

Modeling Approaches of Competitive Sorption and Transport of Trace Metals and Metalloids in Soils: A Review

H. M. Selim* and Hua Zhang

Competition among various heavy metal species for available adsorption sites on soil matrix surfaces can enhance the mobility of contaminants in the soil environment. Accurate predictions of the fate and behavior of heavy metals in soils and geologic media requires the understanding of the underlying competitive-sorption and transport processes. In this review, we present equilibrium and kinetic models for competitive heavy metal sorption and transport in soils. Several examples are summarized to illustrate the impact of competing ions on the reactivities and mobility of heavy metals in the soil-water environment. We demonstrate that equilibrium Freundlich approaches can be extended to account for competitive sorption of cations and anions with the incorporation of competition coefficients associated with each reaction. Furthermore, retention models of the multiple-reaction type including the two-site nonlinear equilibrium-kinetic models and the concurrent- and consecutive-multireaction models were modified to describe commonly observed time-dependent behaviors of heavy metals in soils. We also show that equilibrium Langmuir and kinetic second-order models can be extended to simulate the competitive sorption and transport in soils, although the use of such models is limited due to their simplifying assumptions. A major drawback of the empirically based Freundlich and Langmuir approaches is that their associated parameters are specific for each soil. Alternatively, geochemical models that are based on ion-exchange and surface-complexation concepts are capable of quantifying the competitive behavior of several chemical species under a wide range of environmental conditions. Such geochemical models, however, are incapable of describing the time-dependent sorption behavior of heavy metal ions in competitive systems. Further research is needed to develop a general-purpose model based on physical and chemical mechanisms governing competitive sorption in soils.

SOIL CONTAMINATION of heavy metals such as Cd, Cu, Hg, Pb, Ni, Zn, As, and Cr from mining, industrial, agricultural, and geologic sources poses serious environmental risk worldwide. Several of the elements are on top of the priority pollutants list because of their toxicity to humans and the ecosystem (Adriano, 2001). Transport of heavy metals in the vadose zone and aquifers can lead to further pollution of surface and groundwater (Selim and Amacher, 1997).

During the last three decades, a large number of studies have been performed to identify the dominant controlling mechanisms for the fate and overall behavior of heavy metals in the soil-water environment. Most investigations have focused on describing the sorption and transport of heavy metals under field conditions and in laboratory and greenhouse experiments. Adsorption-desorption on the surface of solid minerals and organic matter is one of the dominant reactions impacting the fate and transport of heavy metals in soils. In contaminated sites, several heavy metal species are often encountered in the soil-water environment. Competition among the various heavy metal species for available adsorption sites on soil matrix surfaces is a commonly observed phenomenon (Murali and Aylmore, 1983; Kretzschmar and Voegelin, 2001; Bradl, 2004; among others). In fact, competitive adsorption and desorption of heavy metals by minerals and soil organic matter has significant importance for their fate and mobility in soils and aquifers. Selective sorption among competing heavy metal ions may greatly impact their bioavailability in soils (Gomes et al., 2001). Enhanced mobility as a result of competitive sorption has often been observed for several trace metal contaminants in soils.

The adsorption of heavy metal by clay minerals, metal oxides, and organic materials has generally been explained by two types of reaction mechanisms: (i) ion exchange in the diffuse layer as a result of electrostatic forces and (ii) surface complexation through the formation of strong covalent bonds between heavy metal ions and specific reaction sites on the surfaces of minerals or organic matters. The ion-exchange reaction is also referred to as *nonspecific sorption* and the surface complexation is referred to as *specific sorption* (Sposito, 1994; Sparks, 1998). A variety of models have been developed with the specific goal of predicting the competitive-sorption behavior of heavy metals in soils. Equilibrium ion-exchange models and surface-complexation

Copyright © American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America. 5585 Guilford Rd., Madison, WI 53711 USA. All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

J. Environ. Qual. 42:640–653 (2013)

doi:10.2134/jeq2012.0323

Received 21 Aug. 2012.

*Corresponding author (mselim@agctr.lsu.edu).

H.M. Selim, School of Plant, Environmental, and Soil Sciences, Louisiana State Univ., Baton Rouge, LA 70803; H. Zhang, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China. Assigned to Associate Editor Andrew Tye.

Abbreviations: SRS, Sheindorf-Rebhun-Sheintuch.

models have been incorporated into geochemical models to simulate reactions among multiple heavy metals in the soil-water environment (Allison et al., 1991; Tipping, 1994; Kinniburgh et al., 1996; Hiemstra and Van Riemsdijk, 1999; Parkhurst and Appelo, 1999). Such models were used to simulate with varying degree of success the competitive sorption and transport of several heavy metals in soils and aquifers (e.g., Smith and Jaffé, 1998; Serrano et al., 2009). Geochemically based models, however, require a detailed description of chemical and mineral composition of solution and porous media, as well as numerous reaction constants. In fact, several of the required parameters are either unavailable or unreliable under most conditions (Goldberg and Criscenti, 2008). Moreover, the inherent heterogeneity of natural porous media often impedes the application of chemical reaction based models. As a result, sorption reactions are frequently simulated using empirical models of the equilibrium type such as the Freundlich and Langmuir (e.g., Kinniburgh, 1986; Selim, 1992; Janetti et al., 2012). A major advantage of empirical models is their simplicity. Unlike the complex surface-complexation models, equilibrium models can be applied to a wide range of conditions with a minimal number of adjustable parameters. A major limitation of the empirical models is that the model parameters are not applicable outside the specific conditions under which the parameters were obtained. Numerous studies have demonstrated that the fitted Freundlich and Langmuir parameters depend heavily on environmental conditions including pH, ionic strength, reaction time, and competing ions (e.g., Mesquita and Vieira e Silva, 2002; Heidmann et al., 2005; Arias et al., 2006; Zhu et al., 2010).

In most geochemical models, sorption processes are often considered as instantaneous where equilibrium conditions are attained in a relatively short time (minutes or several hours). Traditionally, heavy metal sorption studies have been performed based on batch equilibration experiments within a short period of reaction time (hours or days). In the last two decades, numerous studies have demonstrated the lack of reaction equilibrium of contaminants in soils (e.g., Selim 1992; Tye et al., 2003; Crout et al., 2006; Bearup et al., 2012). Laboratory experiments using kinetic approaches have demonstrated that sorption of most reactive chemicals in soils was time dependent at various time scales (Selim and Amacher, 1997). For several heavy metals, a slow but significant reaction phase may exist due to (i) the transport of ion species from bulk solution to the reaction sites on mineral surfaces and (ii) the chemical kinetics of reactions such as ion exchange, the formation of inner sphere surface complexes, precipitation into distinct solid phases, or surface precipitation on minerals. According to Sparks (1998), the kinetics of adsorption-desorption need to be considered for accurate simulation of the fate of heavy metals in the soil-water environment. More recently, several time-dependent experiments have demonstrated the significant influence of competitive sorption on the reaction rates of metals and metalloids in soils (Waltham and Eick, 2002; Shi et al., 2005; Zhang and Selim, 2008).

Retention and Transport

Competitive sorption of interacting ions often results in complex breakthrough patterns during their transport in soils and geologic media. Therefore, describing heavy metal transport

requires retention models that account for their governing mechanisms. The one-dimensional reactive convective-dispersive transport equation is the most frequently used model for describing the transport of dissolved chemicals in soils (Selim, 1992):

$$\frac{\partial \theta C_i}{\partial t} + \rho \frac{\partial S_i}{\partial t} = \frac{\partial}{\partial z} \theta D \frac{\partial C_i}{\partial z} - \frac{\partial q C_i}{\partial z} \quad [1]$$

where S is the amount of adsorption (mg kg^{-1}), C is the dissolved concentration (mg L^{-1}), i indicates i th component in the system, D is the dispersion coefficient ($\text{cm}^2 \text{h}^{-1}$), q is Darcy's water flux density (cm h^{-1}), θ is the soil moisture content ($\text{cm}^3 \text{cm}^{-3}$), ρ is the soil bulk density (g cm^{-3}), z is distance (cm), and t is the reaction time (h). Retention reactions of a solute from the soil solution by the matrix of soils and geologic media is accounted for by the term $\partial S_i / \partial t$ in Eq. [1]. Retention reactions of heavy metals have been quantified based on several approaches. A number of transport models simulate heavy metal sorption based on the local equilibrium assumption (LEA), in which the reaction of an individual solute species in the soil is assumed to be sufficiently fast and an apparent equilibrium may be observed at a time scale considerably shorter than that of transport processes. The local equilibrium assumption is the basis for several commonly used models including ion-exchange, surface-complexation, Freundlich, and Langmuir models. A discussion of the various models from the perspective of competitive sorption and transport is given below. In contrast to the LEA, for most heavy metals, time-dependent retention in soils has been commonly observed (for a review, see Zhang, 2011). As a result, a number of formulations have been introduced to describe their kinetic sorption behavior in soils. Models that account for time-independent reactions have been incorporated into the convective-dispersive transport Eq. [1] to predict the movement of heavy metals in soils. Examples of kinetic models include the first-order, Freundlich kinetic, irreversible, and second-order models. Commonly used equilibrium and kinetic models are summarized in Table 1.

Another class of models is that of the multireaction, multistep, or multisite equilibrium-kinetic models. Basic to multireaction and multisite models is the idea that the soil is a heterogeneous system with different constituents (clay minerals, organic matter, Fe and Al oxides, carbonates, etc.), with sites having different affinities or energies for heavy metal sorption.

Table 1. Equilibrium and kinetic retention models.

Model	Formulation†
Linear equilibrium	$S = K_d C$ (Eq. [5])
Freundlich equilibrium	$S = K_f C^n$ (Eq. [4])
Langmuir equilibrium	$S/S_r = K_L C / (1 + K_L C)$ (Eq. [9])
First-order kinetic	$\partial S / \partial t = k_f (\theta / \rho) C - k_d S$ (Eq. [2])
Freundlich kinetic	$\partial S / \partial t = k_f (\theta / \rho) C^n - k_d S$ (Eq. [3])
Langmuir kinetic	$\rho (\partial S / \partial t) = k_f \theta (S_{\max} - S) C - k_d \rho S$
Irreversible (sink-source)	$\partial S / \partial t = k_s (\theta / \rho) (C / C_p)$
Pseudo-first-order kinetic	$\partial S / \partial t = \kappa (S_{\text{eq}} - S)$
Pseudo-second-order kinetic	$\partial S / \partial t = \omega (S_{\text{eq}} - S)^2$
Second-order irreversible	$\partial S / \partial t = k_s (\theta / \rho) C (S_{\max} - S)$
Kinetic power model	$\partial S / \partial t = K (\theta / \rho) C^n S^m$
Mass transfer	$\partial S / \partial t = K (\theta / \rho) (C - C^*)$

† S_{\max} , maximum sorbed amount; S_{eq} , amount sorbed at equilibrium; k_f , κ , and ω , rate coefficients (d^{-1}); n and m , dimensionless parameters.

