentrations only the very high concentration range is considered. Obviously, both models are not capable of adequately describing the data due to dependency of parameter values on initial concentration.

So far it has been shown that the rate coefficients are dependent on the initial concentration. If the models are not sensitive towards rate coefficient changes, then simulations using average rate coefficients should adequately predict the experimental results well. The third condition used to test the predictive capability of both models was application of the rate coefficients determined at an initial concentrations of 1 mg/L in the simulation of the kinetic retention at initial concentrations of 0.01 and 100 mg/L. In both cases, the multireaction model underestimated the actual experimental data (Figure 4.12). Here, the relative concentration $(C/C_0)$ is plotted
Figure 4.10. Freundlich K parameter determined from kinetic data using equations [4.9] for the three and five parameter fit as a function of the initial concentrations.
Figure 4.11. Langmuir K parameter for site one determined from kinetic data using equations [4.9] for three- and five-parameter fit as a function of the initial concentrations.
versus time on a linear scale. The results for the second-order model are presented in Figure 4.13. The simulation for the 100 mg/L initial concentration clearly underestimated the experimental data more than the multireaction model did. The 0.01 mg/L simulation (dashed line) almost completely overlapped with the model fit of the 1 mg/l initial concentration, indicating the inflexibility of the second-order model at the low concentration range.

Zinc retention in four soils could generally be described using the multisite models, however the models were not valid over a wide range of concentrations. Therefore, these models could not be used to explain all observed phenomena. Due to the dependency of the rate coefficients on the initial concentration both models failed to simulate the data using average rate coefficients assuming one reversible and irreversible site (three parameter, $k_1$, $k_2$, $k_{irr}$) as well as two reversible sites and one irreversible site (five parameter, $k_1$, $k_2$, $k_3$, $k_4$, $k_{irr}$). However, the multireaction model showed clearly more flexible behavior than the second-order. Such differences may be explained as follows: If the sorption maximum of the second-order model was much larger then the input concentration, the model behaved essentially as a linear first-order model. This was due to the term $(S_T F - C)$ and $(S_T (1 - F) - C)$ in equations [4.6] and [4.7], where $S_T F$ and $S_T (1 - F)$ must be much greater than $C$ in order to become a constant. Even when the fraction of site two is small this term can be approximated by a constant especially for low concentration (e.g. 0.01 mg/L). In contrast the multireaction model remained a system of nonlinear equations due to the terms $C^n$ and $C^m$. 
Figure 4.12. Simulations of the kinetic zinc sorption for the initial concentrations of 0.01 and 100 mg/L (dashed line) using the rate coefficients determined from the multireaction model fit at the initial concentration of 1 mg/L (solid line).
Figure 4.13. Simulations of the kinetic zinc sorption for the initial concentrations of 0.01 and 100 mg/L (dashed line) using the rate coefficients determined from the second-order model at the initial concentration of 1 mg/L (solid line).
The continued reaction after the first two days of reaction was accounted for by the first-order irreversible sorption. At low initial concentrations $k_{irr}$ was greater than at higher initial concentrations which agreed with the observation made in a previous paragraph. Since the measured rate coefficients were not constant, one must view these as pseudo rate coefficients.

In order to explain the kinetic behavior of zinc sorption in all four soils, one has to consider the processes involved. Fast reactions were observed for ion exchange. These may be represented by site one in both multisite models. However, the Freundlich and the Langmuir equations represent only a special case of ion exchange. Considering that the zinc/calcium ratio of the initial concentration varied from 1/3 to 1/30,000, these equations cannot be applied to ion exchange. Other reactions such as surface complexation may be fast processes. However, the accessibility of such fast reacting sites may be different from each other. The irreversible reactions may be a diffusion process of zinc into the iron oxide minerals. This is supported by the fact that prolonged reaction did not occur in Eustis soil, which is almost free of iron oxides (Table 4.1).

4.4. Concluding Remarks

The attempt to distinguish one fast reversible, one slow reversible, and one irreversible reaction has its origin in the observation made during time-dependent sorption of heavy metals in soils and soil minerals. Considering the results of the applications of multisite models based on Freundlich and Langmuir equations, it may
be concluded that curve fitting alone cannot be used as a tool to distinguish different reaction sites in a soil. Moreover, multisite models apparently do not have predictive capability for a wide range of concentrations. In order to improve such models specific mechanisms have to be assumed and the models modified accordingly. Since heavy metals are specifically and nonspecifically sorbed, competition with other ions such as calcium and magnesium and specific reaction on mineral surfaces should be considered. Furthermore, the kinetic behavior needs to be studied in more detail in order to elucidate the diffusion controlled processes involved. Surface reaction are usually fast. Therefore, reaction mechanisms may not be rate limiting for either of the sorption process. However, certain sites may not be easily accessible to the ions involved.

The phenomena observed for zinc sorption agree with previous work on the kinetic heavy metal sorption. The presence of certain minerals may control such behavior as continued sorption after two days. In this study it is proposed, that the presence of oxide/hydroxide minerals contributes to prolonged reaction of zinc in soil. In addition, the physical composition of these soil constituents may contribute to particular diffusion processes, such as surface, pore, and solid phase diffusion. The experimental design is a key to understanding kinetic processes in soil when transport is involved.
5.1 Introduction

The fundamental difference in the modelling approaches of heavy metal retention are based on the theoretical assumptions underlying a particular model. In general, chemical models such as surface complexation models involve assumptions regarding the chemical nature of the bonding of a metal with a surface. Hence a meaningful application for such models requires that the system is well understood. This is often not the case, especially for soils, which are often referred to as 'ill-defined' systems (Leckie, 1988). Alternatively, ion exchange models are not based on such precise assumptions and thus provide an easier means of describing retention processes. Although, the nature of the reactions are unknown, the ion exchange approach can be used to determine an equilibrium constant (Gaines and Thomas, 1953). However, the simplest approach is to measure the heavy metal sorbed by a soil for given conditions such as pH and the background solute. Hence the information obtained is associated with very particular environmental conditions and no generalization is possible.

Chemical models such as surface complexation models are used for systems in which Na is used as an indifferent background solute. However, soils from humid regions often contain large amounts of Ca and very little Na. Without relaxing the fundamental assumptions surface complexation models are therefore limited in applications to heterogeneous soil systems. The applications of surface complexation
models to competitive sorption of metals are restricted to very few studies (Cowan et al., 1991). Thus, the treatment of soil systems remains based on the measurement of the sorption for particular environmental conditions. More precisely, heavy metal sorption is primarily investigated as affected by solution pH, heavy metal concentration, and type and concentration of the background solute.

In contrast to surface complexation modelling, the affinity of heavy metals to minerals and soils has been described by ion exchange selectivity coefficients. Instead of describing the heavy metal/proton competition, the ion exchange approach has been used to evaluate heavy metal/Ca sorption. In fact, cation exchange experiments were used to determine competitive heavy metal-Ca sorption, Zn-Ca among others, on clay minerals, on soils containing different adsorbates such as montmorillonite, kaolinite, iron hydroxides, and humus as well as soil (Bittel and Miller, 1974; Abd-Elfattah and Wada, 1981; Harmsen, 1977). They found that the selectivity coefficients increased up to two orders of magnitude in the low concentration range of the heavy metal (also, see Hendrickson and Corey, 1981). Abd-Elfattah and Wada (1981) explained this behavior by specific sorption of the heavy metal cations on oxide surfaces. Tiller et al. (1984a, 1984b) used an extraction method to show that heavy metals compete with Ca as well as with protons. Furthermore, Kiekens (1990) reported not only variable selectivity but also adsorption-desorption hysteresis for a Zn/Ca soil system.

Kinetic studies are not as wide spread as equilibrium sorption investigations. Generally, static batch reactors have been used to determine the retention of heavy
metals. The sorption exhibits initially fast retention followed by slow uptake which can proceed for weeks or months (Christensen, 1984; Aringherie et al., 1985; Barrow, 1986; Amacher et al., 1988; Brümmer et al., 1988). The modelling of the kinetics of sorption has been attempted using simple rate laws. Generally, zero, first, or second order rate laws are not very successful over a large range of initial concentrations and large time intervals (minutes to weeks). In fact, Aringherie et al. (1985) assumed concentration dependent rate coefficients in order to describe kinetics of Cd sorption by an organic soil. Selim and Amacher (1988) used up to 3 different rate laws simultaneously in order to achieve good agreement between the model and the experimental data. Nevertheless, the pseudo rate coefficients were dependent on the initial concentration. This was also true for the multireaction model where the kinetics were described with n-th order rate laws based on the Freundlich equation (Amacher et al., 1988). In contrast to these empirical approaches the cation exchange kinetics of Cd, Zn, and Ca, among other cations on peat was investigated by Bunzl et al. (1976). They concluded that film diffusion was the rate limiting step.

The disadvantages of the equilibrium modelling approaches reviewed above can be summarized as follows: (i) chemical models cannot describe 'ill-defined' systems, (ii) binary ion exchange approaches cannot account for hysteresis phenomena as well as for ternary effects such as proton competition, and (iii) single solute isotherm approach disregards ion competition and lack generality. Similarly, mechanistic approaches of modelling the sorption kinetics cannot account for the chemical heterogeneity. The description of ion exchange kinetics is usually based on diffusion
controlled processes as well as electrostatic effects as described by the Nernst-Planck equation. Since, these processes may not be identifiable, the concepts of modelling the ion exchange kinetics may be only partially applicable to soil. Furthermore, single solute modelling approaches are limited to describing the sorption kinetics at narrow ranges of initial concentrations and time intervals. Hence, concepts other than multiple sites need to be invoked in order to improve the description of heavy metal sorption kinetics at varying concentrations and large time intervals. To overcome these shortcomings we will first derive a sorption model based on the most common reactions used to describe sorption of heavy metals by soils, soil minerals, and organic matter. In particular Ca competition as well as specific sorption of heavy metals will be emphasized in order to derive simple isotherm expressions. Then we will derive a kinetic model based on the assumption that heavy metal/Ca exchange is fast and possibly diffusion controlled, and that other processes such as surface precipitation and solid solution formation are slower than the ion exchange. The model is then applied to Zn sorption to an acid surface soil measured by batch and short column experiments.

5.2. Theoretical

5.2.1. Describing the Sorption of 'High Affinity' and 'Low Affinity' Ions

Generally, trace metals are very strongly sorbed to soils and soil minerals such that values of the distribution coefficient \(K_D = s/c\) may exceed 10,000 (Bunzl and Schimmack, 1991). Therefore, we refer to trace metals as 'high affinity ions'. In
contrast, Ca concentrations in soils are very high in comparison to heavy metals. Since Ca among other ions are exchangeable cations, which are largely bound by electrostatic forces, we refer to them as 'low affinity ions'.

Since soil consists of different reactive solids, different types of reactive surfaces can be identified. Clay minerals such as montmorillonite have strongly acidic sites on their faces, weakly acidic surface functional groups on the edges as well as electrostatic sites due to isomorphous substitutions. Furthermore, oxides and oxyhydroxides of iron and manganese as well as organic matter such as humic and fulvic acids are dominated by variable charge surfaces, on which heavy metals can be adsorbed. In general, heavy metals can form inner- and outersphere complexes with these soil constituents, and can therefore exhibit low to very high affinities towards soil colloids. In addition, some heavy metals such as Zn and Cd may form surface precipitates with oxides at concentrations far below the solubility product of Zn or Cd hydroxide (Farley et al., 1985; Dzombak and Morel, 1986). Heavy metal ions may also penetrate the lattice of minerals such as goethite (Brümmer et al., 1988). In fact, White and Yee (1986) showed that alkali ions penetrate amorphous silicates (obsidian) at 25°C. Considering that soils contain weakly crystalline minerals such as ferrihydrite, this process is quite likely to occur.

In order to describe the sorption of heavy metals in soils one can write the following general equation for a heavy metal sorbed to a surface (Sposito, 1984):
\[
\text{aSH} + p\text{M}^{m+} + q\text{L}^{1-} + x\text{H}^+ + y\text{OH}^- \rightleftharpoons (S)_a\text{M}_p(\text{OH})_y\text{H}_x\text{L}_q^\delta + a\text{H}^+
\]

where \(S\) denotes the surface site, \(\text{M}\) is a metal cation, \(\text{L}\) is a ligand, \(a, p, q, x,\) and \(y\), are stoichiometric coefficients, \(m\) and \(l\) are the valencies of the cation and ligand, respectively, and \(\delta = pm + x - a - ql - y\) is the valency of the surface complex.

Equation [5.1] represents a generalized form of reactions taking place at the solid/solution interface and is commonly used for surface complexation models describing the sorption of metals and/or ligands on oxide minerals. Models based on this reaction have been used to describe the change of surface charges and \(\text{pH}\) in aquatic oxide and oxyhydroxide systems with and without heavy metal ions. Due to the complex composition of soils and the interaction between minerals and organic matter, few scientists applied surface complexation models to soils (Goldberg and Sposito, 1982; Charlet and Sposito, 1987; Zachara et al., 1989). Reaction [5.1] may also describe the complexation of metals and humic substances (Sposito, 1986).

Furthermore, the structural properties of substances which make up the soil organic matter such as humic acids are not fully known, thus, preventing a rigorous theoretical treatment of the chemical processes. Moreover, Honeyman (1984) showed that sorptive additivity of binary mixtures of oxides is rather the exception than the rule. Similarly, Altmann and Leckie (1988) showed that mixtures of oxides and humic acids were controlled by the organic acids at compositions of 25% humic acid or more.

Though it is desirable to develop and apply a sound theoretical model to soil systems,
no model is as yet available which can satisfactorily account for the complexity of the soil and soil solution. Besides the interactions of soil colloids, soils contain considerable amounts of Ca so that heavy metals are almost always affected by the soil solutions composition. In fact, Cowan et al. (1991) attempted to model the effect of Ca on the sorption of Cd on ferrihydrite with the triple layer model and nonelectrostatic surface complexation model with limited success. At the lowest concentration of $0.005 \ M$ Ca the models failed to describe Cd sorption behavior. However, this concentration is closest to the Ca activity of $10^{-2.5}$ found in acid to neutral soils (Lindsay, 1978).