Therefore, a heavy metal species is likely to react with various constituents (sites) by different mechanisms. As a result, a single equilibrium or chemical kinetic reaction is unlikely to be the dominant mechanism in heterogeneous soils with multiple sites having different energies for heavy metal sorption. Below, an overview of multireaction and multisite models and simulations in competitive systems is presented. Table 2 provides a summary of the various competitive models discussed.

First-Order and Freundlich Models

The first-order kinetic approach is perhaps one of the earliest single forms of reactions used to describe sorption with time for several dissolved chemicals in soils. This may be written as

$$\frac{\partial S}{\partial t} = k_f \left(\frac{\theta}{\rho} \right) C - k_b S \quad [2]$$

where the parameters k_f and k_b represent the forward and backward rates of reactions (h^{-1}), respectively, for the retention mechanism. The first-order reaction was first incorporated into the classical convection–dispersion equation by Lapidus and Amundson (1952) to describe solute retention during transport under steady-state water flow conditions.

Based on Eq. [2], for any reaction time t , a linear relation between S and C is obtained. In other words, first-order kinetics yields isotherms, which represent the amount sorbed S vs. the concentration in solution C , a linear relationship, for any given time of reaction; however, linear isotherms are not often encountered for heavy metals in soils. In fact, there is an extensive body of literature that documents the nonlinear behavior of sorption isotherms (for a review, see Sauvé et al., 2000). Isotherms that exhibit nonlinear or curvilinear retention behavior are illustrated in Fig. 1 to 3 for Cu, As(V), and Ni, respectively (Selim and Ma 2001; Zhang and Selim, 2005; Liao and Selim, 2010). To describe such nonlinear behavior, the first-order model of Eq. [2] is extended to include nonlinear kinetics:

$$\frac{\partial S}{\partial t} = k_f \left(\frac{\theta}{\rho} \right) C^b - k_b S \quad [3]$$

where b is a dimensionless parameter commonly <1 . Estimated values for b for the isotherms illustrated in Fig. 1 to 3 were 0.601 to 0.696 for Cu, 0.221 to 0.328 for As(V), and 0.545 to 0.515 for Ni. Such values illustrate that b is time invariant and may be considered a sorption characteristic for a given soil. This nonlinear reaction (Eq. [3]) is fully reversible, where the magnitudes of the rate coefficients dictate the extent of kinetic behavior of retention of the solute from the soil solution. For small values of k_f and k_b , the rate of retention is slow, and strong kinetic dependence is anticipated. In contrast, for large values of k_f and k_b , the retention reaction is a rapid one and should approach quasi-equilibrium in a relatively short time. In fact, at large times, when the rate of retention approaches zero, Eq. [3] yields

$$S = K_F C^b, \text{ where } K_F = \left(\frac{\theta k_f}{\rho k_b} \right) \quad [4]$$

Equation [4] is analogous to the Freundlich equilibrium equation (Kinniburgh, 1986), where K_F is the solute partitioning coefficient ($\text{cm}^3 \text{g}^{-1}$). Therefore, the parameter K_F may be regarded as the ratio of the rate coefficients for sorption (forward reaction) to that for desorption or release (backward reaction).

The parameter b represents the order of the nonlinear or concentration-dependent reaction and illustrates the extent of heterogeneity of sorption sites on soil matrix surfaces. In other words, sorption sites have different affinities for heavy metal retention by matrix surfaces, where sorption by the highest energy sites takes place preferentially at the lowest solution concentrations before sites of lower energies. At increasingly higher concentration, sorption takes place at sites of decreasing affinities, which results in nonlinear or concentration-dependent isotherms of S vs. C . A direct implication of such nonlinear behavior is that at low concentrations, solutes are considerably less susceptible to transport than at higher concentrations.

For the simple case where b in Eq. [4] is 1, we have the commonly used linear form:

$$S = K_d C, \text{ where } K_d = \left(\frac{\theta k_f}{\rho k_b} \right) \quad [5]$$

where the parameter K_d is the solute distribution coefficient ($\text{cm}^3 \text{g}^{-1}$), which is distinctly different from the Freundlich parameter K_F . There are numerous examples of K_d values for the retention of various cations and heavy metals (see Sparks, 1989; Buchter et al., 1989; Sauvé et al., 2000). The lack of nonlinear or concentration-dependent behavior of sorption patterns, as indicated by the linear case of Eq. [5], is indicative of a homogeneous system. For linear behavior, the sorption-site energies of matrix surfaces are best regarded as relatively uniform, and the mobility of a heavy metal is independent of the concentration in the soil solution.

Second-Order and Langmuir Models

An alternative to first- and n th order models is the second-order kinetic approach. Such an approach is commonly referred to as the *Langmuir kinetic model* and has been used for predictions

Table 2. Competitive retention models.

Model	Formulation
Sheindorf–Rebhun–Sheintuch equilibrium model	$S_i = K_i C_i (\sum_{j=1}^I \alpha_{ij} C_j)^{n_i - 1}$ (Eq. [10])
Sheindorf–Rebhun–Sheintuch kinetic model	$\partial(S_i)/\partial t = k_{i,j} (\theta/\rho) C_i (\sum_{j=1}^I \alpha_{ij} C_j)^{n_i - 1} - k_{d,i} (S_i)$ (Eq. [19])
Competitive Langmuir equilibrium model	$S_i/S_{\max} = K_i C_i / (1 + \sum_{j=1}^I K_j C_j)$ (see Eq. [9])
Competitive Langmuir kinetic model	$\partial S_i / \partial t = (\lambda_i) (\theta/\rho) C_i (S_{\max} - \sum_{j=1}^I S_j) - (\lambda_b) S_i$ (Eq. [12])
Vanselow ion exchange	${}^V K_{ij} = [(a_i^*)^{v_j} / (a_j^*)^{v_i}] [(C_j)^{v_j} / (C_i)^{v_i}]$ (Eq. [23–24])
Gaines and Thomas ion exchange	${}^G K_{ij} = [(\gamma_j)^{v_j} / (\gamma_i)^{v_i}] (S_j/C_j)^{v_j} (S_i/C_i)^{v_i}$ (Eq. [25])
Rothmund–Kornfeld ion exchange	$(S_j)^{v_j} / (S_i)^{v_i} = {}^R K_{ij} [(C_j)^{v_j} / (C_i)^{v_i}]^n$ (Eq. [26])
Elovich ion exchange	$\partial S_i / \partial t = a \exp(-BS)$ (Eq. [30])
Fractional power model	$S_i = \kappa t^\beta$ (Eq. [31])
Parabolic diffusion model	$S_i / (S_{\text{eq},i}) = (4/\sqrt{\pi}) \sqrt{(D_m t / r^2)} - (D_m t / r^2)$ (Eq. [29])

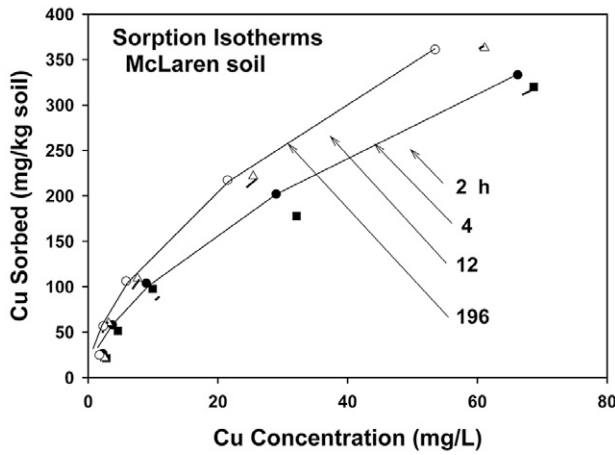


Fig. 1. Adsorption isotherms for Cu on McLaren soil at different retention times.

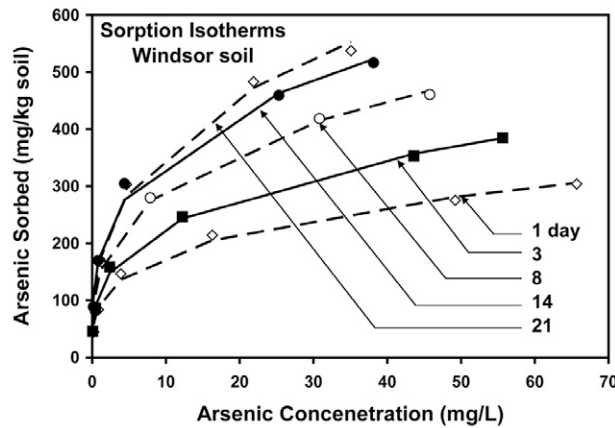


Fig. 2. Adsorption isotherms for As(V) on Windsor soil at different retention times.

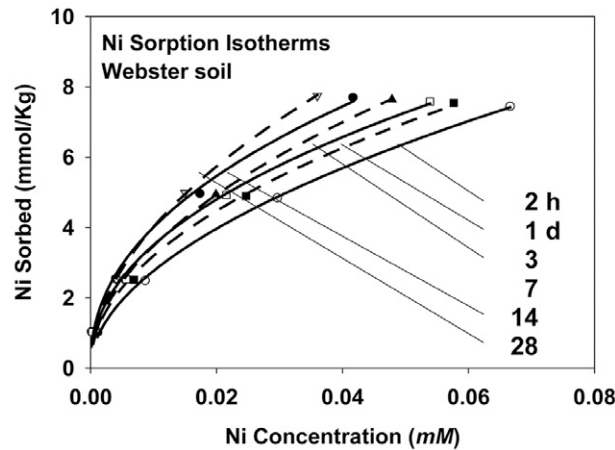


Fig. 3. Adsorption isotherms for Ni on Webster soil at different retention times. The solid and dashed curves are based on the Freundlich equation.

of several reactive solutes, including heavy metals, in several soils (Murali and Aylmore, 1983; Selim and Amacher, 1997). Based on the second-order formulation, it is assumed that the retention mechanisms are site specific, where the rate of reaction is a function of the solute concentration present in the soil solution phase (C) and the amount of available or unoccupied sites, ϕ ($\mu\text{g g}^{-1}$ soil), by the reversible process

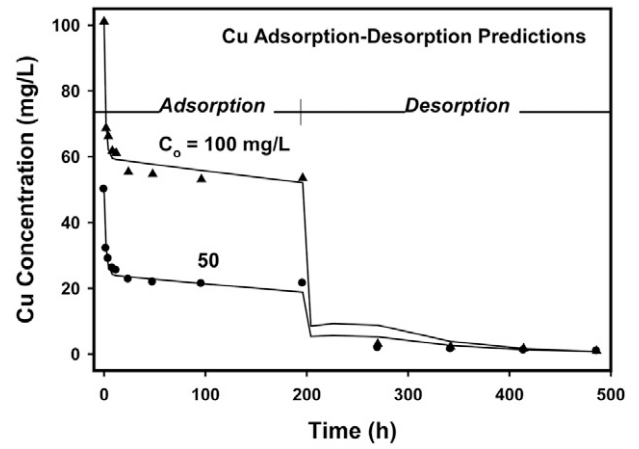


Fig. 4. Experimental results of Cu in soil solution for McLaren soil vs. time during adsorption and desorption for initial concentration $C_o = 50$ and 100 mg L^{-1} . The solid curves are simulations using the second-order model.



where k_f and k_b are the associated rate coefficients and S is the total amount of solute retained by the soil matrix. As a result, the rate of solute retention may be expressed as

$$\begin{aligned} \rho \frac{\partial S}{\partial t} &= k_f \theta \phi C - k_b \rho S \\ &= k_f \theta (S_T - S) C - k_b \rho S \end{aligned} \quad [7]$$

where S_T is the total number of sorption sites. As the sites become occupied by the retained solute, the number of vacant sites approaches zero ($\phi \rightarrow 0$) and the amount of solute retained by the soil approaches that of the total capacity of sites, i.e., $S \rightarrow S_T$. Vacant specific sites are not strictly vacant. They are assumed occupied by H, OH, or other specifically sorbed species. An example of the capability of this kinetic approach in describing the retention of heavy metals in soils is illustrated in Fig. 4. Copper adsorption with time in a McLaren soil was well described by the model across a wide range of input Cu concentrations. Model predictions for adsorption as well as desorption for two initial Cu concentrations are illustrated in Fig. 4.

The above formulation (Eq. [7]) yields the commonly known Langmuir equilibrium model for adsorption on solid surfaces. For large times (as $t \rightarrow \infty$), i.e., when the reaction achieves local equilibrium, the rate of retention becomes

$$k_f \theta \phi C - k_b \rho S = 0, \text{ or } \frac{S}{\phi C} = \left(\frac{\theta}{\rho} \right) \frac{k_f}{k_b} = \omega \quad [8]$$

where ω is the ratio of the forward and backward rate coefficients. Upon further rearrangement of Eq. [8], the second-order formulation, at equilibrium, obeys the widely recognized Langmuir isotherm equation (Kinniburgh, 1986):

$$\frac{S}{S_T} = \frac{K_L C}{1 + K_L C} \quad [9]$$

where the parameter K_L is now equivalent to ω of Eq. [8] and is the Langmuir equilibrium constant. Langmuir formulation is often

expressed in a similar form to Eq. [9], where the total amount sorbed, S_{p} , is replaced by the maximum sorbed amount, S_{max} .

Competitive Retention Models

It is generally accepted that competing ions strongly affect heavy metal retention and release in soils. Industrial waste and sewage sludge disposed of on land often contain appreciable amounts of heavy metal such as Cu, Zn, Cd, and Ni and thus create a risk for croplands, as well as animals and humans. Several competitive models of the equilibrium and kinetic type have been developed to describe reactivities and mobility in multiple-ion systems. An example of metal ion competition is presented in the traditional manner as isotherms in Fig. 5 and 6 (Liao and Selim, 2009). These isotherms were described using the Freundlich model. The extent of nonlinearity of Ni and Cd isotherms are depicted by the dimensionless parameter b and are not influenced by the input concentration of the competing ion. For Windsor and Olivier soils, Ni adsorption decreased significantly across

the entire range of concentrations of the competing ion (Cd); however, Cd adsorption was less affected by the competing Ni ions in both soils. For the neutral Webster soil, Ni was not appreciably affected by the presence of Cd, especially at low Ni concentrations. This may be due to the fact that, for a single-component system, Ni adsorption was much stronger than Cd for the Webster soil. Another explanation of the competitive Ni sorption behavior is that retention is perhaps due to Ni-layered double hydroxide precipitates, which may be considered irreversible on soils and minerals (Voegelin and Kretzschmar, 2005). This process may lead to significant long-term stabilization of the metal within the soil profile (Ford et al., 1999).

Sheindorf–Rebhun–Sheintuch Model

The Sheindorf–Rebhun–Sheintuch (SRS) equation was developed to describe competitive or multicomponent sorption where it is assumed that single-component sorption follows the

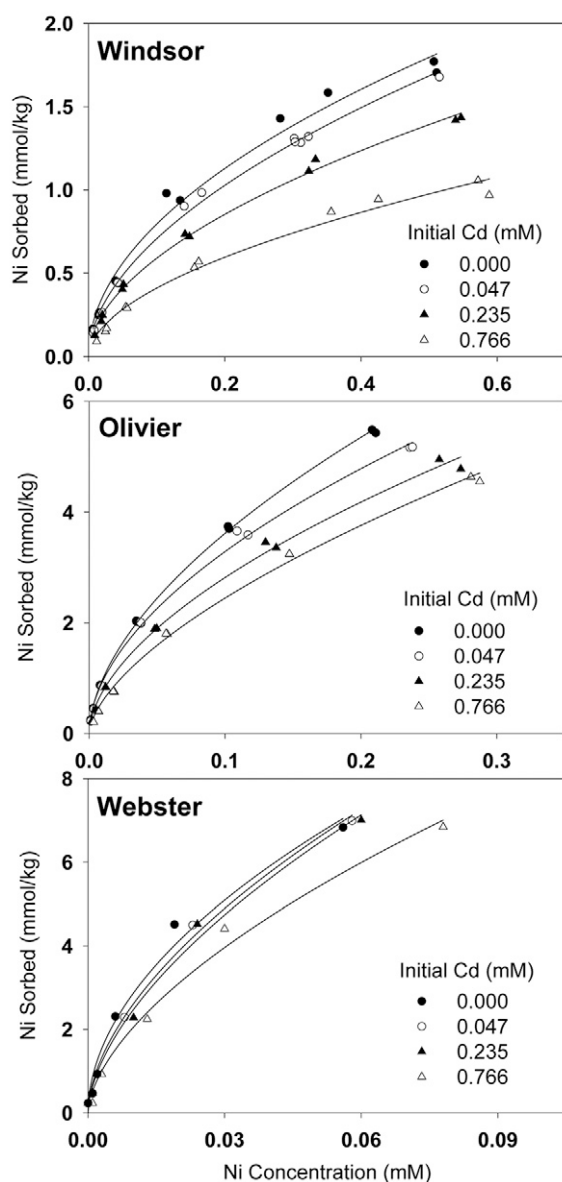


Fig. 5. Competitive adsorption isotherms for Ni in the presence of different concentrations of Cd. Solid curves are Freundlich model calculations.

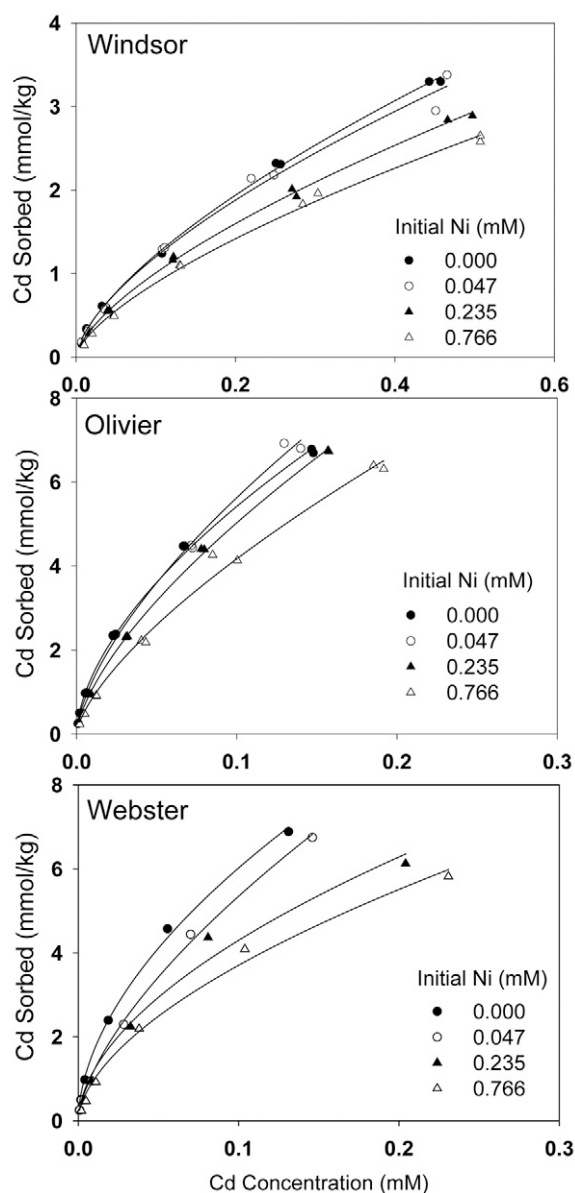


Fig. 6. Competitive adsorption isotherms for Cd in the presence of different concentrations of Ni. Solid curves are Freundlich model calculations.