Here a simplified sorption model is proposed which explicitly accounts for the heterogenous sorption behavior of the different cations. The cation which has a high affinity towards the soil components is denoted as $M$, e.g. the heavy metal cation, whereas the cation with a low affinity is $N$, e.g. calcium. Considering two sites $S$ and $X$ one can write the following reactions:

\[
SH + M^{m+} \rightleftharpoons SM + H^+ \quad K_{SM} \quad [5.2]
\]

\[
SH + N^{n+} \rightleftharpoons SN + H^+ \quad K_{SN} \quad [5.3]
\]

\[
mXH + M^{m+} \rightleftharpoons X_mM + mH^+ \quad K_{XM} \quad [5.4]
\]

\[
nXH + N^{n+} \rightleftharpoons X_nN + nH^+ \quad K_{XN} \quad [5.5]
\]

where $K$ denotes the equilibrium constant, $n$ and $m$ are the valencies of the metal $M$ and $N$, whereas $X$ and $S$ denote the different sites, respectively. Equations [5.2] and
[5.3] are similar to the approach taken by James and Parks (1982) without considering the electrostatic effects of the complexation reaction on the surfaces. In fact, Davis and Kent (1990) classified reactions like [5.2] and [5.3] as non-electrostatic surface complexation models. In contrast, equations [5.4] and [5.5] represent ion exchange reactions. According to Sposito (1989) ion exchange reaction are defined by the process in which an ion in solution will replace an ion associated with a solid, and therefore, no mechanisms of reaction are considered. Furthermore, readily exchangeable ions are bound only by electrostatic forces e.g. by outersphere complexation or are present in the diffuse ion swarm.

In order to develop a simple sorption model we assume that the high affinity heavy metal ion M will be strongly sorbed to site S, whereas metal N will be weakly sorbed. Specifically, if $K_{SM}$ is several orders of magnitude greater then $K_{SN}$, the high affinity metal will compete with protons, whereas the other metal N will react primarily with site X.

Based on the assumption that both ions M and N have the same affinity towards site X, we can derive an ion exchange reaction of M and N for site X by multiplying equation [5.4] with n and [5.5] with m. Combining both equations will yield:
mX_{nN} + nM^{m+} \rightleftharpoons nX_{mM} + mN^{n+} \quad K_{MN} = \frac{(K_{XM})^n}{(K_{XN})^m} \quad [5.6]

The simplest model accounting for specific sorption and competition between M and N consists of reaction [5.2] and [5.6]. Reaction [5.2] can be rewritten as an isotherm expression:

\[
\frac{[SM]}{S_T} = \frac{K_{SM}^*[M^{m+}]/[H^+]}{1 + K_{SM}^*[M^{m+}]/[H^+]} \quad [5.7]
\]

and

\[
S_T = [SH] + [SM] \quad [5.8]
\]

where the brackets [ ] denote concentration, $S_T$ is the total amount of surface sites ($M^{-1}$ soil) and $K^*$ denotes the affinity coefficient. Since only the divalent cations Zn and Ca are considered in this paper, equations [5.7] and [5.8] may be further simplified. Furthermore, it is assumed that the pH is nearly constant such that equation [5.7] can be rewritten:

\[
\frac{s}{s_T} = \frac{K_{SP}M}{1 + K_{SP}M} \quad [5.9]
\]

where $s_T$ denotes the maximum sorption capacity ($M M^{-1}$ soil), $K_{SP}$ is the affinity coefficient ($L^3 M^{-1}$) which is equal to $K_{SM}^*[H^+]$, $SP$ stands for specific or high affinity sorption, $s$ is the amount of solute sorbed ($M M^{-1}$ soil), and $M$ the amount of solute in solution ($M L^{-3}$). It should be noted that equation [5.9] is commonly referred to as the Langmuir equation.
The ion exchange reaction can be expressed with the empirical selectivity coefficient:

\[
K_{MN}^* = \frac{(N^{m+})^m [X_m M]^n}{(M^{m+})^n [X_n N]^m}
\]  \hspace{1cm} [5.10]

where \( K_{MN}^* \) stands for the selectivity coefficient, brackets [ ] are concentration and parenthesis ( ) denote activity. If the valencies \( m \) and \( n \) are not equal equation [5.10] can not be reduced to a simple isotherm equation. For homoalvalent ion exchange (\( m = n \)) equation [5.8] can be simplified:

\[
\frac{q_M}{q_T} = \frac{K_{EX}^M /N}{1 + K_{EX}^M /N}
\]  \hspace{1cm} [5.11]

and

\[
q_T = mX_m M + nX_n N = q_M + q_N
\]  \hspace{1cm} [5.12]

where \( K_{EX} \) is the separation factor, \( q_M \) is the amount of solute \( M \) sorbed (\( M M^{-1} \) soil), \( q_N \) is the amount of solute \( N \) sorbed (\( M M^{-1} \) soil), and \( q_T \) is the total amount of exchange sites (\( M M^{-1} \) soil). Furthermore, equations [5.10] and [5.11] are related through \( K_{EX} = (K_{MN}^*)^{1/n} \).

This sorption model should be viewed as an empirical approach, which lumps the overall sorption process into a competitive sorption between of metal \( M \) and \( N \) retained by site \( X \) and a high affinity, noncompetitive sorption of \( M \) onto site \( S \). In particular, site \( S \) should consist of all reactions of \( M \) with the solid phase for which metal \( N \) cannot compete. This may include coordination of \( M \) with surface functional
groups metal N does not react with and possibly surface precipitation of M. Hence, the Langmuir equation may not be the only mathematical description of these reactions. Furthermore, the low affinity competitive reaction site X may represent all reactions which involve both metals M and N. Since the definition of the sites are based on the competitiveness of M and N, the reaction mechanisms may include innersphere and outersphere complexation for both sites.

The heterogeneity of soils implies that the selectivity coefficient as defined in equation [5.6] may not be constant. Instead, it is conceivable that the competition is better described by a variable selectivity coefficient. In order to account for heterogeneity we rewrite equations [5.13] and [5.14]:

\[
\frac{s}{s_T} = \frac{K_{SP} M^\lambda_1}{1 + K_{SP} M^\lambda_1} \quad [5.13]
\]

and

\[
\frac{q_M}{q_T} = \frac{K_{EX}(M /N)^\lambda_2}{1 + K_{EX}(M /N)^\lambda_2} \quad [5.14]
\]

where \(\lambda_1\) and \(\lambda_2\) are the heterogeneity factors. Equation [5.13] is known as the general Langmuir-Freundlich equation (Kinniburgh, 1986), whereas equation [5.14] is referred to as the Rothmund-Kornfeld equation (Sposito, 1981). Since, the ion exchange site is dominated by the exchangeable ions, we assume that the maximum sorption capacity of equation [5.14] is in the order of magnitude of the cation exchange capacity and the sum of exchangeable cations.
Since heterogeneity may be expressed differently one can summarize the model with the following equation (Chapter 2 and 3):

$$\Gamma = \sum_{i=1}^{\text{max}} \Gamma_i^T \left\{ \frac{(k_i \xi_i)^\lambda}{1 + (k_i \xi_i)^\lambda} \right\}^{\mu_i} \tag{5.15}$$

where $\Gamma$ denotes the total amount of solute sorbed to the solid phase ($M M^{-1}$ soil), $\text{max}$ is the maximum number of sites, $i$ is the site number, $\Gamma_i^T$ is the maximum sorption capacity for site $i$ ($M M^{-1}$ soil), $k_i$ is the affinity coefficient for site $i$, $\xi$ is either the solution activity (concentration) or the activity (concentration) ratio of two solutes. The exponents $\lambda_i$ and $\mu_i$ are heterogeneity coefficients. A general description of equation [5.15] is given elsewhere (Chapter 2 and 3). In particular, the model employed here can be obtained by setting the maximum number of sites $\text{max}=2$ and the exponents $\lambda_1=1$ and $\mu_1=1$. Site $i=2$ is the ion exchange site, whereas site $i=1$ represents the noncompetitive, high affinity sorption. Accordingly, the maximum sorption capacity terms can be expressed by $\Gamma_1^T=s_T$ and $\Gamma_2^T=q_T$. In addition, the solution activity or concentration term can be reduced to $\xi_1=M$ and $\xi_2=M/N$.

5.2.2. Modelling the Kinetics

The kinetics of heavy metal sorption is strongly affected by the initial concentration of the heavy metal as shown by Amacher et al. (1986). More precisely, the higher the initial concentration the faster the apparent equilibrium state is reached. In order to qualitatively explain the observed phenomena, one may argue that at least
two reactions take place; one is relatively fast and dominates at the high concentration range. The second reaction is slower and dominates at low concentrations, whereas it may not be detected at high concentrations of Zn. Hence, the model presented here should be viewed as an attempt to quantify this explanation. Based on the assumption that the sorption can be represented by a competitive site for the high and low affinity ions and noncompetitive sites for only the high affinity ions, a kinetic model is developed in this section. The following three kinetics sites are considered: (i) a diffusion controlled ion exchange site, (ii) a reversible noncompetitive site for M only, and (iii) an irreversible noncompetitive site for M.

(i) Since the accessibility of ion exchange sites may be restricted by the spatial arrangement of the reactive solid soil components, such as aggregation, and their interaction, diffusion controlled processes may govern the kinetics of sorption. The spatial arrangement of soil particles may be very complex, so that the geometry is not well defined. Therefore, we represent the kinetics by employing a mass transfer coefficient as follows (Flühler and Jury, 1983; Parker and Jardine, 1986):

\[
\frac{dq_m}{dt} = k_m (q_m^* - q_m) \quad [5.16]
\]

\[
\frac{dq_n}{dt} = k_m (q_n^* - q_n) \quad [5.17]
\]

where \( t \) denotes the time (T), \( k_m \) is the mass transfer coefficient (T\(^{-1}\)) and \( q_m^* \) and \( q_n^* \) are the amount of solute M and N sorbed at equilibrium (M M\(^{-1}\) soil). The mass transfer coefficient is based on the assumption that a steady state diffusion process
controls the transport of solute from the solution to the sorption site. According to Hines and Maddox (1985) the mass transfer coefficient can be derived from either steady state film or particle diffusion, where the mass transfer coefficient is linearly related to the effective diffusion coefficient. Applying this approach to this sorption model implies that in addition to the solution species M and N, and the sorbed species s, qM, and qN, the two dummy variables qM* and qN* must be introduced. Therefore, two additional algebraic equations based on the selectivity coefficient (equation [5.11]) and mass balance on the exchanger need to be introduced:

\[ 0 = K_{EX} M^{\lambda_2} q_N^* - N^{\lambda_2} q_M^* \] \[ 0 = q_T - q_M^* - q_N^* \]

(ii) In addition to the diffusion controlled kinetics the high affinity site S is assumed to be controlled by fractional-order kinetics \((1+\lambda_1)\) as follows:

\[ \frac{ds}{dt} = k_1 \theta M^{\lambda_1} (s_T - s) - k_2 s \]

where \(k_1\) denotes the forward rate coefficient \(((M L^{-3})^{\lambda_1} T^{-1})\) and \(k_2\) is the backward rate coefficient \((T^{-1})\). It should be emphasized that the rate coefficients are apparent rate constants rather than true meaningful parameters. Nevertheless, the affinity coefficient \(K_{SP}\) should be related to the apparent rate coefficients for sufficiently long times \((K_{SP}=k_1/k_2)\).
(iii) The model presented here allows irreversible reactions as well. A process may be treated as irreversible if the time a reaction needs to reach equilibrium largely exceeds the time of observation. Here we apply a second-order rate law:

$$\frac{ds^{irr}}{dt} = k_{irr} \theta M (s_T^{irr} - s^{irr})$$  \[5.21\]

where \(s^{irr}\) denotes the amount sorbed to the irreversible site (M M\(^{-1}\) soil) and \(k_{irr}\) is the apparent irreversible rate constant (M\(^{-1}\) L\(^3\) T\(^{-1}\)). It should be noted that the second-order rate law becomes a pseudo first-order for large values of the maximum sorption capacity \(s_T^{irr}\) for this irreversible site. The rationale of defining a maximum sorption capacity of the irreversible site is based on observations that only a certain percentage of heavy metals sorbed to soils can be recovered by extraction methods (Cavallaro and McBride, 1984). The irreversibility may therefore be viewed as a reaction whose backward reaction rate considerably exceeds the time span of observation and hence the sorption is the only process observed. Further justification for the irreversible sorption of Zn onto soil has been reported by Kiekens (1990). Since heavy metals associate with the iron mineral fraction in soils after long equilibration times (Levy et al., 1992), one cannot rule out that the desorption may be surface controlled kinetics such as most weathering reactions (Stumm and Wollast, 1990).

5.2.3. Sorption and Desorption under Flow Conditions

Sorption data obtained using static batch experiments involve a reaction vessel, for example a centrifuge tube which contains a relatively small amount of soil and
a larger amount of a solution. However, natural soil systems have considerably lower solution/soil ratios, which may be closely simulated in soil columns studies. In addition, during leaching experiments the reaction products in the solution are constantly removed, whereas in batch experiments the reaction product remains in the soil solution. In fact, Miller et al. (1989), Hodges and Johnson (1987), and Schweich et al. (1983) showed that sorption data obtained under flow conditions are different from those obtained using batch experiments. In order to use sorption data for transport predictions one needs to employ an experimental technique which closely resembles the transport process of interest.