Freundlich equation (Sheindorf et al., 1981). The derivation of the SRS equation was based on the assumption of an exponential distribution of adsorption energies for each component. Specifically, the SRS model was developed to describe competitive equilibrium sorption for multicomponent systems where the sorption isotherms of a single component follow the Freundlich equation. A general form of the SRS equation can be written as

$$S_i = K_i C_i \left(\sum_{j=1}^l \alpha_{ij} C_j \right)^{n_i} \quad [10]$$

where the subscripts i and j denote metal components i and j , l is the total number of components, and α_{ij} is a dimensionless competition coefficient for the adsorption of component i in the presence of component j . The parameters K_i and n_i are the Freundlich parameters representing a single-component system i as described in Eq. [4] above. By definition, α_{ij} equals 1 when $i = j$. If there is no competition, i.e., $\alpha_{ij} = 0$ for all $j \neq i$, Eq. [10] yields a single-species Freundlich equation for component i identical to Eq. [4]. The estimated $\alpha_{\text{Ni-Cd}}$ values for Ni adsorption in the presence of Cd were larger than 1 for the Windsor and Olivier soils, indicating a noticeable decrease of Ni in the presence of Cd. In contrast, the $\alpha_{\text{Ni-Cd}}$ for Ni adsorption on the Webster soil was <1 , which is indicative of little influence of competing Cd ions (Liao and Selim, 2009). These results are in agreement with the competitive sorption reported by Antoniadis and Tsadilas (2007). Such small $\alpha_{\text{Ni-Cd}}$ implies that Ni adsorption in the Webster soil was least affected in a competitive Ni–Cd system in comparison with the other two soils. Moreover, the estimated $\alpha_{\text{Cd-Ni}}$ for Cd adsorption was 0.61 for Windsor and 0.82 for Olivier soils, whereas the Cd–Ni competitive coefficient was 4.00 for the Webster soil. Although the SRS equation may be regarded as a multicomponent model and does not imply certain reaction mechanisms, differences in competitive sorption between the neutral and the two acidic soils were illustrated based on the SRS models' competitive selectivity parameters. In fact, Roy et al. (1986) suggested that the SRS parameters could be used to describe the degree of competition under specific experimental conditions. Calculated results using the estimated $\alpha_{\text{Ni-Cd}}$ are given in Fig. 7 and 8 and illustrate the capability of the SRS model to describe experimental data for competitive adsorption of Ni and Cd (Liao and Selim, 2009). An F test indicated that there was no statistical difference between our experimental results and SRS model calculations (at the 95% confidence level). Based on these calculations, the SRS model was capable of quantifying competitive adsorption for Ni and Cd. For both Ni and Cd, however, the SRS model deviated considerably from the experimental data for high concentrations of the competing ions. This finding is consistent with the application of the SRS model made earlier by Gutierrez and Fuentes (1993) and illustrates the need for model improvement to better describe competitive adsorption of heavy metals across the entire range of concentrations.

The suitability of the multicomponent SRS equation for describing the competitive adsorption isotherms of trace elements on soil and soil minerals has been investigated by several researchers. A general procedure for applying the SRS equation is first to obtain the Freundlich distribution coefficient K_F and reaction exponent b or n by fitting the single-component isotherms to the Freundlich

equation, followed by estimating the competition coefficients α_{ij} through fitting the experimental isotherms of binary and ternary mixtures to the SRS equation (Roy et al., 1986). Although the SRS equation does not imply specific reaction mechanisms, the competition coefficients α_{ij} in the equation can be used to evaluate the relative selectivity of the sorbent to the heavy metal species. The SRS equation with competition coefficients estimated through nonlinear least squares optimization has been demonstrated to successfully describe the experimental competitive adsorption isotherms of Ni and Cd on three different soils (Liao and Selim, 2009). Gutierrez and Fuentes (1993) used the SRS equation to represent the competitive adsorption of Sr, Cs, and Co in Ca-montmorillonite suspensions. They found that the SRS competition coefficients α_{ij} obtained from experimental data of binary mixtures successfully predicted the competitive adsorption of the ternary mixture Sr–Cs–Co. Similarly, Bibak (1997) found that values of SRS competitive coefficients obtained from binary sorption experiments successfully predicted sorption data of the ternary solute mixture Cu–Ni–Zn. The SRS equation was successfully used to describe the competitive sorption of Cd, Ni, and Zn on a clay soil by Antoniadis and Tsadilas (2007). In addition, the SRS equation was also used by Wu et al. (2002) in representing the competitive adsorption of MoO_4^{2-} , SO_4^{2-} , SeO_4^{2-} , and SeO_3^{2-} on a $\gamma\text{-Al}_2\text{O}_3$ surface, using relative affinity coefficients instead of competitive coefficients. The relative affinity coefficients were calculated as the ratios of the proton coefficients of competing anions. The simulation result showed that the sorption affinity of anions on the $\gamma\text{-Al}_2\text{O}_3$ surface decreased in the order $\text{MoO}_4^{2-} > \text{SeO}_3^{2-} > \text{SeO}_4^{2-} > \text{SO}_4^{2-}$.

Competitive Langmuir Model

The Langmuir equation (Eq. [9]) can be extended to account for competitive sorption of multiple heavy metals in multicomponent systems (Murali and Aylmore, 1983):

$$S_i = \frac{K_{L_i} C_i S_{\max}}{1 + \sum_j K_{L_j} C_j} \quad [11]$$

The multicomponent Langmuir approach assumes that there is only one set of sorption sites for all competing ions. Furthermore, the model also assumes that the presence of competing ions does not affect the sorption affinity of other ions. To describe the time-dependent sorption of competing ions, the multicomponent second-order kinetic equation was proposed in the form (Murali and Aylmore, 1983)

$$\frac{\partial S_i}{\partial t} = (\lambda_f)_i \frac{\theta}{\rho} C_i \left(S_{\max} - \sum_{i=1}^l S_j \right) - (\lambda_b)_i S_i \quad [12]$$

Moreover, for the case where negligible competition is assumed among the various ions, Eq. [12], on omitting the subscript i , is reduced to the second-order formulation Eq. [7] discussed above.

Although the concept of a competitive Langmuir model has been proposed since three decades ago (Murali and Aylmore, 1983; Bradl, 2004; Janetti et al., 2012), its applications in modeling metal sorption on soils are scarce. Recently, Vidal et al. (2009) tested a two-metal Langmuir model with three parameters (S_{\max} , K_{L1} , and K_{L2}) and a two-site Langmuir model ($S_{\max1}$, $S_{\max2}$, K_{L1} , and K_{L2}) for describing the competitive adsorption among three metal pairs, i.e., Zn–Pb, Cu–Pb, and Pb–Cd. Their results, shown in

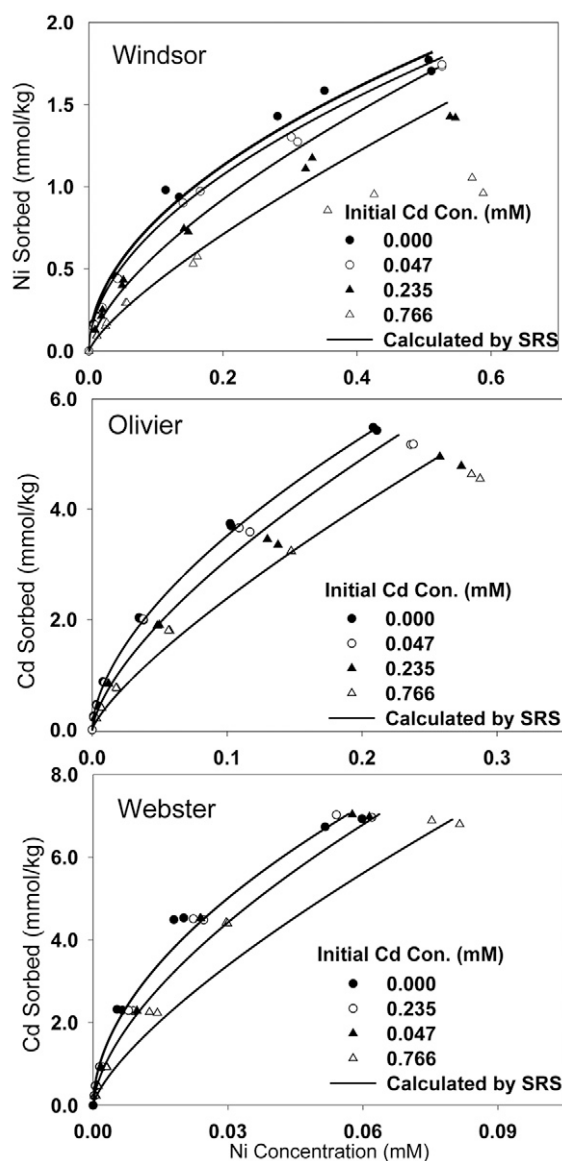


Fig. 7. Competitive adsorption isotherms for Ni in the presence of different concentrations of Cd. Solid curves are Sheindorf-Rebhun-Sheintuch model calculations.

Fig. 9, indicated that both modeling approaches were suitable to model the sorption of metals in binary mixtures; however, fitted Langmuir parameters were dependent on the concentrations of the competing metals, which limited applicability of the models. Based on maximum likelihood and model quality criteria, Janetti et al. (2012) compared extended Langmuir and modified Langmuir models, among a set of competitive-sorption models, for describing Cu–Zn sorption in two Israel soils and a Ni–Cd sorption data set (Liao and Selim, 2009). Their results showed that the extended Langmuir was among the best performing competitive-sorption models.

Competitive Multireaction Model

Kinetic (time-dependent) sorption models of the Freundlich type were developed to simulate the sorption of solutes during their transport in soils and aquifers (Selim, 1992). Zhang and Selim (2007) extended the equilibrium Freundlich approach to account for kinetic competitive or multiple-component systems. Specifically, the model accounts for equilibrium and kinetic

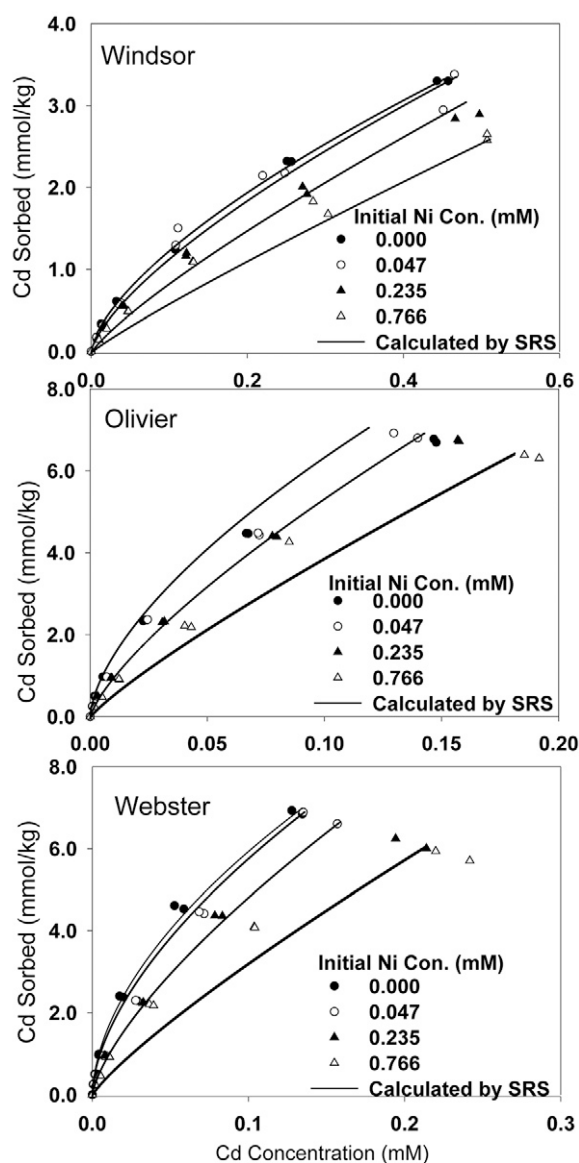


Fig. 8. Competitive adsorption isotherms for Cd in the presence of different concentrations of Ni. Solid curves are Sheindorf-Rebhun-Sheintuch model calculations.

adsorption in a way similar to the SRS equation described above. This model represents a modification of the multireaction model (MRM), which accounts for equilibrium and kinetic retention of the reversible and irreversible types (see Fig. 10). The MRM accounts for linear as well as nonlinear reaction processes of equilibrium and kinetic (reversible and irreversible) types. The model with reversible as well as irreversible sorption of the concurrent and consecutive types is shown in Fig. 10. In this model, S_e represents the amount retained on equilibrium sites (mg kg^{-1}), S_1 and S_2 represent the amounts retained on reversible kinetic sites (mg kg^{-1}), S_s represents the amount retained on consecutive irreversible sites (mg kg^{-1}), and S_{ir} represents the amount retained on concurrent irreversible sites (mg kg^{-1}).

The retention reactions associated with the MRM are expressed as

$$S_e = K_e \left(\frac{\theta}{\rho} \right) C^b \quad [13]$$

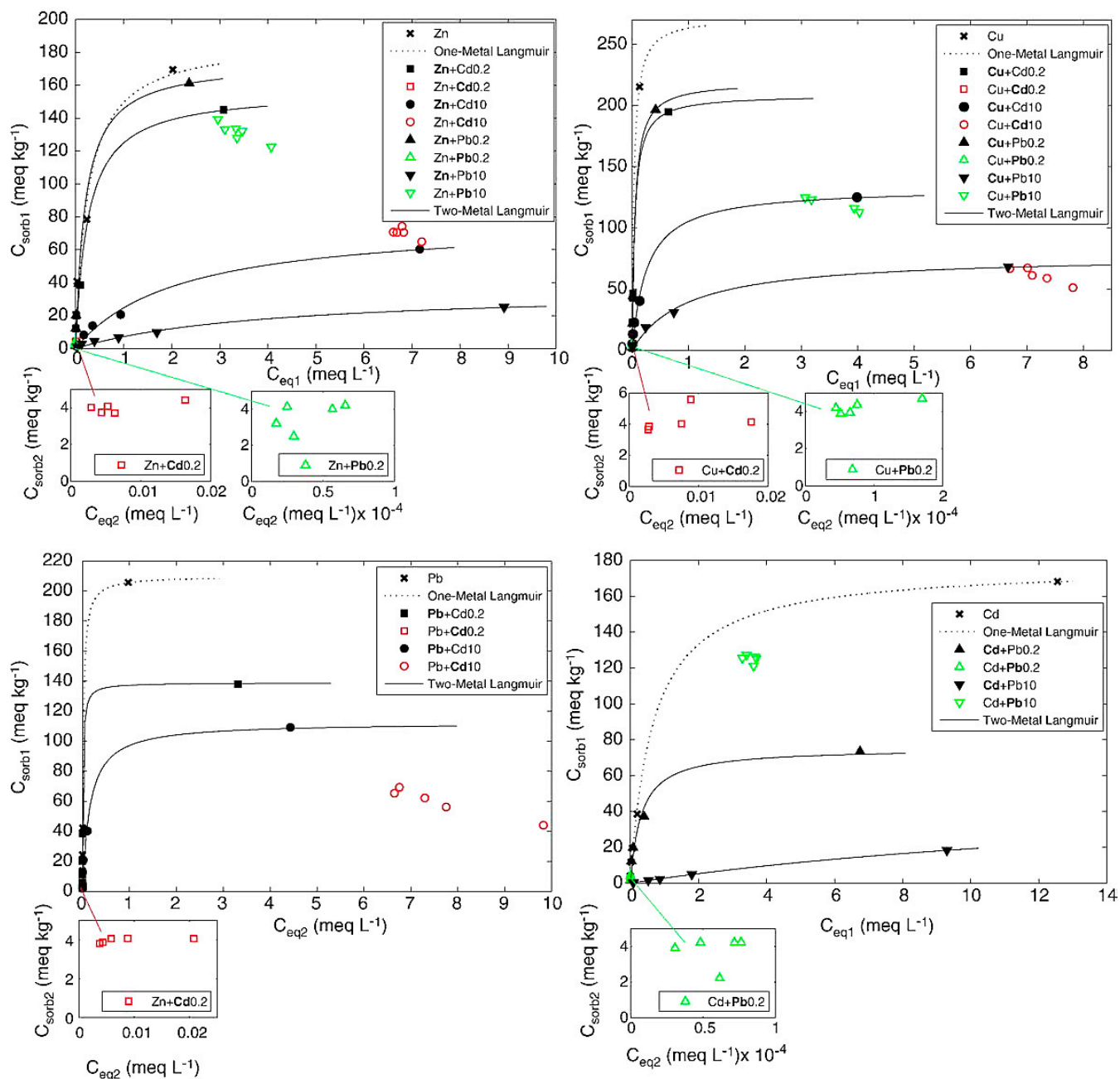


Fig. 9. One-metal and two-metal Langmuir fitting of the sorption isotherms. The amplified areas show data on sorption of the competitive metal at 0.2 mmol L⁻¹ (reproduced with permission from Vidal et al., 2009).

$$\frac{\partial S_1}{\partial t} = k_1 \left(\frac{\theta}{\rho} \right) C^n - k_2 S_1 \quad [14]$$

$$\frac{\partial S_2}{\partial t} = \left[k_3 \left(\frac{\theta}{\rho} \right) C^m - k_4 S_2 \right] - k_s S_2 \quad [15]$$

$$\frac{\partial S_s}{\partial t} = k_s S_2 \quad [16]$$

$$S_{irr} = k_{irr} \left(\frac{\theta}{\rho} \right) C \quad [17]$$

where t is the reaction time (h); ρ is the soil bulk density (g cm⁻³); θ is the water content (cm³ cm⁻³); b is the reaction order; C is the concentration in solution (mg L⁻¹); K_c is a dimensionless equilibrium constant (cm³ g⁻¹); k_1 and k_2 (h⁻¹) are the forward and backward rate coefficients, respectively, associated with S_1 and n is the reaction order; k_3 and k_4 (h⁻¹) are the forward and backward rate coefficients, respectively, associated with S_2 and m is the reaction order; k_s (h⁻¹) is the irreversible rate coefficient; and k_{irr} (h⁻¹) is the rate coefficient associated with S_{irr} . In the above equations, we assumed $n = m$ because there is no method for estimating n or m independently. Zhang and Selim (2007) modified the MRM to account for competitive Freundlich type retention such that:

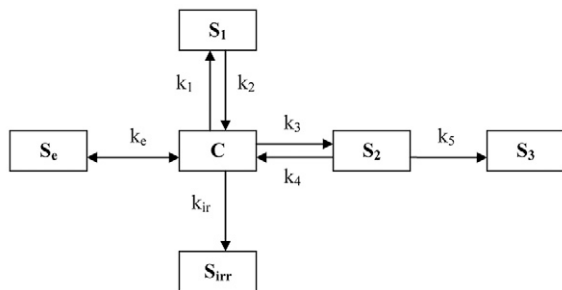


Fig. 10. Schematics of the multireaction model for retention of reactive chemicals in soils, where C is the solute concentration in the solution phase, S_e is the amount retained on equilibrium-type sites, S_1 is the amount retained on kinetic Type 1 sites, S_2 is the amount retained on kinetic Type 2 sites, S_3 is the amount retained irreversibly by consecutive-type reaction, S_{irr} is the amount retained by concurrent-type reaction, and K_e , k_1 , k_2 , k_3 , k_4 , k_5 , and k_{irr} are reaction rates.

$$(S_e)_i = K_{e,i} C_i \left(\sum_{j=1}^l \alpha_{i,j} C_j \right)^{n_i-1} \quad [18]$$

$$\frac{\partial (S_1)_i}{\partial t} = k_{1,i} \frac{\theta}{\rho} C_i \left(\sum_{j=1}^l \alpha_{i,j} C_j \right)^{n_i-1} - k_{2,i} (S_1)_i \quad [19]$$

$$\frac{\partial (S_2)_i}{\partial t} = k_{3,i} \frac{\theta}{\rho} C_i \left(\sum_{j=1}^l \alpha_{i,j} C_j \right)^{n_i-1} - (k_{4,i} + k_{s,i}) (S_2)_i \quad [20]$$

$$\frac{\partial (S_s)_i}{\partial t} = k_{s,i} (S_s)_i \quad [21]$$

$$\frac{\partial (S_{irr})_i}{\partial t} = k_{irr,i} \frac{\theta}{\rho} C_i \quad [22]$$

When competition is ignored, i.e., α_{ij} for all $j \neq i$, Eq. [17] yields single-species n th-order kinetic sorption. Examples of the capability of this approach to describe the transport of competitive As(V) and P behavior in soil columns are given in Fig. 11 (Zhang and Selim, 2007), where As(V) and P BTCs exhibit extensive asymmetry and nonequilibrium conditions appear dominant, as indicated by the drop in As(V) and P concentrations in response to flow interruption (or stop flow). These simulations demonstrated that competitive retention for As(V) and P with time was successfully predicted using this kinetic approach with model coefficients based on single-component kinetic batch results.