Using short columns or disk flow systems represents an alternative to batch or column experiments and it resembles the transport conditions more realistically than batch experiments. Small amounts of soil for such flow systems also reduce the run time and simplify the treatment of solute mixing. The mathematical description of flow systems is based on mass balance considerations of the control volume and can be given by (Skopp and McCallister, 1986):

\[
\frac{d}{dt}(c + \frac{\rho \Gamma}{\theta}) = \frac{AJ}{V_0} (c_{in} - c_{out}) \tag{5.22}
\]

where \(c\) denotes the solute amount in solution (M L\(^{-3}\)), \(\Gamma\) is the solute amount sorbed to the soil (M M\(^{-1}\) soil), \(c_{in}\) is the solute concentration of the incoming solution (M L\(^{-3}\)), \(c_{out}\) is the solute concentration of the effluent (M L\(^{-3}\)), \(A\) is the cross sectional area of the column (L\(^2\)), \(J\) is the solute flux (L T\(^{-1}\)), and \(V_0\) is the volume of the column or reactor (L\(^3\)). In general \(c_{in}\) is a known function of time which can be
controlled by the experimental design, whereas the effluent concentration $c_{\text{out}}$ is usually measured. In order to use equation [5.22] one needs to relate the concentration inside the control volume ($c$) to the in and out flowing concentrations ($c_{\text{in}}$ and $c_{\text{out}}$). A differential mass balance inside of the control volume based either on convective-dispersive or convective transport will yield partial differential equations, either the second order convective-dispersive equation or a first order wave equation. Here we adopted the assumption made by Skopp and McCallister (1986) which equates $c = c_{\text{out}}$.

For reactive solutes, two cases should be distinguished; (i) local equilibrium sorption and (ii) kinetics of sorption. For the first case equation [5.24] may be simplified for a single solute system as:

$$\int_{c_{\text{in}}}^{c} \frac{R(c^*)}{c_{\text{in}} - c^*} \, dc^* = \frac{\lambda}{V_0} \frac{A J}{V_0} (t - t_D) = \frac{V - V_D}{V_0}$$

[5.23]

where $c^*$ is a dummy variable, $t_D$ is the lag time (T), $V_D$ the lag volume ($L^3$), and $R$ is a retardation factor given by:

$$R(c) = 1 + \left[ \frac{\rho}{\theta} \right] \frac{\partial \Gamma}{\partial c}$$

[5.24]

It should be noted, that for equilibrium conditions the effluent concentration is independent of solute flux, rather, it dependents on the total amount of solute passed through the flow system.
For the second case, the kinetics of sorption, one needs to combine equation [5.22] with a kinetic rate law \( r(c, \Gamma') \) to obtain a system of two ordinary differential equations:

\[
\frac{dc}{dt} = \frac{AJ}{V_0} (c_{in} - c) - r(c, \Gamma) \tag{5.25}
\]

\[
\frac{d\Gamma}{dt} = r(c, \Gamma) \tag{5.26}
\]

Based on equations [5.23] through [5.26] two different methods can be used to determine whether or not the process is controlled by kinetics or equilibrium reactions. First, experiments may be repeated at different flow rates. Plotting the effluent concentration for different flow rates as a function of the corrected volume \((V/V_0)\) should yield the same curves, if the local equilibrium assumption is valid. If the curves are different, kinetic processes determine the breakthrough behavior. Alternatively, the flow of solute into the system may be interrupted \((J=0)\). If the effluent concentration exhibits a jump after restarting the flow, kinetics is the predominant factor of the system. In fact, during the interruption period equation [5.26] governs the sorption/desorption process which is equivalent to the equations describing static batch reactors.

In order to apply equation [5.25] one needs to apply the rate laws [5.16], [5.17], [5.20], and [5.21]. The mass balance equations of species M and N can be written as follows:
\[ \frac{dM}{dt} = \frac{AJ}{V_0} (M_{in} - M) - \left( \frac{\rho}{\theta} \right) k_m (q_M^* - q_M) \]
\[ - k_1 M \lambda_i \rho (s_T - s) + k_2 \rho s - k_{irr} M \rho (s_T^{irr} - s^{irr}) \]  
\[ \frac{dN}{dt} = \frac{AJ}{V_0} (N_{in} - N) - \left( \frac{\rho}{\theta} \right) k_m (q_N^* - q_N) \]

The above 2 equations together with equations [5.16] through [5.21] form a system of differential/algebraic equations, with 6 first-order ordinary differential and 2 algebraic equations. This system of equations was solved using the differential/algebraic system solver DASSL (Petzold, 1983) and is summarized in Table 5.1.

The initial conditions can be specified as follows:

\[ M(0) = M_0 \]  
\[ N(0) = N_0 \]  
\[ q_M(0) = q_{M0} \]  
\[ q_N(0) = q_{N0} \]  
\[ q_M^*(0) = q_{M0}^* \]  
\[ q_N^*(0) = q_{N0}^* \]
Table 5.1. Summary of the model equations describing the kinetics of sorption in a two species system under batch and flow conditions.

<table>
<thead>
<tr>
<th>DESCRIPTION</th>
<th>EQUATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass balance of M</td>
<td>[ \frac{dM}{dt} = \frac{AJ}{V_0} (M_{in} - M) - \left( \frac{\rho}{\theta} \right) k_m (q_M^* - q_M) - k_i M^\lambda \rho (s_T - s) + k_2 \rho s - k_{ir} M \rho (s_T - s^{ir}) ]</td>
</tr>
<tr>
<td>Mass balance of N</td>
<td>[ \frac{dN}{dt} = \frac{AJ}{V_0} (N_{in} - N) - \left( \frac{\rho}{\theta} \right) k_m (q_N^* - q_N) ]</td>
</tr>
<tr>
<td>Mass transfer kinetics of M</td>
<td>[ \frac{dq_M}{dt} = k_m (q_M^* - q_M) ]</td>
</tr>
<tr>
<td>Mass transfer kinetics of N</td>
<td>[ \frac{dq_N}{dt} = k_m (q_N^* - q_N) ]</td>
</tr>
<tr>
<td>Ion exchange equilibrium</td>
<td>[ 0 = K_{EX} M^\lambda q_N^* - N^\lambda q_M^* ]</td>
</tr>
<tr>
<td>Mass (charge) balance of exchanger</td>
<td>[ 0 = q_T - q_N^* - q_M^* ]</td>
</tr>
<tr>
<td>High affinity apparent rate law</td>
<td>[ \frac{ds}{dt} = k_i \theta M^\lambda (s_T - s) - k_2 s ]</td>
</tr>
<tr>
<td>Irreversible apparent rate law</td>
<td>[ \frac{ds^{ir}}{dt} = k_{ir} \theta M (s_T^{ir} - s^{in}) ]</td>
</tr>
</tbody>
</table>
where the subscript 0 denotes the value at \( t=0 \). In order to model not only step input functions and steady state flow, we let the input concentrations and the flux be a function of time:

\[
M_{in} = M_{in}(t) \quad \text{and} \quad N_{in} = N_{in}(t) \quad [5.37]
\]

\[
J = J(t) \quad [5.38]
\]

In particular the following functions are used in this paper:

\[
M_{in}(t) = M_{in,1} \quad \text{and} \quad N_{in}(t) = N_{in,1} \quad \text{for} \quad t \leq t_p \quad [5.39]
\]

\[
M_{in}(t) = M_{in,2} \quad \text{and} \quad N_{in}(t) = N_{in,2} \quad \text{for} \quad t > t_p \quad [5.40]
\]

\[
J(t) = J_i \quad \text{for} \quad t < t_i \quad \text{and} \quad t \geq t_e \quad [5.41]
\]

\[
J(t) = 0 \quad \text{for} \quad t \geq t_i \quad \text{and} \quad t < t_e \quad [5.42]
\]

where \( t_p \) denotes the duration of a concentration input pulse, \( t_i \) and \( t_e \) are the starting and ending times of flow interruption, \( J_i \) is the solution flux, \( M_{in,1} \) and \( N_{in,1} \) are the pulse concentrations of \( M \) and \( N \), respectively, and \( M_{in,2} \) and \( N_{in,2} \) are the concentrations of \( M \) and \( N \) after the pulse, respectively.
5.3. Materials and Methods

5.3.1. Soil and Soil Preparation

The soil used in this study was the acid Ap horizon of the Windsor soil from New Hampshire and is classified as a mixed mesic Typic Udipsamment. This soil was air-dried and passed through a 2-mm sieve before use. Subsequently the soil was analyzed for pH by the 1:1 soil/water paste method (McLean, 1982), for organic matter by the acid-dichromate oxidation method (Nelson and Sommers, 1982), for free iron oxides by the dithionite-citrate-bicarbonate method (Mehra and Jackson, 1960), and for the cation exchange capacity (CEC) by the method of Gillman (1979). The soil had a pH of 5.3, the total organic carbon was 2.03 %, and the sum of cations was 2.0 cmol_c kg^{-1}. The free and amorphous Fe_2O_3 content was 1.23 % and 0.42 %, respectively. Also, the Al_2O_3 and MnO_2 was 0.56 and 0.042 %, respectively. The soil texture consisted of 76.8 and 20.5 % sand and silt, respectively.

5.3.2. Batch Experiments

Reagent-grade zinc nitrate tetrahydrate and calcium nitrate tetrahydrate were used. Radioactive ^{65m}Zn (9.25 \times 10^{12} \text{ Bq kg}^{-1}) was used as a tracer to monitor the extent of Zn reactivity with the soil.

The retention of Zn was studied in batch experiments as outlined by Amacher et al. (1986). Initial concentrations of Zn in the soil solutions were 0.153, 0.765, 1.53, 7.65, 15.3, 30.6, 76.5, 153, 765, and 1530 \mu mol L^{-1} (0.01, 0.05, 0.1, 0.5, 1, 2, 5, 10, 50, and 100 mg L^{-1}). The background solution composition for the Zn
solutions was 0.005 \( M \) \( \text{Ca(NO}_3\text{)}_2 \). The radioactive zinc was added to the solutions in order to follow the extent of the retention.

The retention experiments were carried out as follows. Duplicate 4.0-g samples of each soil were added to preweighed 50-mL polypropylene centrifuge tubes. Forty mL of Zn solution was then added to the duplicate samples of each soil and the samples were vortex mixed. The centrifuge tubes were agitated by placing them in a shaker set to shake at 120 osc/min. The Zn samples were shaken 15 min every 6 hr. After 2, 5, 8, 24, 48, 72, 96, 144, 192, 240, and 288 hr, the samples were centrifuged for 5 min at 2500 rpm, aliquots of 250 \( \mu\text{L} \) of the supernatant were withdrawn for \( ^{65}\text{Zn} \) counting by liquid scintillation spectrometry, the pH of the supernatant was measured, and the samples were reweighed, vortex mixed, and returned to the shaker.

Details of the calculations for the amounts of Zn retained by the soils are outlined elsewhere (Amacher et al., 1986). Concentrations of Zn in the sample solutions were calculated from the specific activities of the initial solutions and the measured activities of the sample aliquots. Correction for radionuclide decay was avoided by counting the initial solutions each time the samples were counted. The amounts of each metal retained by the soils were calculated from the difference between the initial concentrations in solution and the concentrations in solution at each sampling time with a correction for the amounts removed for counting.
5.3.3. Short Column Experiments

The disk flow apparatus consisted of a 47 mm polycarbonate filter holder (Nuclepore Swin Lok Holder) and two 0.45 μm membranes (Gelman GN-6 Metricel Membranes). Three grams of air-dried soil was evenly distributed on the membrane, which was previously placed on the female part of the filter holder. The second membrane was then used to cover the soil and the male part of the filter holder was used to seal the flow apparatus. The soil was initially wetted with approximately 200 ml of 1 M Ca(NO₃)₂ to ensure Ca saturation of the exchange sites. Then approximately 500 mL of 0.005 M Ca(NO₃)₂ was introduced to reduce the ionic strength to the desired level. After this equilibration a Zn(NO₃)₂ pulse at concentrations at either 2.65 \times 10^{-5} \text{ M} or 2.51 \times 10^{-7} \text{ M} in a 0.005 M Ca(NO₃)₂ solution were applied to the disk flow apparatus. The high concentration solution was analyzed using inductively coupled plasma (ICP) spectroscopic analysis. The low concentration solution was initially spiked with the radio isotope ⁶⁵ᵐZn at an activity of 9.25 \times 10^{12} \text{ Bq kg}^{-1} and analyzed by liquid scintillation counting (LSC). Since previous work has shown that slow sorption kinetics is most pronounced at low concentrations, this study will emphasize the low concentration runs of both the sorption and desorption. In order to prove that kinetics are indeed dominant during flow processes the interruption technique was applied. The sorption experiment at the low Zn concentration was performed at a flow rate of approximately 10 ml min⁻¹. This sorption experiment was repeated three times. After completion of each experiment the flow was interrupted for 0.5 min, 24 h, and 30 days. The desorption
experiment was then carried out at approximately the same flow rate. Table 5.2 summarizes the conditions of the sorption and desorption experiments carried out using short columns.

5.4. Results and Discussion

5.4.1. Parameter Constraints

Before describing the experimental and modelling results in detail, we need to address some important features of the model. First, the model should be viewed as a lumped parameter approach to the description of the chemical and mass transfer phenomena. Second, the lumped parameters should be related to meaningful chemical and physical processes. Even though some of the parameters cannot be derived explicitly, they should be qualitatively interpreted and evaluated as meaningful model elements. If the parameters can be identified in terms of their physical or chemical meaning, their values should be determined independently. Nevertheless, for a heterogeneous system such as soils independent parameter determination may not be feasible or possible. Therefore, the parameter values should be restricted to a certain range which seems to agree with theoretical or empirical considerations. Furthermore, a model with several parameters is generally capable of describing any arbitrary curves, hence parameter values obtained by employing least square parameter optimization techniques may yield meaningless results. In order to avoid
Table 5.2. Flow rate, concentrations, and interruption time of the sorption and desorption disk flow experiments.