Ion-Exchange Models

Ion exchange is considered an instantaneous process representing (nonspecific) sorption mechanisms and a fully reversible reaction between heavy metal ions in the soil solution and those retained on charged surfaces of the soil matrix. In a standard mass-action formulation, the exchange reaction for two competing ions i and j , having valences v_i and v_j , respectively, may be written as

$${}^T K_{ij} = \frac{(a_i^*)^{v_j}}{(a_j^*)^{v_i}} \quad [23]$$

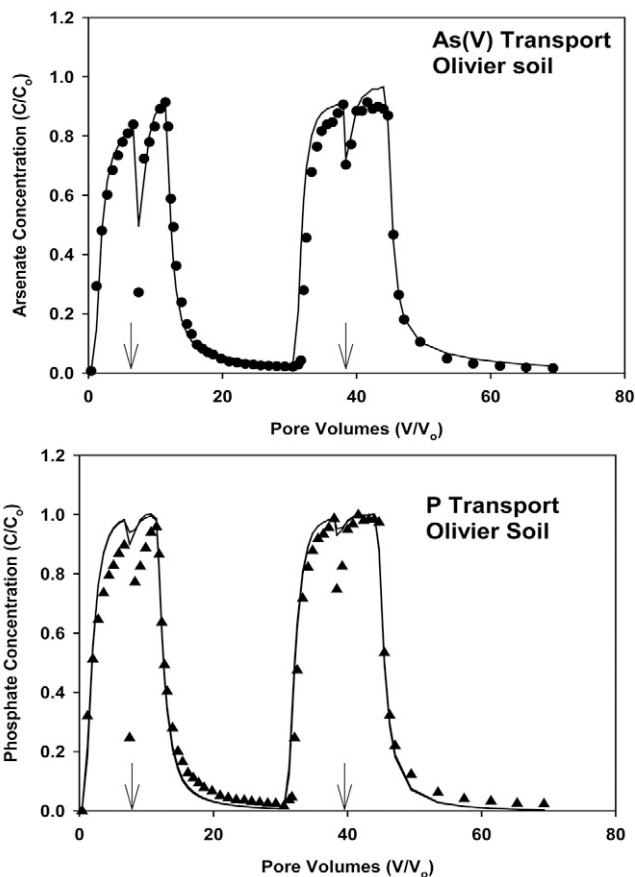


Fig. 11. Experimental As(V) and P breakthrough curves in Olivier soil. Solid curves are simulations using the competitive multireaction model. Arrows indicate when stop flow occurred.

where ${}^T K_{ij}$ is the thermodynamic equilibrium constant and a and a^* (omitting the subscripts) are the ion activity in soil solution and on the exchanger surfaces, respectively. Based on Eq. [23], the Vanselow selectivity coefficient ${}^V K_{ij}$ can be denoted as

$${}^V K_{ij} = \frac{{}^T K_{ij}}{\left[\frac{(\zeta_j)^{v_j}}{(\zeta_i)^{v_i}} \right]} \quad [24]$$

where ζ is the activity coefficient on the soil surface. It is recognized that in soils, ion exchange involves a wide range of thermodynamically different sites. As a general practice, the activity coefficient for a solid phase is commonly set equal to 1. In addition, the much simpler Gaines and Thomas (1953) selectivity coefficient ${}^G K_{ij}$ may be used, where

$${}^G K_{ij} = \frac{(\gamma_j)^{v_i}}{(\gamma_i)^{v_j}} \left(\frac{s_i}{C_i} \right)^{v_j} \left(\frac{s_j}{C_j} \right)^{v_i} \quad [25]$$

This formulation is more conveniently incorporated into the convection–dispersion transport Eq. [1]. In Eq. [25], γ_i and γ_j are dimensionless solution-phase activity coefficients where $a_i = \gamma_i C_i$. In addition, the terms s_i and s_j are dimensionless, representing the solid-phase concentrations expressed in terms of equivalent fractions, $s_i = S_i/\Omega$, with Ω the cation exchange or adsorption capacity of the soil ($\text{mmol}_c \text{ kg}^{-1}$ soil) and S_i the concentration

(mmol_c kg⁻¹) of adsorbed-phase soil. Although Ω is often assumed as invariant, it has been observed to be dependent on the soil pH and the counter ions present in the soil. Moreover, there are several other ways to express the adsorbed-phase concentration on a fractional basis, including that of a molar rather than an equivalent fraction.

Several studies have indicated that the affinity of heavy metals to soil matrix surfaces increases with decreasing heavy metal fraction on the exchanger surfaces (Abd-Elfattah and Wada, 1981; Harmsen, 1977; Selim et al., 1992; Hinz and Selim, 1994). Using an empirical selectivity coefficient, it was shown that Zn affinity increased up to two orders of magnitude for low Zn surface coverage in a Ca background solution (Abd-Elfattah and Wada, 1981). Mansell et al. (1988) successfully relaxed the assumption of constant affinities and allowed the selectivity coefficients to vary with the amount adsorbed on the exchange surfaces.

The Rothmund–Kornfeld model incorporates variable selectivity based on the amount of adsorbed or exchanger composition. The approach is empirical and provides a simple equation that incorporates the characteristic shape of binary exchange isotherms as a function of the equivalent fraction of the amount sorbed as well as the total concentration in solution. Harmsen (1977) and Bond and Phillips (1990) expressed the Rothmund–Kornfeld model as

$$\frac{(s_i)^{v_j}}{(s_j)^{v_i}} = {}^R K_{ij} \left[\frac{(c_i)^{v_j}}{(c_j)^{v_i}} \right]^n \quad [26]$$

where n is a dimensionless empirical parameter associated with the ion pair i – j and ${}^R K_{ij}$ is the Rothmund–Kornfeld selectivity coefficient. This equation is best known as a simple form of the Freundlich equation that applies to ion-exchange processes. As pointed out by Harmsen (1977), the Freundlich equation may be considered as an approximation of the Rothmund–Kornfeld equation valid for $s_i \ll s_j$ and $c_i \ll c_j$, where

$$s_i = {}^R K_{ij} (c_i)^n \quad [27]$$

This equilibrium Rothmund–Kornfeld ion-exchange equation was used by Hinz and Selim (1994) to describe the exchange isotherms of Zn–Ca and Cd–Ca as well as the breakthrough curve of Zn and Cd in uniformly packed columns of Windsor and Olivier soils. They concluded that the Rothmund–Kornfeld ion-exchange equation well described binary ion-exchange isotherms but overestimated the extent of retardation during Zn and Cd transport in soils. Examples of experimental and simulated breakthrough curves are given in Fig. 12.

Numerous studies have indicated that ion exchange is a kinetic process in which equilibrium is not instantaneously reached. The observed kinetic or time-dependent ion-exchange behavior is probably a result of the transport of initially sorbed ions from exchange sites to the bulk solution and the reverse process of the transport of replacing ions from the bulk solution to exchange sites. Specifically, the rate of ion exchange is dependent on the following processes: (i) diffusion of ions in the aqueous solution; (ii) film diffusion at the solid–liquid interface; (iii) intraparticle

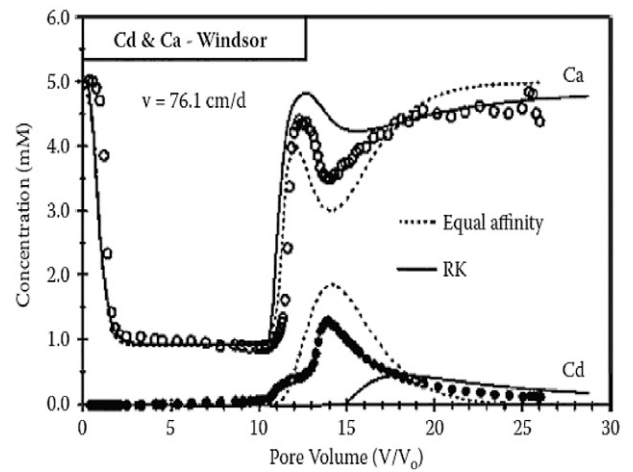


Fig. 12. Cadmium and Ca breakthrough curves in Windsor soil at various ionic strengths. Predictions were based on equal affinity (selectivity coefficient $K_f = 1$) and the Rothmund–Kornfeld equation. A constant pore water velocity (v) was maintained.

diffusion in micropores and along pore wall surfaces; and (iv) interparticle diffusion inside solid particles (Sparks, 1989). Due to the complexity of the kinetic processes, during last three decades several kinetic rate formulations have been proposed. Such formulations have been applied to describe sorption–desorption kinetic results for heavy metal ions. The pseudo-first-order or mass-action model is perhaps the most commonly used approach, where the kinetic rate is assumed to be a function of the concentration gradient on the exchange surfaces (Plazinski et al., 2009). For the exchangeable amount S (omitting the subscript i), the rate equation can be expressed as (Selim et al., 1992)

$$\frac{\partial S}{\partial t} = \alpha (S_{eq} - S) \quad [28]$$

where α is an apparent rate coefficient (d⁻¹) for the kinetic-type sites and S_{eq} is the amount sorbed at equilibrium (as $t \rightarrow \infty$). For large values of α , S approaches S_{eq} in a relatively short time, and equilibrium is rapidly achieved. In contrast, for small α , kinetic behavior should be dominant for extended periods of time. Expressions similar to the above model have been used to describe mass transfer between mobile and immobile water in porous media (Coats and Smith, 1964) as well as chemical kinetics (Parker and Jardine, 1986). To simulate the transport of Cd in different soils, Selim et al. (1992) developed a multicomponent transport model that incorporates the kinetics of ion exchange and specific sorption in the advection–dispersion equation. Based on the assumption of mass transfer or diffusion as the rate-limiting step, a first-order mass-transfer equation with an apparent rate coefficient was incorporated into the transport equation. The simulation results in Fig. 13 demonstrate that the model with kinetic ion exchange adequately predicted Cd breakthrough curves for a Eustis soil. The simulations shown also demonstrate the effect of the value of the apparent rate coefficient α on Cd predictions.