<table>
<thead>
<tr>
<th>CASE(1)</th>
<th>PROC. (2)</th>
<th>Zn Concentration (3)</th>
<th>Ca Concentration (3)</th>
<th>q(4)</th>
<th>Pulse Length (5)</th>
<th>Time (6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>molar concentration</td>
<td>molar concentration</td>
<td>ml min⁻¹</td>
<td>ml</td>
<td>min</td>
</tr>
<tr>
<td>S1</td>
<td>S</td>
<td>2.62 × 10⁻⁵</td>
<td>5.01 × 10⁻³</td>
<td>11.82</td>
<td>1476.9</td>
<td>125.0</td>
</tr>
<tr>
<td>S2</td>
<td>S</td>
<td>2.51 × 10⁻⁷</td>
<td>5.01 × 10⁻³</td>
<td>9.51</td>
<td>760.4</td>
<td>80.0</td>
</tr>
<tr>
<td>S3</td>
<td>S</td>
<td>2.51 × 10⁻⁷</td>
<td>5.01 × 10⁻³</td>
<td>8.82</td>
<td>705.5</td>
<td>80.0</td>
</tr>
<tr>
<td>S4</td>
<td>S</td>
<td>2.51 × 10⁻⁷</td>
<td>5.01 × 10⁻³</td>
<td>9.48</td>
<td>758.5</td>
<td>80.0</td>
</tr>
<tr>
<td>S1</td>
<td>D</td>
<td>0</td>
<td>5.01 × 10⁻³</td>
<td>3.17</td>
<td>2013.7</td>
<td>636.0</td>
</tr>
<tr>
<td>S2</td>
<td>D</td>
<td>0</td>
<td>5.01 × 10⁻³</td>
<td>9.43</td>
<td>1131.9</td>
<td>120.0</td>
</tr>
<tr>
<td>S3</td>
<td>D</td>
<td>0</td>
<td>5.01 × 10⁻³</td>
<td>8.02</td>
<td>962.3</td>
<td>120.0</td>
</tr>
</tbody>
</table>

(1) case: 1 - analysis by inductively coupled plasma spectrophotometer, S - analysis by liquid scintillation counting, 1, 2, 3 - replicates; (2) process: S - sorption, D - desorption; (3) concentr.: Zn - zinc concentration, Ca - calcium concentration; (4) q: flow velocity in ml/min; (5) pulse l.: pulse length in volume (VOL.) or time (TIME); (6) T₁: time of how long the flow was interrupted; for the sorption experiments this time refers to the interruption between sorption and desorption experiment.
ambiguous parameter values we choose to heuristically fit the model to the experimental data. More precisely, we assumed a certain range of parameter values and then applied a trial and error procedure to fit the model to the measured data.

In order to clarify the usefulness of the model presented in this chapter, we need to emphasize which phenomena shall be described by the model. First, the sorption of Zn in a Ca background solution under static batch conditions should be described as affected by large variations of the initial Zn concentration. Second, the sorption and desorption kinetics under flow conditions should be modelled.

As pointed out by Sposito (1989) readily exchangeable cations are primarily adsorbed by electrostatic forces. This implies that the value of the maximum sorption capacity (q_max) for the ion exchange site should be in the range of the cation exchange capacity and the sum of exchangeable cations (section 5.2.2.). This parameter was therefore determined independently by a batch experiment where the soil was extracted with NH_4OAc adjusted to the soil pH (Chapter 3). Since electrostatic forces dominate the ion exchange site, the affinity of both divalent ions should be close to equal. Hence, the affinity coefficient K_{EX} for the exchange reaction should not differ from unity by more than one order of magnitude. However, the affinity may be still a function of the exchanger composition and thus heterogeneity can be accounted for by the exponent λ_2. For values of λ_2 less than one, the affinity of Zn towards the exchangers increases with decreasing concentration. In order to estimate what value of λ_2 is meaningful one needs to employ the assumption that the affinity of Zn and Ca to be adsorbed onto the exchange site should be in the same order of magnitude. For
very low values of the heterogeneity coefficient $\lambda_2$ this assumption may not hold since the affinity increases more than one order of magnitude with decreasing Zn concentration. This constraint on the heterogeneity factor can only be determined qualitatively.

The diffusion controlled kinetics of the ion exchange site is expressed in terms of only one parameter, the mass transfer coefficient ($k_m$). Bunzl and Schimmack (1991) showed that film diffusion may be the rate limiting step in the reactions with half lives in the range of 5 to 30 seconds. Hence, mass transfer coefficients should range from 0.01 to 1.0 h$^{-1}$. For flow systems the use of a mass transfer coefficient depends on the pore water velocity. At very slow velocities the mass transfer may not be rate limiting and hence the local equilibrium assumption is valid. In addition, other authors have also described the sorption kinetics during transport with a mass transfer coefficient (Flühler and Jury, 1983; Parker and Jardine, 1986).

In contrast to the ion exchange site, high affinity sorption sites should have considerably higher values for the forward apparent rate coefficient than for the backward. Furthermore, the heterogeneity factor $\lambda_1$ should not be constrained to values close to one. Even though the kinetics applied for the high affinity site is nonlinear, the rate controlling step may involve more than one process such as particle diffusion in micropores or into mineral lattices. Hence, the parameters of the high affinity site cannot easily be constrained and therefore the parameters are subjected to fitting procedures.
In addition to the high affinity site, the irreversibility of some reaction may need to be assumed, since it is well known that heavy metals can not be extracted from soils using exchangeable ions (Kiekens, 1990). This implies that this site may only be detected during a desorption study.

5.4.2. Batch Kinetics

In order to demonstrate the ability of the model to describe the kinetics of Zn sorption at various initial conditions the following input concentrations were chosen 0.153, 15.3 and 1530 μmol L⁻¹. Figure 5.1 shows the data with the model fitting. First, the data exhibits the same phenomena previously reported by Amacher et al. (1988), that is the time dependent retention reaches an apparent equilibrium faster at high concentrations than at lower ones. In order to document the reproducibility of the experimental procedure both duplicated measurements were plotted. The agreement of the model fit with the data is excellent. All three curves were obtained using the same model parameter; only the initial conditions varied. The parameter values used to model the batch data are listed in first column of Table 5.3 where the bold values represent the parameters not subjected to the curve fitting. According to the parameter constraints the maximum sorption capacity of the ion exchange site (q_T) was 10 mmol kg⁻¹ (20 mmol_c kg⁻¹) soil as measured with the NH₄OAc method. Furthermore, the affinity coefficient K_{EX} was assumed to be 1. In order to obtain a good model fit to the data the heterogeneity factor λ₂ and the mass transfer coefficient k_m were adjusted. The maximum sorption capacity (s_T) for the high affinity site was
Figure 5.1. The sorption kinetics of Zn in Windsor soil at three initial concentrations 0.153 (O), 15.3 (□), and 1530 (◊) μmol/L as a function of time.
Table 5.3. Parameter values for different simulations of Zn sorption and desorption in the batch and the disk flow reactor. The bold values were kept constant during the parameter fitting.

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>BATCH</th>
<th>SHORT COLUMN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>$k_1$ ((mmol L$^{-1}$ h$^{-1}$))</td>
<td>0.41</td>
<td>10.0</td>
</tr>
<tr>
<td>$k_2$ (h$^{-1}$)</td>
<td>0.01</td>
<td>2.0</td>
</tr>
<tr>
<td>$s_T$ (mmol kg$^{-1}$ soil)</td>
<td>0.25</td>
<td>0.50</td>
</tr>
<tr>
<td>$\lambda_1$</td>
<td>0.815</td>
<td>0.815</td>
</tr>
<tr>
<td>$K_{EX}$</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$q_T$ (mmol kg$^{-1}$ soil)</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>$\lambda_2$</td>
<td>0.850</td>
<td>0.850</td>
</tr>
<tr>
<td>$k_m$ (h$^{-1}$)</td>
<td>0.60</td>
<td>75.0</td>
</tr>
<tr>
<td>$k_{irr}$ (mmol L$^{-1}$ h$^{-1}$)</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>$s_{T_{irr}}$ (mmol kg$^{-1}$ soil)</td>
<td>-</td>
<td>0.25</td>
</tr>
</tbody>
</table>

chosen to be 1 to 2 orders of magnitude lower than the cation exchange capacity.

The other parameters were varied until the model showed good agreement with the experimental data.

So far only three initial concentrations have been considered. In order to confirm that the proposed kinetic sorption model applies to all concentrations used in this study the amount sorbed was simulated as a function of the solution concentration for 2, 24, and 288 h using the parameter values presented in the first column of Table 5.3. Since the concentration range covers 4 orders of magnitude, the results are plotted on a logarithmic scale and presented in Figure 5.2. The model exhibits good
Figure 5.2. Zn isotherms measured as a function of equilibration time and model prediction using the model parameters presented in Table 5.3.
agreement with the data especially at low concentrations. Hence, the major features of the data are well described by the model.

Model predictions of the concentrations of the ion exchange and the high affinity sites along with solution concentrations were plotted as a function of time, in order to demonstrate how the different sites influence the sorption behavior. At the highest concentration the ion exchange prevails over the specific sorption so that the influence of the high affinity site is negligible (top graph in Figure 5.3). This indicates that Zn behaves essentially as an exchangeable cation. The dashed curve clearly indicates the relative insignificance of the high affinity site \( s \). For \( M_0 = 0.0153 \, \text{mM} \), the sorption is almost equally influenced by the ion exchange and high affinity sites. In particular, the ion exchange takes place early so that within the first day the amount of Zn sorbed to the ion exchange sites \( q_M \) exceeds the amount sorbed to the high affinity site \( s \). After approximately 12 hours the amount of Zn sorbed to the ion exchange site \( q_M \) reaches a maximum, followed by desorption, caused by increasing uptake by the high affinity sites. For the lowest initial concentration, the ion exchange site caused initial rapid uptake of some 70% within the first 24 hours which was followed by a much slower noncompetitive sorption process (bottom graph in Figure 5.3).

The concentration dependency of the competition between the ion exchange and the high affinity sites for Zn was further clarified by plotting the model predicted relative amount of Zn sorbed to the high affinity site \( s/(q_M + s) \) as a function of Zn in the soil solution after 2, 24, and 288 hours of sorption (Figure 5.4). For batch
Figure 5.3. Relative concentrations of solution concentration ($M/M_0$), amount sorbed to the ion exchange site ($q_M/M_0$) and to the high affinity site ($s/M_0$) of Zn in Windsor soil for 1529, 15.3, and 0.153 μmol L$^{-1}$ initial solution concentrations.
Figure 5.4. Simulated relative amount of Zn sorbed to the high affinity site as a function of solution concentration for the batch reactor at 2, 24, and 288 hours.
kinetics we can distinguish three regions in this plot. At low concentrations less than $10^{-2}$ mM the high affinity sites dominate the overall sorption. More precisely, the amount of Zn retained by the high affinity sites was strongly time dependent and it makes up the majority of the sorbed Zn up to 84%. A transition zone at concentrations between $10^{-2}$ to about $10^{-1}$ mM is characterized by the rapid change of the relative high affinity sorption. Here, the ion exchange site (q) retains equal amounts of Zn as compared to the high affinity sorption (s). In fact, for 24 and 288 h sorption times the ion exchange site retains between 30 and 60% of the total amount of Zn sorbed. At concentration above $10^{-1}$ mM the ion exchange makes up more than 60% of total amount sorbed. In addition, the overall retention kinetics is considerably faster at high concentrations, since the sorption process may be controlled by ion exchange.

At high initial concentrations the sorption may be modelled with an ion exchange approach because the influence of the high affinity sorption sites were very small (top graph in Figure 5.3). However, at low initial concentrations the ion exchange is the dominant mechanism in describing the initial fast Zn retention. Therefore, modelling the kinetics of sorption, the ion exchange site plays an important role at all concentrations, whereas the high affinity site can be neglected at high concentrations.
5.4.3. Short Column Kinetics

So far the proposed model has been successfully applied to the batch reactor experiments. In order to prove the versatility of the model we attempted to describe the sorption and desorption of Zn under flow conditions. The advantage of using a flow system is that the desorption can be investigated more easily than under static batch conditions. Furthermore, faster sorption and desorption can be examined and the stopped flow technique can be applied to provide essential information regarding the slow processes. The time frame in this investigation ranged from minutes to one month, whereas the time limits of the batch experiments ranged from 2 hours to 2 weeks. The broader time interval of the short column experiments, as well as the incorporation of both the sorption and desorption, requires generality of the model.

Figure 5.5 shows the amount of sorbed Zn as a function of flow time for three different interruption times. The experimental conditions are presented in Table 5.2. The flow rate for all runs ranged from 8 to 10 ml min\(^{-1}\) and the pulse concentration was 2.5 \(10^{-7}\) \(M\) Zn. An interruption of less than 0.5 minutes is shown in the upper graph of Figure 5.5. Clearly, the desorption is nearly complete. With increasing interruption time, the recovery decreases rapidly. After a 24 hour flow interruption the recovery is nearly 50\% (center graph in Figure 5.5) whereas an interruption time of 30 days yielded a recovery of only 20\% (bottom graph of Figure 5.5). In order to support these observations we plotted the amount of Zn in the effluent as a function of flow time (Figure 5.6). Here the flow interruption is demonstrated by the concentration jump after the change of input solution. After the 0.5 minute
Figure 5.5. The sorption of Zn in short columns with interruptions of 0.5 min (top graph), 24 hours (center graph), and 30 days (bottom graph). The lines are simulations with parameters given in Table 5.3.
interruption no jump is observed (upper graph in Figure 5.6). In contrast the 24 h and 30 day interruption exhibit a concentration decrease of 50 and 75 % respectively (center and bottom graph in Figure 5.6). It is obvious that the sorption process did not reach equilibrium for possibly more than 30 days. Hence, the desorption takes place when the sorption process is not completed. In fact, one may not rule out that desorption and sorption may take place simultaneously at different sites.