Other kinetic expressions have also been used to describe the kinetic exchange of ions in minerals and soils (Sparks, 1998). The parabolic diffusion model is based on the assumption of diffusion-controlled rate-limited processes in media with a homogeneous particle size. The parabolic diffusion equation was derived from Fick's second law of diffusion in a radial coordinate system:

$$\frac{S_i}{(S_{eq})_i} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{D_m t}{r^2}} - \frac{D_m t}{r^2} \quad [29]$$

where r is the average radius of soil or mineral particles and D_m is the molecular diffusion constant.

The Elovich model is another empirical kinetic retention model, which may be expressed as

$$\frac{\partial S_i}{\partial t} = a \exp(-BS_i) \quad [30]$$

where a is the initial adsorption rate and B is an empirical constant. Jardine and Sparks (1984) compared the first-order, parabolic diffusion, and Elovich approaches described above to describe the kinetic exchange of K and Ca in clay minerals and soils. They found that the pseudo-first-order model provided the best overall goodness-of-fit to the experimental results.

Recently, a fractional power approach was introduced by Serrano et al. (2005) having the form

$$S = \kappa t^\beta \quad [31]$$

where κ and β are empirical constants. They compared the overall sorption kinetics of Pb and Cd for single and binary systems. Their results showed that the simultaneous presence of the competing metal did not affect the estimated apparent sorption rate, which indicated that the rate-limiting processes of the sorption of heavy metal ions were not impacted by the competing ions. Although the empirical kinetic formulas were relatively easy to implement, the rate constants obtained from limited sets of experimental conditions were not readily applicable to other conditions (Shi et al., 2005; Zhang and Selim, 2008).

Surface-Complexation Models

Surface-complexation models have been used to describe an array of equilibrium-type chemical reactions including proton dissociation, metal cation and anion adsorption reactions on oxides and clays, organic ligand adsorption, and competitive-adsorption reactions on oxide and oxide-like surfaces (Allison et al., 1991; Parkhurst and Appelo, 1999). The application and theoretical aspects of surface-complexation models were extensively reviewed by Goldberg (1992) and Sparks (2003). Surface-complexation models are chemical models based on a molecular description of the electric double layer using equilibrium-derived adsorption data.

Surface complexes can exist as inner sphere surface complexes or outer-sphere surface complexes. Inner sphere surface complexes are strong complexes involving either ionic or covalent bonding without water molecules between the adsorbing ion and the surface functional group. Outer sphere surface complexes are less stable complexes involving electrostatic bonding, with at least one water molecule between the adsorbing ion and the surface functional group. For heterogeneous soils, multisurface models can be developed to include sorption of chemical components on various reaction sites on the surfaces of minerals and organic materials (Hiemstra and Van Riemsdijk, 1999; Weng et al., 2001, 2002). A list of the complexation mass action equations and the associated equilibrium reaction coefficients were given by Goldberg (1992) and Zhang and Selim (2012).

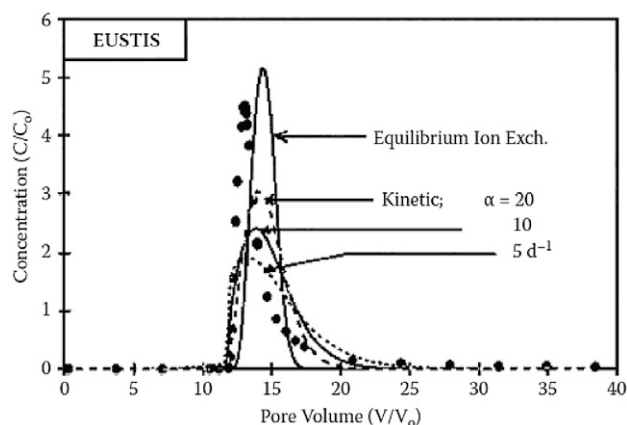


Fig. 13. Measured (closed circles) and predicted breakthrough curves for Cd in Eustis soil. Curves are predictions using an equilibrium model and a kinetic ion-exchange model with different apparent kinetic rate coefficients α .

In the past two decades, several models have been developed to describe the competitive adsorption of metals and metalloids on soil organic matter (Dudal and Gerard, 2004; Jeong et al., 2007). The NICA–Donnan model (Kinniburgh et al., 1996) combined the nonideal competitive adsorption (NICA) model (Benedetti et al., 1996) for specific binding and a Donnan-type model for nonspecific binding of an electrolyte. The model considers site heterogeneity, nonideality, multicomponent competition, and electrostatic interactions for ion binding to humic substances. In contrast to the continuous site distribution concept used in the NICA–Donnan model, the Windermere humic aqueous model (WHAM; Tipping, 1993, 1994) utilizes a discrete distribution of carboxylic- and phenolic-type functional groups to represent the behavior of organic materials. Both models have been successfully applied to simulate the adsorption of heavy metals and metalloids on the surfaces of humic substances (e.g., Weng et al., 2001, 2002). Extensive data sets of model parameters have been compiled for the models (Milne et al., 2003), which greatly enhanced their capacity for simulating complex reaction patterns for various metal ions. More recently, Shi et al. (2008) incorporated the WHAM model into a reversible two-site kinetic adsorption model to describe time-dependent adsorption and desorption of Zn in soils. Their model predicted the redistribution from monodentate to bidentate sites as an important mechanism during desorption of Zn from the soil surface.

Surface complexation models, in combination with ion-exchange models, have been used with various degrees of success to describe competitive sorption and transport of heavy metals in soils (Bradbury and Baeyens, 2005; Heidmann et al., 2005; Serrano et al., 2009; Voegelin et al., 2001). For example, Serrano et al. (2009) used a nonelectrostatic equilibrium model with both surface-complexation and ion-exchange reactions to describe the competitive sorption of Pb and Cd on three acid soils across a range of pH values and metal concentrations. The model included surface-complexation sites on an Fe-oxyhydroxide mineral, clay mineral edges, and an Al-oxyhydroxide as well as two different exchange sites to account for the ion-exchange capacity attributed to the phyllosilicate minerals smectite, weathered illite, and kaolinite and organic matter. The concentrations for specific types of surface sites were estimated from the experimentally measured mineral and chemical composition of the soils. As demonstrated

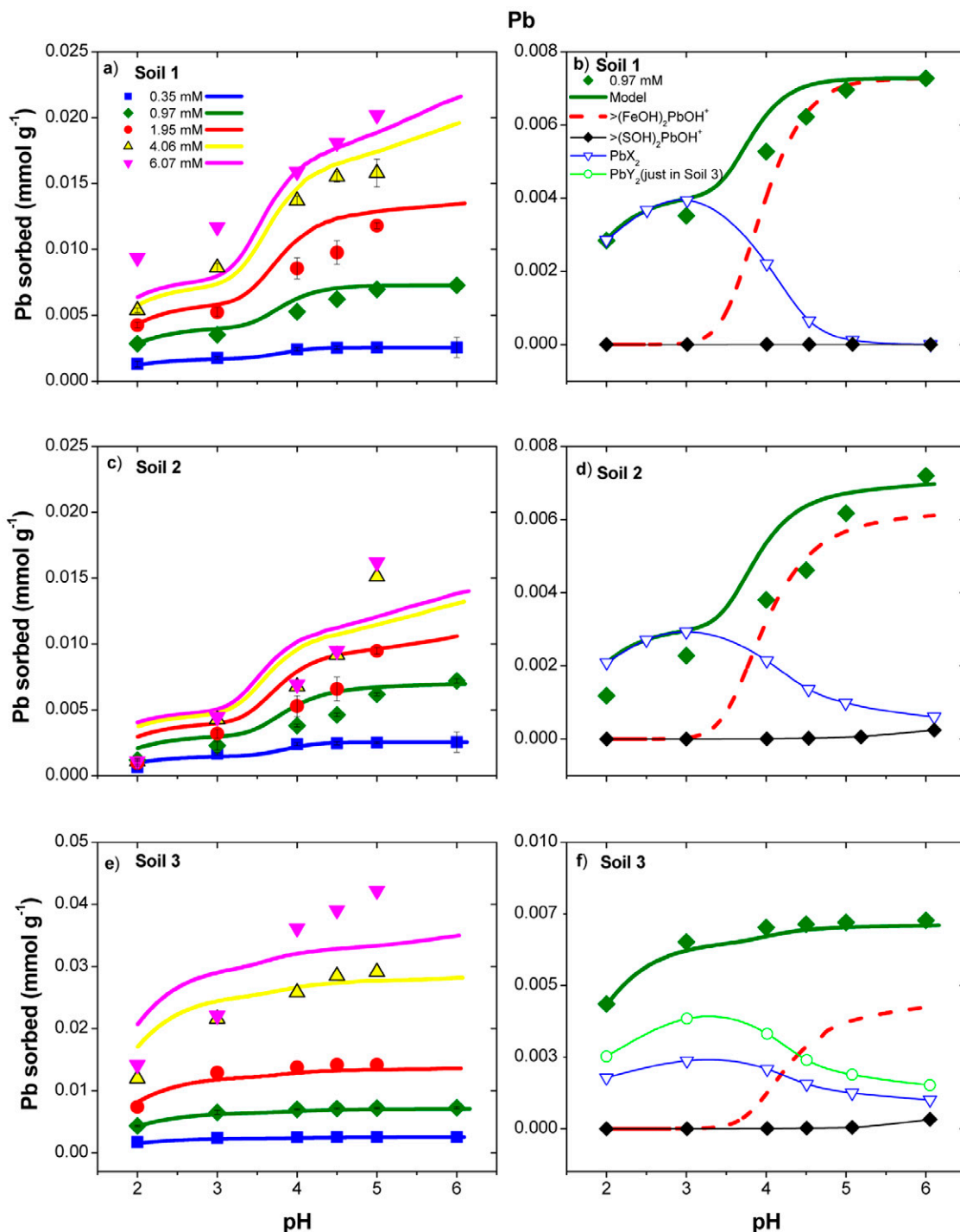


Fig. 14. Lead adsorption in binary-metal systems (Cd present): experimental data (points) and model fit (lines) are shown for (a) Soil 1, (c) Soil 2, and (e) Soil 3; model results for surface speciation of sorbed Pb at a total concentration of 0.91 mmol L^{-1} are shown for (b) Soil 1, (d) Soil 2, and (f) Soil 3 (reproduced with permission from Serrano et al., 2009).

by Fig. 14, their model results matched well the experimental data for Pb sorption in binary systems across the range of concentration and pH studied for all three soils. Voegelin et al. (2001) incorporated the convective-dispersive equation (Eq. [6]) into surface-complexation modeling to predict the competitive sorption of Cd, Zn, and Ni during transport in soils. Their study indicated that heavy metal adsorption in acidic soils is perhaps reversible where time-dependent reactivities are negligible. An example of their experimental and model calculations for Ca and Zn, with Ca breakthrough curves, is shown in Fig. 15.