Ideally the parameter used to model the batch experiments discussed earlier should be applicable to the short column data. Due to the different experimental conditions the same parameters could not be used to model this data set. However, the cation exchange capacity (q_T), the affinity coefficient ion exchange (K_EX), and the heterogeneity factor (λ_2) were not changed for all simulations ( bold values in Table 5.3). Furthermore, the parameters of the high affinity site were varied in order to obtain the closest fit to the data. First we attempted to change only the apparent rate coefficient since different experimental conditions may affect the overall kinetic sorption behavior. However, no satisfactory fit was obtained and therefore the ratio of k_1/k_2 had to be changed along with maximum sorption capacity (s_T).

Furthermore, since the stopped flow technique was applied, the model needs to describe the sorption/desorption over as much as 30 days. Only by invoking an irreversible site could the observed phenomena be described.

For short column simulations I and II k_1 was approximately 25 times the value used for the batch experiment and k_2 was about 200 times greater than that for the batch data. Hence, the overall affinity was decreased; however the sorption and
Figure 5.6. Effluent concentration curves of Zn in short column runs with 0.5 min (top graph), 24 hours (center graph) and 30 days (bottom graph) interruptions. Simulations are the lines with values presented in Table 5.3.
desorption kinetics were faster, i.e. closer to instant equilibrium than the batch kinetics. Furthermore, the mass transfer coefficient of the ion exchange reaction was increased from 0.6 to \( 75 \text{ h}^{-1} \). In addition the irreversible site was invoked with rate coefficients ranging from 0.001 to 0.05 mmol\(^{-1}\) L\(^3\) h\(^{-1}\). The highest value was sufficient to predict the 0.5 min and 24 h interruption, however, the model grossly overestimates the experimental data for the desorption curve after the 30 d interruption (simulation I, Figure 5.5). When decreasing both the irreversible and reversible pseudo rate coefficients (simulation II) the amount sorbed is lower for the sorption and desorption as compared to the other simulations. The predicted desorption curve after the 30 day interruption is grossly underestimated. Simulation III shows excellent agreement with the experimental data for sorption and desorption after the 30 d interruption. The only difference between simulation I and III is the smaller \( k_{irr} \) of simulation III. In contrast to the 30 d interruption desorption prediction, the 24 h interruption simulation yielded a better fit for run I than for run III (Figure 5.5). Simulation IV differs from the other predictions in that \( k_1 \) and \( k_2 \) were both 25 times larger than that used for the batch experiments. Also, the mass transfer coefficient \( (k_m) \) is greater than \( 10^4 \) and hence for ion exchange the local equilibrium assumption is valid. In contrast to the other simulations the \( k_{irr} \) used was 0.001 mmol\(^{-1}\) L\(^3\) h\(^{-1}\). Thus, the irreversible site is least important for this simulation. The ratio of \( k_1/k_2 \) in case IV was the same for both the batch and short column simulations. Once the system reaches a quasi equilibrium state, the affinity coefficient for the batch and the short column system appears to be equal. Hence, the short column simulation IV
resembles most closely the parameter obtained from the batch experiments. In all cases, the shape of the simulated breakthrough curve underestimates the measured values for the sorption, whereas the desorption is overestimated for all interruption times (Figure 5.5).

In Figure 5.6 the effluent curves of the short columns are presented along with the simulations. Clearly, the 0.5 min interruption does not show any significant concentration jump for both the simulated and experimental curves. However, the simulated breakthrough curves appear earlier than the experimental. This phenomenon may be related to the mixing behavior of the solute. The assumption of \( c = c_0 \) taken here (after Skopp and McCallister, 1986) may need to be modified. Nevertheless, the concentration jump after the 24 h and 30 d interruption are predicted fairly well so that qualitative agreement between the model and the experimental data are observed. In order to evaluate the simulations more closely only the solution concentration shortly before and after the interruption was plotted as shown in Figure 5.7. Clearly, simulation III predicts the concentration after the interruption of 30 d best, whereas simulation II shows best agreement for the 24 h interruption data set. However, the measured effluent concentration is considerably lower than the predicted one. Simulation IV underestimates the effluent before and after all interruptions.

The short column data set at the highest concentration (2.62 \( 10^{-5} \) \( M \)), revealed that no kinetics is detectable after a 24 h interruption. The filled square in Figure 5.8 is the first data point measured after the 24 h interruption. Clearly no jump was detected and hence the slow kinetics was not measurable at this concentration. The
Figure 5.7. Experimental and simulated effluent concentrations of Zn shortly before and after the 0.5 min (top graph), 24 h (center graph), and 30 d (bottom graph) interruptions.
Figure 5.8. Effluent curve of Zn with an input concentration of $2.61 \times 10^5 M$ with a 24 h interruption. The lines indicate simulations and the solid square (■) denotes the first data point measured after the 24 h interruption.
Zn breakthrough was simulated with the parameters given in Table 5.3 and all of the simulations reproduced the observed phenomenon; that is, the ion exchange seems to mask the slower high affinity sorption.

5.4.4. Discussion

The experimental data and the model predictions presented here reveal that the sorption of Zn by an acidic soil treated as an equilibrium or a kinetic process is highly concentration dependent. In order to justify such a modelling approach we attempted to relate our approach to previous research. Alkaline earth element competition with heavy metals on iron oxides surfaces has been described using the triple layer and a nonelectrostatic surface complexation model (Cowan et al., 1991). In particular, the authors assumed that Ca is competing with Cd on the same plane in order to obtain a satisfactory fit. In fact, equations [5.2] and [5.3] are identical to the ones used for Cd and Ca innersphere and outersphere complexation of the triple layer and the nonelectrostatic surfaces complexation models (Cowan et al, 1991). Furthermore, bidendate outersphere complex formation of Ca with iron oxide has the form of reaction [5.4] and [5.5]. In order to predict the ion exchange equilibria of two competing cations other than protons James and Parks (1982) developed a surface complexation model for permanent charge clay minerals. They utilized reactions of the form of equations [5.2] and [5.3]. This approach was based on the early work by Garrels and Christ (1956) who defined a high and low affinity adsorption site for permanent charge clay minerals but neglected the electrostatic effects. Furthermore,
reactions of heavy metals with organic matter as well as humic and fulvic acid have been represented by reactions of the type given by equations [5.2] through [5.5] (Gamble et al., 1983; Perdue et al., 1983). Overall, equations [5.2] to [5.5] represent a common description of surface reactions of soil minerals and organic matter.

Since soils are heterogeneous 'ill defined' systems, chemical models which account for heterogeneity are still not available and hence the assumption concerning the bonding nature need to be relaxed. In order to describe the effect of Ca on the sorption of heavy metals, approaches other than surface complexation modelling have been applied. As mentioned previously, ion exchange of heavy metals with Ca has been studied for minerals and soils (Harmsen, 1977; Abd Elfattah and Wada, 1981). One common observation was that when the heavy metals were added to the soil, the solution pH decreased (Abd Elfattah and Wada, 1981). Hence, the affinity of the heavy metals to exchange preferentially with protons of surface functional groups is greater than that of Ca. The selectivity coefficients are generally dependent on the exchanger composition as well as the degree of Ca saturation (Abd Elfattah and Wada, 1981). Furthermore, Tiller et al. (1979) and Tiller et al. (1984a, b) used a fast Ca extraction method to distinguish two different sorbed heavy metal fractions. They found that the Ca extractable Zn fraction (nonspecific) is less pH dependent than the remaining fraction (specific). Since their terminology of nonspecific and specific sorption is not consistent with the definition given by Sposito (1984) and Schindler (1990). We did not adopt their terms in this work. However, their findings are in agreement with the ion exchange approach by Abd-Elfattah and Wada (1981), that is
the heavy metal sorption is partially controlled by Ca competition and partially, perhaps, by other specific reactions. Also, Wolf et al. (1977) interpreted the effect of Ca on the sorption of various heavy metals on peat with the $K_D$ (distribution coefficient s/c) approach. They suggested that competition of the heavy metal ions with Ca as well as preferential sorption to acid surface functional groups controls the overall sorption. More recently, Harter (1992) investigated the sorption of several heavy metals by a surface soil as affected by Ca presence. He also concluded that the heavy metals compete only partially with Ca. In fact, when Co and Cu were added to the Ca saturated soil the amount of Ca released was less than the amount of heavy metal added. Other researchers investigated ionic strength effects of heavy metal competition with Ca in soils and minerals (Garcia-Miragaya and Page, 1976; Petruzelli, 1985). They also concluded that competition is primarily governing the overall sorption behavior.

Independent of the soils and soil materials as well as the method of data interpretation used for studying the effect of Ca on heavy metal sorption, the results have two important commonalities; (i) heavy metals compete with Ca and (ii) heavy metals are sorbed on sites which seem to be unaffected by Ca. Thus, the observed phenomena can be viewed as a support for explicitly defining a competitive ion exchange and a noncompetitive high affinity site (Equations [5.10] and [5.11]). By defining two different sites this sorption model has to be viewed as an empirical approach derived from experimental and theoretical considerations. Also, the ion exchange approach loses its thermodynamic significance. Moreover, chemical models
have a limited ability to account for heterogeneity. With the exception of Dzombak and Morel (1990), who extended the diffuse layer model by defining a high and low affinity site in the same plane, chemical models usually do not account for heterogeneity. When attempting to model the chemical behavior of heterogeneous surfaces assumptions on the nature of bonding have to be relaxed and hence the modelling becomes a descriptive tool such as the local isotherm approximation by Nederlof et al. (1990). In order to avoid additional sites we choose to describe heterogeneity by the exponents $\lambda_1$ and $\lambda_2$ which are a measure for the width of a close to normal site affinity distribution (Sposito, 1984). Furthermore, in heterogeneous soils the equilibrium may not be reached after long times such as several months, so that the equilibration time cannot be well defined. Therefore, the kinetic model was developed based on the assumption that equilibrium may not be reached for several months.

The empirical nature of our model becomes even more evident when the kinetics of sorption is considered. Even though equilibrium information can be obtained from chemical kinetics the converse is not true; that is, no kinetic information can be deduced from equilibrium data (Atkins, 1986). Hence, the model formulation chosen here is based on the observations obtained from previous research. More precisely, sorption and transport studies have revealed that exchangeable ions react relatively fast with soil. In fact, Ca and Mg exchange in a stirred tank reactor has been examined by Seyfried et al. (1989). They found that the local equilibrium assumption was valid to adequately describe their data even when using flow rates up
to 2.2 mL min\(^{-1}\). Furthermore, the transport of exchangeable ions in soil columns was predicted adequately with the local equilibrium approach (Lai and Jurinak, 1971; Valocchi et al., 1981; Gaston and Selim, 1990a). In addition, Harter and Lehmann (1983) attempted to experimentally distinguish the contribution of ion exchange to heavy metal sorption by employing a batch kinetic technique. They assumed that the initial fast retention is controlled by ion exchange.

Nonequilibrium of ion exchange is usually attributed to physical nonequilibrium e.g. diffusion controlled processes caused by soil structural properties such as aggregation. Two approaches are commonly applied to describe physical nonequilibrium in soils; (i) the mobile/immobile or two-region approach (Selim et al., 1987; Mansell et al., 1988; Gaston and Selim, 1990b) or (ii) the mass transfer coefficient approach (Parker and Jardine, 1986). The first approach requires the determination of an immobile water fraction in the soil, among others. An independent measurement of the parameters may not be possible and therefore we chose the second approach which required only one parameter, namely the mass transfer coefficient (Equations [5.16] and [5.17]).

Since Ca competition as well as sorption speed is used to distinguish the sites, the chemical reactions (Equations [5.2] and [5.3]) of the high affinity site should be viewed as an incomplete description of the processes taking place. For example, surface complexation in a well defined system may take place very fast. In fact, relaxation methods are commonly used to determine the kinetics of surface complexation where the time range may be several orders of magnitude lower than the
ones for flow methods (Sparks and Zhang, 1991). Hence, under flow conditions the
local equilibrium assumption may be valid for some reactions. Therefore, the ion
exchange site as described by Equation [5.14] may include innersphere complexation.
If indeed higher energy bonding needs to be represented by the ion exchange
expression, concentration dependent selectivity should be anticipated. From this point
of view the presence of the heterogeneity factor \( \lambda_2 \) is essential for the model to
work. This also implies that the slow high affinity sorption sites represent processes
such as: diffusion into micropores (Smit et al., 1978), hindered diffusion, surface
restructuring, surface precipitation (Dzombak and Morel, 1986), and diffusion into the
solid phase (Brügger et al., 1988). As shown previously the batch sorption process
can be described with only one high affinity site, whereas the desorption in thin disk
flow systems require an additional irreversible site.

The model presented here is in accordance with the observed phenomena by
other researchers and the results presented in this paper. In principle the batch and
the short column experiments show similar phenomena, however, the rate coefficients
are considerably different. Since batch experiments were designed to prevent particle
abrasion through moderate agitation, it is proposed here that the initial kinetics of the
first 24 hours reflect the experimental conditions. More precisely, the initial sorption
rate is most likely controlled by diffusion of Zn from the solution to the sorption sites.
This process may be slower under static batch conditions since the reaction product
is not removed and the soil solution ratio is small (1:10). In contrast, the short
column experiment was carried out with a soil solution ratio of approximately 1:1 so
that the diffusion through the bulk solution to the solid phase is minimal. Thus, the substantially slower rate coefficient of the batch experiment column can therefore be explained with incomplete mixing of the soil suspension. Hence, both the mass transfer coefficient \( (k_m) \) and the forward coefficient \( (k_f) \) are dependent on the experimental condition. Furthermore, the slow sorption kinetics in the short column experiment was expressed by the irreversible site since the reversible noncompetitive site had a considerably higher rate coefficient. At high initial concentrations the batch and short column experiments show very similar results, that is an apparent equilibrium is reached after short times. In fact the slow kinetics can not be detected by stopped flow technique or the batch method. Overall, the kinetics of Zn sorption at high concentrations behaves essentially as that of a readily exchangeable cation. Hence the local equilibrium assumption may be applied to the transport results. The success of the approach has been presented elsewhere (Chapter 3). Hence, the model given here describes the sorption of Zn adequately over a wide range of concentrations. Also, it can be used to deduce, at least qualitatively, the concentrations ranges where the local equilibrium assumption might be valid.

5.5. Summary and Conclusion

A model was developed to describe the sorption/desorption of Zn in an acid soil at various concentrations under static batch and dynamic flow conditions. The basic assumptions for the model were: (i) the presence of low affinity competitive sites governing Ca/Zn ion exchange, (ii) the presence of high affinity noncompetitive sites
governing higher energy bonding of Zn with surface functional groups for which Ca cannot compete, (iii) the two types of sites may be heterogeneous so that the affinity increases with decreasing Zn sorption, (iv) the maximum sorption capacity of the competitive site is approximately equivalent to the sum of exchangeable cations, (v) maximum sorption capacity of the high affinity sites are considerable lower than that of the low affinity competitive sites, (vi) the kinetics of the competitive site is diffusion controlled and was described using a mass transfer coefficient, (vii) the kinetics of the high affinity site was described using pseudo rate coefficients, and (viii) an additional irreversible process was incorporated and described by a second order reaction. This model may be classified as an empirical two species/multisite model. The model was capable of describing quantitatively Zn sorption measured with a static batch reactor as a function of time over four orders of magnitude of initial concentrations. Zn sorption and desorption measured by a short column experiment was qualitatively described by the model, however, the rate coefficients were at least two orders of magnitude greater than those from the batch data set. The irreversible site was necessary to satisfactorily predict the desorption at an input concentration of $2.51 \times 10^{-7} \, M$. At high Zn concentrations the sorption is controlled by the fast ion exchange site which was demonstrated by the sorption batch experiment and the stopped flow technique of the short column experiments. The model adequately described this behavior.

The model presented in this paper exceeds conceptually other modelling attempts of heavy metal sorption kinetics in heterogeneous soil systems as follows...
(Aringhieri et al., 1985; Amacher et al., 1988; Selim and Amacher, 1988); (i) the sorption sites can be explicitly related to possible chemical reactions; (ii) based on the reactions and assuming that the system is heterogeneous some model parameter can be constrained to a certain range of value; (iii) an important model parameter can be determined independently, e.g. the maximum sorption capacity for the ion exchange site equals the sum of exchangeable cations. Furthermore, the model development takes into account other approaches including surface complexation models, ion exchange approaches, the distribution coefficient \((K_D)\) approach, extraction methods, and kinetic studies. Thus, the model derivation can be viewed as an attempt to synthesize the essential findings of several approaches and present a lumped parameter approach for describing the observed phenomena. Future research should emphasize the independent methods for the measurement of the different sites.
CHAPTER 6
THE MEASUREMENT OF ZN SORPTION AND DESORPTION KINETICS
IN TWO SOILS AS INFLUENCED BY ORGANIC MATTER AND IRON OXIDE REMOVAL USING A DISK FLOW APPARATUS

6.1 Introduction

Heavy metal sorption by soils has been shown to be a function of pH, sorbate concentration, and background solute (Alloway, 1991). Since such studies are based on macroscopic observations, we do not know which soil colloids govern the sorption behavior. Two principal ways have been employed to elucidate the effects of soil colloids on the sorption: (i) a 'synthetic' soil can be made from the mixtures of pure minerals and/or organic acids (Honeyman, 1984; Altmann and Leckie, 1987) or (ii) colloids of a natural soil can be removed or separated (Cavallaro and McBride, 1984; Shuman, 1976; Mangaroo et al., 1965). The advantage of the first approach is that the individual colloids are well known. However, the interaction between these colloids are based on the experimental conditions such as sorbent/sorbate ratio and solution/soil ratio and takes place within short time. In contrast colloidal interactions in natural soils are caused by pedological processes during soil genesis. Hence, taking into account the interactions of colloids in natural soils, the second approach seems to be more appropriate. In addition to the determination of which colloid governs the sorption, the measurement of sorption is dependent on the type of experimental procedure.
Batch experiments are standard procedures in determining equilibrium data, whereas flow methods are employed for the collection of kinetic data. It has been observed that chemical data obtained from column experiments are different from data obtained from static batch experiments (Miller et al., 1989; Hodges and Johnson, 1987). Due to this fact, prediction of reactive flow in soil columns based on static batch experiments may yield inconclusive results (Persaud et al., 1983) which is why chemical data should be determined in a flow system.

Since batch type experiments are usually carried out at a high solution/soil ratio the data may not be applicable to transport processes as shown by Green and Obien (1969) and Dao and Lavy (1978) for pesticide movement. An alternative to batch experiments are short column or disk flow experiments. Miller et al. (1989), Hodges et al. (1987), and Akratanakul et al. (1983) showed that the batch results were mostly underestimating the sorption of ions on soils and minerals with respect to short column results. The use of long columns for determination of equilibrium parameters has been attempted by Green and Corey (1971) for pesticides and by Schweich et al. (1983) for ion exchange. Furthermore, solutes which are highly retarded require a long leaching time in order to reach the input concentration at the effluent. In addition, the mixing effects in the flow direction (hydrodynamic dispersion) also need to be accounted for. Therefore, short column or disk flow experiments are preferable over long column experiments, since the former is faster to carry out and simpler to evaluate.
Even though equilibrium data can be obtained from disk flow experiments (Helfferich, 1962; Schweich and Sardin, 1981), most researchers use this method for the determination of kinetic rate coefficients. Jardine and Sparks (1984) determined the rate coefficients of K sorption on soils and clay minerals using short column experiments. Their analysis depends on the assumption that the rate of reaction follows first order kinetics. Later, Skopp and McCallister (1986) gave a more rigorous analysis of the use of disk flow systems for determining reaction kinetics. They presented a number of analytical solutions for special cases of sorption reactions. In another study the kinetics of Cd sorption to goethite has been determined by short column experiment assuming second order kinetics by Theis et al. (1988).

The objectives of this paper are to measure the kinetics of Zn sorption and desorption under flow conditions by two acid soils with and without removal of organic matter and iron oxide. Furthermore, we will distinguish between equilibrium and kinetics using experimental methods.

6.2. Theoretical

In order to present a meaningful discussion of the disk flow experiment some theoretical aspects of the evaluation of the data are presented here. The equation describing solute transport in a thin disk can be given as follows (Skopp and McCallister, 1986):

\[ V_T \frac{d}{dt}(\theta c + \rho s) = A J (c_{in} - c_{out}) \]  

[6.1]
where \( c \) denotes solution concentrations \((\text{M} \text{L}^{-3})\), \( s \) is the amount of solute sorbed \((\text{M} \text{M}^{-1} \text{soil})\), \( t \) is time \((\text{T})\), \( V_T \) the total volume of the disk or short column \((\text{L}^3)\), \( A \) is the cross sectional area \((\text{L}^2)\), \( J \) is the flux \((\text{L} \text{T}^{-1})\), \( \theta \) is the volumetric water content \((\text{L}^3 \text{L}^{-3})\), \( \rho \) is the bulk density \((\text{M} \text{L}^{-3})\), and the subscripts in and out denote the inflow and outflow concentrations, respectively. This equation is used when dispersion and the concentration gradient in the flow direction can be neglected. However, if this is not the case the right hand side of equation [6.1] will be expressed by a differential mass balance inside the control volume. Assuming either diffusive, convective, or convective-dispersive transport, the equation [6.1] then becomes a partial differential equation: either the diffusion, the convection, or the dispersion-convection equation. However, use of an algebraic relationship between the concentration \( c \) within the control volume, and the inflow and outflow concentration, simplifies the mathematical treatment of the disk flow system. In fact, Skopp and McCallister (1986) equate \( c \) and \( c_{\text{out}} \), whereas Biggar et al. (1978) assume that \( c \) is the arithmetic average of \( c_{\text{in}} \) and \( c_{\text{out}} \). When applying equation [6.1] to equilibrium studies, one can show that the outflow curve is independent of the time; but rather, it is dependent on the outflow volume. Introducing the retardation factor \( R \):

\[
R\ (c) = 1 + \frac{\rho}{\theta} \frac{\partial s}{\partial c} \tag{[6.2]}
\]

so that equation [6.1] may be rewritten as:
where $V$ is the volume of solution passed through the short column ($L^3$), $V_0$ is pore space ($L^3$), and $c^*$ denotes the integration dummy variable. The left hand side of equation [3] may have a closed form solution depending on the form of the retardation factor and the functional relationship between $c_{out}$ and $c$. The right hand side is the integrated form of the time derivative and is equivalent to the volume of solution passed through the column. Performing experiments with the same soil and solution at different velocities, the breakthrough curves should be identical when plotted as a function of the effluent volume, provided the local equilibrium assumption is valid. However, if kinetic reactions are controlling the sorption process, the breakthrough curves should exhibit different shapes. Hence, conducting experiments at different flow velocities should give the appropriate information on either the equilibrium or kinetic processes. Alternatively, the flow may be interrupted for a given time duration. Such an interruption should yield a change in concentration if time dependent sorption dominates the retention process.

An alternate representation of the disk flow data is to compute the amount of sorbed solute as a function of time. This can be done by numerical integration using the trapezoidal method. More specifically, the following equation can be used:

$$s_j = \frac{\theta}{\rho} q \left[ t_j c_i - \frac{1}{2} \sum_{j=1}^{n} (t_j - t_{j-1}) (c_j + c_{j-1}) \right]$$  \[6.4\]
where \( q (= J \cdot A) \) denotes the flow \( (L^3 \cdot T^{-1}) \), \( n \) is the number of data points, and \( c_j \) is the solution concentration at time \( t_j \).

6.3. Materials and Methods

The soils used are listed in Table 6.1. The first soil is the Windsor loamy sand, an entisol from New Hampshire, which was also treated with hydrogen peroxide \((H_2O_2)\) in order to oxidize the organic matter. Then a subsample was taken and the iron oxide/hydroxide was removed with the dithionite-citrate method (Mehra and Jackson, 1961). After both treatments the soil was air-dried and ground to obtain a good mixture of the clay, silt, and sand fraction. Finally the soil was passed through a 2 mm sieve.

The disk flow apparatus consisted of a 47 mm polycarbonate filter holder (Nuclepore Swin Lok Holder), and two 0.45 \( \mu \)m membranes (Gelman GN-6 Metricel Membranes). Three grams of air-dried soil was evenly distributed on the membrane, which was previously placed on the female part of the filter holder. Then the second membrane was used to cover the soil and the male part of the filter holder was used to seal the flow apparatus. In order to prevent leaking of the filter holder at high velocities and high pressures, teflon tape was used to seal the thread of the filter holder. The soil was initially wetted with approximately 200 ml \( 1 \; M \) \( Ca(NO_3)_2 \) to ensure Ca saturation of the exchange sites. Then approximately 500 ml of \( 0.005 \; M \) \( Ca(NO_3)_2 \) was introduced to reduce the ionic strength to the desired level. After this equilibration a \( Zn(NO_3)_2 \) pulse at concentrations at either \( 2.62 \times 10^{-5} \; M \) or \( 2.51 \times 10^{-7} \).
Table 6.1. Taxonomic classification and selected soil properties of the Windsor and Mahan soil.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Horizon</th>
<th>Taxonomic Classification</th>
<th>pH</th>
<th>OM %</th>
<th>Fe₂O₃ %</th>
<th>CEC⁺⁺</th>
<th>Clay Mineralogy *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Windsor</td>
<td>Ap</td>
<td>Mixed, mesic Typic Udipsamment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>OH-VR &gt; KA &gt; IL</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.4</td>
<td>1.87</td>
<td>1.22</td>
<td>15.9</td>
<td>KA &gt; VR &gt; IL</td>
</tr>
<tr>
<td>Mahan</td>
<td>Bt</td>
<td>Clayey, kaolinitic Typic Hapludult</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>KA &gt; VR</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.6</td>
<td>0.50</td>
<td>2.17</td>
<td>30.0</td>
<td>KA &gt; VR &gt; SM</td>
</tr>
</tbody>
</table>

# Cation exchange capacity - here the same as sum of exchangeable cations
& KA - kaolinite, VR - vermiculite, OH-VR - OH-vermiculite, IL - illite
$M$ in a 0.005 $M$ Ca(NO$_3$)$_2$ solution were applied to the disk flow apparatus. The high concentration solution was analyzed using inductively coupled plasma spectroscopic analysis. The low concentration solution was initially spiked with the radio isotope $^{65}$Zn at a activity of $9.25 \times 10^{12}$ Bq L$^{-1}$ and analyzed by liquid scintillation counting. Since previous work has shown that slow sorption processes are most pronounced at low concentrations (Amacher et al., 1986), this study emphasizes the low concentration runs of both the sorption and desorption. In order to prove that kinetics are indeed dominant during flow process the interruption technique was applied. For untreated, peroxide, and peroxide/dithionite treated Windsor and Mahan soil, the sorption experiments at the low Zn concentration were performed at a flow rate of approximately 10 ml min$^{-1}$. After completion of each sorption experiment the flow was interrupted for 24 h. The desorption experiment was then carried out at the same flow rate. In order to prove that the high flow rate of the desorption experiment was governed by kinetic process the flow was interrupted after approximately 2 h. After discontinuance of 7 to 15 days the flow was restarted for about 4 min at the same rate. Information about the slow sorption and desorption was obtained by comparing these experiments. Furthermore, the interruption test clearly revealed to what extent the process is controlled by kinetics. The experiments at the high Zn concentration were performed without second interruption during the desorption. In addition, the high concentration sorption experiments were carried out at two different velocities, of approximately 3 and 10 ml min$^{-1}$. 
In all cases the experiments are conducted to compare the results with that of the untreated Windsor soil. The Mahan soil's composition is very different from that of the Windsor soil and consists primarily of minerals such as goethite and kaolinite. Therefore, the Mahan soil is an inorganic variable charge soil, whereas the Windsor soil is primarily influenced by organic matter. Table 6.2 summarizes the data of the different sorption and desorption runs.

### 6.4. Results and Discussion

In this study different flow velocities were applied to the high concentration experiments, whereas the interruption test was applied to the sorption and desorption experiments at low Zn concentrations. Table 6.2 summarizes the experimental conditions under which the disk flow experiments were conducted. The velocities used ranged from 3 to 11 ml min$^{-1}$. Previous studies utilized velocities ranging from 1 to 10 ml min$^{-1}$ (Sparks et al., 1980; Theis et al., 1988).

Figure 6.1 shows the outflow concentrations in Mahan soil as a function of the solution volume passed through the soil. In order to show that the concentration range of the high concentration experiments did not overlap with the low concentration runs, the concentration is plotted on a logarithmic scale. Clearly, the concentrations are very different and the results may not be comparable, since different ranges of concentrations are considered. It should be noted that the lowest measured concentration with ICP analysis was greater than the input concentration for the low concentration experiments.
Table 6.2. Flow rate, concentrations, and interruption time of the sorption and desorption disk flow experiments.

<table>
<thead>
<tr>
<th>SOIL$^{(1)}$</th>
<th>CASE$^{(2)}$</th>
<th>PROC.$^{(3)}$</th>
<th>-- CONCENTRATION$^{(4)}$ --</th>
<th>q$^{(5)}$</th>
<th>PULSE LENGTH$^{(6)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Zn</td>
<td>Ca</td>
<td>ml/min</td>
</tr>
<tr>
<td>WU</td>
<td>I1</td>
<td>S</td>
<td>2.62 10$^{-5}$</td>
<td>5.01 10$^{-3}$</td>
<td>3.06</td>
</tr>
<tr>
<td>WU</td>
<td>I2</td>
<td>S</td>
<td>2.62 10$^{-5}$</td>
<td>5.01 10$^{-3}$</td>
<td>11.82</td>
</tr>
<tr>
<td>WU</td>
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<td>S</td>
<td>2.51 10$^{-7}$</td>
<td>5.01 10$^{-3}$</td>
<td>8.82</td>
</tr>
<tr>
<td>WU</td>
<td>S2</td>
<td>S</td>
<td>2.51 10$^{-7}$</td>
<td>5.01 10$^{-3}$</td>
<td>8.82</td>
</tr>
<tr>
<td>WU</td>
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<td>S</td>
<td>2.51 10$^{-7}$</td>
<td>5.01 10$^{-3}$</td>
<td>9.48</td>
</tr>
<tr>
<td>WP</td>
<td>I1</td>
<td>S</td>
<td>2.62 10$^{-5}$</td>
<td>5.01 10$^{-3}$</td>
<td>12.27</td>
</tr>
<tr>
<td>WP</td>
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<td>5.01 10$^{-3}$</td>
<td>9.20</td>
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<td>S</td>
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<td>5.01 10$^{-3}$</td>
<td>2.80</td>
</tr>
<tr>
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<td>S2</td>
<td>S</td>
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<td>5.01 10$^{-3}$</td>
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<td>5.01 10$^{-3}$</td>
<td>12.36</td>
</tr>
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<td>9.38</td>
</tr>
<tr>
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<td>10.24</td>
</tr>
<tr>
<td>M</td>
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<td>5.01 10$^{-3}$</td>
<td>9.47</td>
</tr>
<tr>
<td>M</td>
<td>I2</td>
<td>S</td>
<td>2.62 10$^{-5}$</td>
<td>5.01 10$^{-3}$</td>
<td>3.17</td>
</tr>
<tr>
<td>M</td>
<td>S1</td>
<td>S</td>
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<td>5.01 10$^{-3}$</td>
<td>9.43</td>
</tr>
<tr>
<td>WU</td>
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<td>D</td>
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<td>5.01 10$^{-3}$</td>
<td>8.02</td>
</tr>
<tr>
<td>WU</td>
<td>S1</td>
<td>D</td>
<td>0</td>
<td>5.01 10$^{-3}$</td>
<td>3.30</td>
</tr>
<tr>
<td>WU</td>
<td>S2</td>
<td>D</td>
<td>0</td>
<td>5.01 10$^{-3}$</td>
<td>3.10</td>
</tr>
<tr>
<td>WU</td>
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<td>D</td>
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<td>5.01 10$^{-3}$</td>
<td>9.15</td>
</tr>
<tr>
<td>WP</td>
<td>I2</td>
<td>D</td>
<td>0</td>
<td>5.01 10$^{-3}$</td>
<td>8.73</td>
</tr>
<tr>
<td>WP</td>
<td>S1</td>
<td>D</td>
<td>0</td>
<td>5.01 10$^{-3}$</td>
<td>9.29</td>
</tr>
<tr>
<td>WD</td>
<td>I2</td>
<td>D</td>
<td>0</td>
<td>5.01 10$^{-3}$</td>
<td>3.30</td>
</tr>
<tr>
<td>WD</td>
<td>S1</td>
<td>D</td>
<td>0</td>
<td>5.01 10$^{-3}$</td>
<td>3.30</td>
</tr>
<tr>
<td>M</td>
<td>I2</td>
<td>D</td>
<td>0</td>
<td>5.01 10$^{-3}$</td>
<td>9.43</td>
</tr>
</tbody>
</table>

(1) soil: WU - untreated Windsor soil, WP - peroxide treated Windsor soil, WD - peroxide/dithionite treated windsor soil, M - Mahan soil
(2) case: I - analysis by inductively coupled plasma spectrophotometer, S - analysis by liquid scintillation counting, 1,2,3 - replicates
(3) process: S - sorption, D - desorption
(4) concentration: Zn - zinc concentration, Ca - calcium concentration
(5) q: flow velocity in ml/min
(6) pulse l.: pulse length in volume (VOL.) or time (TIME)
(7) T_i: time of how long the flow was interrupted; for the sorption experiments this time refers to the interruption between sorption and desorption experiment
Figure 6.1. Sorption breakthrough of Zn at two concentrations, $2.65 \times 10^{-5}$ and $2.51 \times 10^{-7}$. 
Figure 6.2 shows Zn sorption onto Mahan soil at two different velocities, 3.14 and 10.24 ml min\(^{-1}\). Both curves are almost identical, since they were plotted against the volume of solution passed through the soil. As mentioned above this could mean that the sorption at such a high concentrations (2.62 \(10^{-5}\) M = 1.71 mg L\(^{-1}\)) may be treated as an equilibrium process. Nevertheless, if small amounts of the solute are adsorbed very slowly, the velocity difference may not be sufficient to show significant differences between the runs.

At the low concentration, the stopped flow technique revealed that the sorption can not be represented by equilibrium reactions (Figure 6.3). The interruption, after the sorption breakthrough produced a concentration jump from approximately 95% to about 65% of the input concentration. Furthermore, the interruption during the desorption run clearly reveals that the process is far from equilibrium. More precisely, the concentration jumps from nearly zero to 55% of the input concentration. These findings confirm previous research carried out under batch conditions (Amacher et al., 1986). The fundamental difference between flow and static batch experiments is that under flow conditions the reaction products in the soil solution are continuously removed. In addition, the physical arrangement of the reactive particles does not change. In contrast, in static batch experiments, the reaction products remain in the soil solution and the soil structure is at least partially destroyed. Furthermore, vigorous shaking may break up soil particles and expose new reaction sites. Hence, prolonged kinetics in such conditions could be interpreted as an experimental artifact.
Figure 6.2. Sorption breakthrough of Zn in Mahan soil plotted as a function of the solution volume passed through the column with an input concentration of $2.62 \times 10^{-5}$. 
Figure 6.3. Sorption and Desorption of Zn in Mahan soil (S1) with an input concentration of $2.5 \times 10^{-7}$ and two flow interruptions.
Also, the difficulty encountered in using kinetic data obtained under batch condition for the modelling of the transport may support the hypothesis that batch experiments do not provide the necessary information to describe solute sorption and kinetic retention. Nevertheless, slow sorption kinetics at low concentration are observed under both static batch and dynamic flow conditions.

The untreated Windsor soil exhibits similar behavior; that is the sorption kinetics are most pronounced at low concentrations whereas the local equilibrium assumption may be valid at high concentrations. In order to show the effects of the different treatments of the soil, the sorption breakthroughs of the high concentration ($2.62 \times 10^{-5} M$) are presented in Figure 6.4. The untreated soil shows a step initial increase and a very flat slope approaching the input concentration. The peroxide treated Windsor soil shows somewhat similar behavior. The initial concentration appears slightly later indicating that more Zn was sorbed in the peroxide altered soil than in the untreated soil. The dithionite treated soil differed significantly from the other samples. In particular, the initial concentration increase is less steep and the concentration reaches 95 % of the input concentration at a later time. Obviously, during the same period of time the dithionite treated soil retained more Zn than the other samples. In order to show the results for the low concentration runs a different data representation was chosen.

The low concentration runs with the untreated, peroxide, and peroxide/dithionite treated Windsor soil revealed even more deviation from each other than at the high concentration. Figure 6.5 shows the amount of sorbed Zn as a function of
Figure 6.4. The sorption of Zn in untreated, hydrogen peroxide, and hydrogen peroxide/dithionite treated Windsor soil at flow rates of approximately 3 mL min⁻¹.
Figure 6.5. The amount of Zn sorbed as a function of time in untreated, hydrogen peroxide, and hydrogen peroxide/dithionite treated Windsor soil.
Figure 6.6. The desorption of Zn after a 24 h flow interruption in untreated, hydrogen peroxide, and hydrogen peroxide/dithionite treated Windsor soil.
Figure 6.7. The desorption of Zn in treated and untreated Windsor soil. The relative amount of sorbed Zn is plotted as a function of time after a 24 h interruption.
time as determined with Equation 6.4. Clearly, the untreated soil retained the least amount of Zn, whereas the peroxide treated soil sorbed about twice as much as the untreated soil. The peroxide/dithionite treated soil retained about 4 times as much as the untreated soil for the same sorption time. The desorption curves are presented in Figure 6.6. The recovery after an interruption of 24 h was very low especially for the peroxide and peroxide/dithionite treated soil. In fact, the absolute amount of recovery after 2 h of Ca(NO$_3$)$_2$ leaching for the untreated, hydrogen peroxide, and hydrogen peroxide/dithionite treated samples was in the same order of magnitude varying from 2 to 4 $\mu$mol kg$^{-1}$. However, the relative recovery as well as the shape of the desorption curves are quite different as shown in Figure 6.7. Both the peroxide and peroxide/dithionite treated soil samples exhibit a recovery of approximately 15%, whereas the recovery of the untreated soil is about 50%. Also, the shape of the two treated samples are very similar.

In addition, the stopped flow technique has been applied to the high and low concentration sorption and desorption runs. The results are comparable to the Mahan soil. More precisely, at low concentrations a concentration jump is clearly visible. In fact the concentration jumps for the untreated Windsor soil is lowest with a 50% drop, followed by the peroxide treated sample with a jump from approximately 0.95 to 0.19 C/C$_0$. Similarly, the peroxide/dithionite treated sample exhibits a jump from 0.80 to 0.13 C/C$_0$. This proves that the sorption in all samples are controlled by kinetics. In contrast, the high concentration sorption experiments did not exhibit concentration jumps between the sorption and desorption runs (Figure 6.9). Hence,
the local equilibrium assumption may be valid for the high concentration \((2.62 \times 10^{-5} \text{ M})\) for all soils used in this study.

In order to obtain information on the slow desorption kinetics the flow was stopped after the desorption for the peroxide and peroxide/dithionite treated samples. An interesting phenomenon is the concentration drop of the peroxide/dithionite sample. Obviously, the sorption did not reach equilibrium after the 24 h interruption between the sorption and desorption. Once the flow was stopped during the Ca leaching, the sorption process was still proceeding such that the solution concentration was further reduced. In contrast, the peroxide treated Windsor soil exhibited an increase, clearly showing that the desorption is a kinetic process, too.

In order to interpret these results, it is necessary to discuss the effects of the peroxide and peroxide/dithionite treatment on the sorption behavior of soils. First, the colloidal interactions in soils need to be addressed. Considering that Windsor is an Ap horizon, the organic matter should play an important role in the sorption behavior of metals. In suspensions of soil colloids organic matter coatings occur on minerals such as goethite, as proposed by Altmann and Leckie (1987) and shown by Lion et al. (1982). Furthermore, macro molecules can interact with soil minerals in various ways; e.g. polymers form chains which partially bond specifically or electrostatically to surfaces. Depending on the macromolecule properties, such as the charge, macromolecules form random coils (noncharged), complete collapsed covers on mineral surfaces (cationic), or cation bridging (anionic) (Oades, 1989; Clapp et al., 1991). Furthermore, organic matter and mineral interactions may be a function of the
Figure 6.8. The 24 h flow interruption (arrow) after the low concentration Zn sorption in untreated, hydrogen peroxide, and hydrogen peroxide/dithionite treated Windsor soil.
Figure 6.9. Results of the 24 h flow interruption (arrow) between the Zn sorption and desorption runs at the high concentration pulse of untreated and treated Windsor soil.
Figure 6.10. Flow interruption during the low concentration desorption experiment of the peroxide and peroxide/dithionite treated Windsor soil.
particle size. In particular, organic/mineral complexes may accumulate in either the fine or the coarse fraction of soil clays depending on the pedogenetic process involved in the soil formation. Also, organic matter often encapsulates Fe and Al polycations. In addition, clay particles may cover the coarse fraction of organic matter, especially plant detritus. As can be seen from this brief overview, both inorganic and organic coatings exist in soils. Furthermore, organic matter contributes significantly to aggregate formation.

Iron oxide occurrences play an important role as sorbent in sorption of ions in soil. The most common iron minerals are goethite and ferrihydrite, which was traditionally referred to as amorphous iron oxide (Schwertmann and Taylor, 1989). In contrast to the former, the latter is weakly crystalline and may have a considerably larger specific surface area than goethite samples. The mineral appearance of iron oxide ranges from well crystallized goethite, lepidocrocite, and hematite, among others, which occur as needles, plates, globular or highly porous, irregular, grass like aggregates. Also, goethite often exhibits faults and cracks within the crystal. In addition to the morphological properties iron oxides contribute to the cementation of soil particles and most likely to the aggregate formation (Schwertmann and Taylor, 1989). In this respect the iron oxides have a similar function as organic matter, even though these soil components are significantly different. Therefore, interactions of colloids in soils may contribute to restricted accessibility of sorption sites.

The effect of the above mentioned colloids on the sorption behavior of ions onto soil has been studied by destruction of organic matter and iron oxides. Mangaroo
et al. (1965), Sequi and Aringhieri (1977), Petruzelli et al. (1981), and Shuman (1988) studied the effect of organic matter destruction or alteration on the sorption behavior of metals. When the soil is treated with hydrogen peroxide, the organic matter is altered so that the structures and interactions between the organic and mineral soil components may be destroyed. Hence, new surfaces may be exposed (Sequi and Aringhieri, 1977) and/or existing reaction sites may become more accessible towards metal sorption. Even though new surfaces may be exposed it depends on the reactivity of the surfaces whether or not the sorption capacity is increased. Although the organic matter destruction with hydrogen peroxide is usually incomplete (Oades, 1989), one should expect a decrease in the soil sorption capacity caused by the diminished organic fraction of the soil. However, both a decrease and/or increase of metal sorption capacity and/or cation exchange capacity (CEC) has been observed by Shuman (1988), Petruzelli et al. (1981), Sequi and Aringhieri (1977), and Mangaroo et al. (1965). Nevertheless, a sorption capacity decrease seems to be more often observed than an increase. Also, the CEC of soils primarily quantifies the sorption caused by electrostatic forces. However, specific sorption sites may have been exposed by organic matter removal.

In contrast to the organic matter destruction, the iron oxide removal by the dithionite method commonly results in CEC increase more often than a decrease (Shuman, 1976; Cavallaro and McBride, 1984; Shuman, 1988; Ghabru et al., 1990). Iron oxide coatings exist primarily on the coarse clay fraction, the silt, and the sand fraction. Depending on the nature of this fraction, these coatings may cover reactive
surfaces such as silicate minerals. For example, Ghabru et al. (1990) showed that iron oxide coating was present on weathered biotite. Using the dithionite method the coatings were removed and the cleavage was clearly visible. They also concluded that most of the iron oxides were associated with the iron bearing minerals such as biotite and amphiboles. Also, the iron oxides in the fine clay fraction are usually present as small discrete particles, whereas the iron oxyhydroxide possibly forms coatings on clay minerals. The treatment of minerals and soils with dithionite-citrate solution will generally increase the CEC due to an increase of reactive surface area (Ghabru et al., 1990) and the reduction of structural Fe of clay minerals (Ericsson et al., 1984).

In summary, the overview reveals that colloidal interactions in the soil may be very important for the sorption behavior of metals. Both the organic matter and iron oxides and oxyhydroxides form coatings on other reactive surfaces. Due to these colloidal interactions, reactive surfaces may be unavailable for metal sorption in soils. This may also imply that the accessibility may be restricted by such colloidal behavior. Hence, the kinetics of sorption are influenced by the removal or alterations of these colloids. In addition, when soils are suspended in solutions, the aggregates may break up and expose new surfaces to the solution. Also, vigorous mixing creates abrasion and thus, surface alterations. Therefore, not only chemical alterations of the colloidal composition, but also, mechanical changes may cause increased reactivity. This may be one reason why sorption data obtained from batch experiments may not agree with those obtained from column studies.
Considering that Windsor soil is an entisol, one expects that it contains parent material, which has not been completely weathered to secondary minerals. In fact, after drying the peroxide/dithionite treated sample, mica in the silt and sand fraction were visible which clearly indicated presence of mica and probably other silicate minerals in the coarse fraction of the soil. After removal of organic matter and iron oxides these minerals may provide reactive surface sites for the sorption of metals similar to the findings of Ghabru et al. (1990). Therefore, the increased sorption after both treatments can be explained by the exposures of new reactive surfaces. The findings concerning the increased sorption capacity are consistent with the findings of previous studies. However, there is marked difference between the low and high concentration of Zn applied to the soils. The difference between the untreated, the peroxide, and the peroxide/dithionite treated Windsor soil is most pronounced at low concentrations. One may speculate that more specific sites have become available through the different treatments. At high concentrations this increase of specific sites may simply not be significant.

The kinetics of the sorption process in the dithionite treated soil sample seems to extend for several weeks as indicated by the interruption test during the Ca leaching. Furthermore, since the desorption kinetics of the treated soil are considerably slower than that of the untreated Windsor soil, possible diffusion into soil minerals or surface controlled reactions may have caused this behavior. Also, since the shape of the desorption curves of the untreated soil exhibits an initial steep drop,
considerable amounts of Zn bound weakly seems to have been released quicker than the remaining sorbed Zn.

6.5. Summary and Conclusions

Disk flow experiments have been used to show that Zn sorption and desorption is a kinetic process especially at concentrations of $10^{-7}$ M in an ultisol and an entisol. Interruption tests were carried out at the termination of the sorption step and prior to and during the desorption experiments at low concentrations ($2.5 \times 10^{-7}$ M). The interruption tests revealed that the high concentration experiments are nearly in an instantaneous equilibrium state. This confirms the findings of previous batch experiments. The interruption test during the desorption runs showed that the desorption process may be very slow, such that the processes involved may be viewed as irreversible for periods of time in the order of hours and days. Also, the destruction of the organic matter with hydrogen peroxide, and the removal of iron oxides and iron oxyhydroxides by the dithionite treatment in the Windsor soil doubled and quadrupled the sorption of Zn at low concentration, respectively. Furthermore, the removal of the iron oxides prolonged the sorption kinetics considerably. This effect was less pronounced for the organic matter removal. The prolonged sorption kinetics may be attributed to the exposure of new less accessible sites. Also, since iron minerals exhibit slow sorption (in the order of weeks) caused by either diffusion into the lattice (Brümmer et al., 1988) or surface precipitation (Dzombak and Morel, 1986) similar processes may cause the slow desorption. In addition, the interaction
of organic matter and secondary iron minerals with other minerals such as coatings and aggregate formation may have reduced the accessibility of reactive surfaces. Hence, a change of colloidal interaction due to the mixing environment may create the observed differences between the batch and columns results. Moreover, the interaction of soil minerals and organic matter should be viewed in terms of soil genesis and micromorphology of the soil components.
CHAPTER 7

SUMMARY AND CONCLUDING REMARKS

This study was conducted to determine various factors influencing the heavy metal transport as measured under controlled laboratory conditions. It was assumed that soil is a chemical heterogeneous system (Chapter 1). The assumption is supported by the fact that chemical models are very difficult to apply successfully without relaxing the underlying assumption of a particular model. Hence, a mechanistic model may then be viewed as an empirical modelling approach.

In this light, the 'parameter lumping' as presented by Altmann and Leckie (1987) is reviewed and applied to water-saturated reactive solute transport in soils (Chapter 2). The description of chemical heterogeneity by various site affinity distribution functions are critically discussed and derived. The relationship between the site affinity distribution function and the transport behavior of reactive solutes was deduced from the sensitivity analysis of the heterogeneity factor. Specifically, the effect of the heterogeneity factor on the breakthrough curves is directly related to the shape and appearance of the site affinity distribution function. Sensitivity analysis revealed that the ratio of maximum sorption capacities of sites and the input solution concentration are most influential on the retardation of the solute front, whereas the heterogeneity factor and affinity coefficient determine the shape of the breakthrough curves.

Since simple isotherm equations such as the Langmuir and Freundlich equations may not describe heavy metal retention adequately over large concentration
ranges (Kinniburgh, 1986), special cases of a generalized isotherm equation were applied to the sorption of Zn and Cd in two acidic soils at 24 and 288 h equilibration times (Chapter 3). The general Langmuir-Freundlich equation provided best predictions of our transport results. Ion exchange experiments of Zn-Ca and Cd-Ca in both soils were successfully described by the Rothmund-Kornfeld equation. When applying these isotherms to transport of Zn in Windsor soil at nearly constant and variable ionic strength, the predicted breakthrough curves were in good agreement with the measured data. However, Cd transport was only qualitatively predicted. The predicted breakthrough curves of Zn and Cd in Olivier soil using isotherm equations and assuming that local equilibrium is valid did not agree with measured data. Employing a mass transfer coefficient, the predictions were slightly improved. Different transport behavior of Zn in Olivier and Windsor soils was attributed to the differences in the mineralogical composition and the structural properties, such as presence of aggregates. Nevertheless, at high concentrations the local equilibrium assumption was valid for Zn transport in Windsor soil.

The use of different equilibration times revealed that the sorption of Zn is time dependent especially at low concentrations. In fact, the kinetics of sorption was most pronounced at the lowest initial concentrations of 0.01 mg L\textsuperscript{-1} whereas fast kinetics was observed at the highest initial concentration of 100 mg L\textsuperscript{-1}. The data of the sorption kinetics of Zn were examined using multireaction and second-order multisite models (Chapter 4). In order to describe the data five pseudo rate coefficients were needed. Furthermore, the rate coefficients were dependent on the initial concentration
and were not related to the 'fitted' affinity coefficients of the Freundlich and Langmuir equations. Therefore, these multisite models are only valid for very narrow concentration ranges and are descriptive tools rather than true useful predictive models.

In order to overcome the shortcomings of these single solute multisite models a new kinetic model was developed (Chapter 5). The basic assumptions for this model can be listed as follows: (i) a low affinity competitive site controls Ca-Zn ion exchange, (ii) a high affinity noncompetitive site control by higher energy bonding of Zn with surface functional groups Ca cannot compete for, (iii) both sites may be heterogeneous so that the affinity increases with decreasing Zn sorption, (iv) the maximum sorption capacity of the competitive site is approximately equivalent to the sum of exchangeable cations, (v) maximum sorption capacity of the high affinity sites are considerable lower than that of the low affinity competitive site, (vi) the kinetics of the competitive site is diffusion controlled and can be described with a mass transfer coefficient, (vii) the kinetics of the high affinity site is described by pseudo rate coefficients, and (viii) an additional irreversible process may be described empirically by a second order reaction. This model may be classified as an empirical two species/multisite model. The kinetic data of batch and disk flow experiments were well described by this model. The model was successfully used to predict the kinetics as a function of Zn loading on Windsor soil. Both experimental data and model predictions revealed that the ion exchange process is a fast one, prevails at high concentrations, and may be described using the local equilibrium assumption.
The Windsor soil used for the kinetic study is a heterogeneous surface soil and hence the soil components which control the sorption behavior are unknown. In order to describe the effects of organic matter and iron oxides on the sorption process, these fractions were removed using hydrogen peroxide and dithionite methods, respectively (Chapter 6). The thin disk experiments revealed that the removal of both soil components increased the sorption, especially at low concentrations, and slowed the rate of reaction. It was concluded that iron coatings and colloidal interactions may be responsible for the difference in the sorption behavior for the treated samples and untreated samples. These colloidal interactions may be viewed as a result of soil genesis. Therefore, kinetics of heavy metal sorption in soil may be strongly related to the micromorphology and mineralogy of soils.

Even though this study includes various experimental techniques applied to various solute concentration ranges, the results from the batch, short column, and long column experiments show certain commonalities. That is, heavy metals such as Zn or Cd behave essentially as exchangeable ions at high concentrations, competing with alkaline earth ions such as Ca. At low concentrations, specific interactions dominate sorption, kinetics and transport. In particular, Zn sorption in Windsor soil can be described as an equilibrium process for concentration above 0.1 mM, below this concentration level kinetic processes may control the overall transport behavior considering a time frame ranging from several minutes to one month. This study also shows that batch techniques may be useful to obtain equilibrium sorption data,
however, the sorption kinetics which are significant for transport processes are best obtained using flow methods where the soil remains less disturbed.

Future research should, therefore, address the measurement of sorption data for transport phenomena. Although, soil testing methods have become almost standardized, the application of soil testing results to transport studies are questionable. Hence, modifications of these tests may be appropriate in order to accommodate the needs for transport predictions. Empirical models need to be rigorously related to processes and methods for determining model parameters independently should be developed.
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Christoph Hinz
Dept. of Civil Engineering
Louisiana State University
Baton Rouge, LA 70803-6405

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Christoph Hinz was born October 25, 1959 in Rheine, Federal Republic of Germany. He was raised in Lingen (Ems), Germany, and in 1978 he graduated from the 'Technisches Gymnasium', Nordhorn. In Fall 1979 he entered the Geology program at the Justus-Liebig University, Giessen and transferred to the Technical University (Rheinisch-Westfälische Technische Hochschule), Aachen in 1981. From spring 1984 to spring 1985 he was a visiting student at the Agriculture Research Organization, the Volcani Center, Institute of Soils and Water, in Israel. He graduated with the degree 'Diplom-Geologe' from the Technical University of Aachen in spring 1986. Since Fall of 1986 he has been enrolled in the Ph.D. program in the Department of Agronomy, and since the Summer of 1991 also in the M.S. program in Engineering Science with the emphasis on environmental engineering.
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