A major drawback of most surface-complexation models is that they are limited to describing equilibrium-type reactions and do not account for kinetic sorption-desorption processes in soils. In heterogeneous soils with a variety of sorbents having different reactivities, time-dependent sorption is often observed. Kinetics or nonequilibrium sorption may arise due to the heterogeneity of sorption sites on matrix surfaces. In fact, various types of surface complexes (e.g., inner sphere, outer sphere, monodentate, bidentate, mononuclear, or binuclear) with contrasting sorption affinities can be formed on mineral surfaces

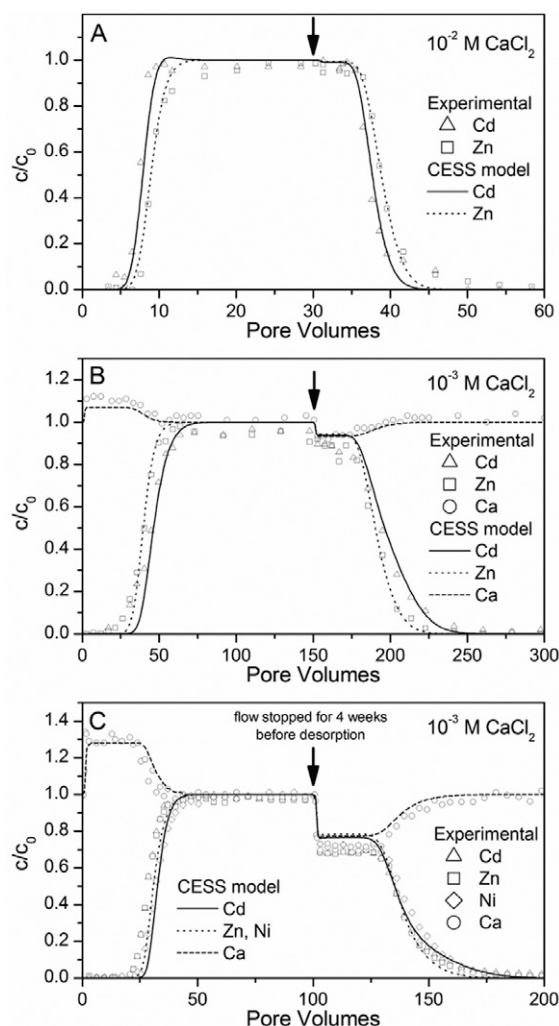


Fig. 15. Coupled breakthrough curves of Cd, Zn, and Ni in (A) in 10^{-2} mol L^{-1} and (B,C) 10^{-3} mol L^{-1} $CaCl_2$ background electrolyte solution. Curves are model calculations (reproduced with permission from Voegelin et al., 2001).

at various surface coverages of metals and metalloids. This heterogeneity of sorption sites may contribute to the observed adsorption kinetics where sorption takes place preferentially on high-affinity sites, followed subsequently by slow sorption on sites with low sorption affinity. Furthermore, the diffusion of ions to reaction sites within the soil matrix has been proposed as an explanation for time-dependent adsorption by many researchers (e.g., Fuller et al., 1993; Raven et al., 1998).

Summary

In this contribution, the framework covering the basics of competitive heavy metal sorption and transport in soils was presented. Commonly used single retention models of the equilibrium type were discussed along with various kinetic-type approaches. Retention models of the multiple-reaction type, including two-site equilibrium-kinetic models, concurrent and consecutive-multireaction models, and the second-order approach were also presented. Several examples were presented for the purpose of illustrating the impact of competing ions on the reactivities and mobility of heavy metals in the soil-water environment. Examples presented here demonstrate the influence of ligand competition for adsorption sites on mineral surfaces.

Furthermore, we demonstrated that the equilibrium Freundlich and Langmuir approaches can be extended to account for competitive retention when multiple heavy metals are present in the soil-water system. Such models may be further modified to describe the frequently observed time-dependent behavior of heavy metals in soils. A major drawback of the Freundlich and Langmuir approaches is that these models are empirically based and their associated parameters are specific for each soil. Geochemical models based on ion exchange and surface complexation require a large number of input parameters, but they have been shown to be capable of quantifying the competitive behavior of several chemical species under a wide range of chemical conditions. Geochemical models are not capable of describing time-dependent sorption in competitive systems, however. Therefore, further research is needed to characterize physical and chemical mechanisms involved in kinetic sorption in soils.

References

- Abd-Elfattah, A., and K. Wada. 1981. Adsorption of lead, copper, zinc, cobalt, and calcium by soils that differ in cation-exchange materials. *J. Soil Sci.* 32:271–283. doi:10.1111/j.1365-2389.1981.tb01706.x
- Adriano, D.C. 2001. Trace elements in terrestrial environments: Biogeochemistry, bioavailability, and risks of metals. 2nd ed. Springer, New York.
- Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. 1991. MINTEQA2/PRODEFA2: A geochemical assessment model for environmental systems. Version 3.0 user's manual. EPA/600/3-91/021. USEPA, Washington, DC.
- Antoniadis, V., and C.D. Tsadilas. 2007. Sorption of cadmium, nickel, and zinc in mono- and multi-metal systems. *Appl. Geochem.* 22:2375–2380. doi:10.1016/j.apgeochem.2007.06.001
- Arias, M., C. Perez-Novo, E. Lopez, and B. Soto. 2006. Competitive adsorption and desorption of copper and zinc in acid soils. *Geoderma* 133:151–159. doi:10.1016/j.geoderma.2005.07.002
- Beaure, L.A., A.K. Navarre-Sitchler, R.M. Maxwell, and J.E. McCray. 2012. Kinetic metal release from competing processes in aquifers. *Environ. Sci. Technol.* 46:6539–6547. doi:10.1021/es203586y
- Benedetti, M.F., W.H. Van Riemsdijk, L.K. Koopal, D.G. Kinniburgh, D.C. Goody, and C.J. Milne. 1996. Metal ion binding by natural organic matter: From the model to the field. *Geochim. Cosmochim. Acta* 60:2503–2513.
- Bibak, A. 1997. Competitive sorption of copper, nickel, and zinc by an Oxisol. *Commun. Soil Sci. Plant Anal.* 28:927–937. doi:10.1080/00103629709369843
- Bond, W.J., and I.R. Phillips. 1990. Approximate solution for cation transport during unsteady, unsaturated soil water flow. *Water Resour. Res.* 26:2195–2205. doi:10.1029/WR026i009p02195
- Bradbury, M.H., and B. Baeyens. 2005. Experimental measurements and modeling of sorption competition on montmorillonite. *Geochim. Cosmochim. Acta* 69:4187–4197. doi:10.1016/j.gca.2005.04.014
- Bradl, H.B. 2004. Adsorption of heavy metal ions on soils and soils constituents. *J. Colloid Interface Sci.* 277:1–18. doi:10.1016/j.jcis.2004.04.005
- Buchter, B., B. Davidoff, M.C. Amacher, C. Hinz, I.K. Iskandar, and H.M. Selim. 1989. Correlation of Freundlich K_d and n retention parameters with soils and elements. *Soil Sci.* 148:370–379. doi:10.1097/00010694-198911000-00008
- Coats, K.H., and B.D. Smith. 1964. Dead-end pore volume and dispersion in porous media. *Soc. Pet. Eng. J.* 4:73–84.
- Crout, N.M.J., A.M. Tye, H. Zhang, S.P. McGrath, and S.D. Young. 2006. Kinetics of metal fixation in soils: Measurement and modeling by isotopic dilution. *Environ. Toxicol. Chem.* 25:659–663. doi:10.1897/05-069R.1
- Dudal, Y., and F. Gerard. 2004. Accounting for natural organic matter in aqueous chemical equilibrium models: A review of the theories and applications. *Earth Sci. Rev.* 66:199–216. doi:10.1016/j.earscirev.2004.01.002
- Ford, R.G., A.C. Scheinost, K.G. Scheckel, and D. Sparks. 1999. The link between clay mineral weathering and the stabilization of Ni surface precipitates. *Environ. Sci. Technol.* 33:3140–3144. doi:10.1021/es990271d
- Fuller, C.C., J.A. Davis, and G.A. Waychunas. 1993. Surface chemistry of ferrihydrite: 2. Kinetics of arsenate adsorption and coprecipitation. *Geochim. Cosmochim. Acta* 57:2271–2282. doi:10.1016/0016-7037(93)90568-H
- Gaines, G.L., and H.C. Thomas. 1953. Adsorption studies on clay minerals: II. A formulation of the thermodynamics of exchange adsorption. *J. Chem. Phys.* 21:714–718. doi:10.1063/1.1698996
- Goldberg, S. 1992. Use of surface complexation models in soil chemical systems. *Adv. Agron.* 47:233–329. doi:10.1016/S0065-2113(08)60492-7
- Goldberg, S., and L.J. Criscenti. 2008. Modeling adsorption of metals and metalloids by soil components. In: A. Violante et al., editors, *Biophysico-chemical processes of heavy metals and metalloids in soil environments*. John Wiley & Sons, New York. p. 215–264.

- Gomes, P.C., M.P.F. Fontes, A.G. da Silva, E.D. Mendonça, and A.R. Netto. 2001. Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. *Soil Sci. Soc. Am. J.* 65:1115–1121. doi:10.2136/sssaj2001.6541115x
- Gutierrez, M., and H.R. Fuentes. 1993. Modeling adsorption in multicomponent systems using a Freundlich-type isotherm. *J. Contam. Hydrol.* 14:247–260. doi:10.1016/0169-7722(93)90027-P
- Harmsen, K. 1977. Behavior of heavy metals in soils. *Ctr. Agric. Publ. Doc.*, Wageningen, the Netherlands.
- Heidmann, I., I. Christl, and C. Leu. 2005. Competitive sorption of protons and metal cations onto kaolinite: Experiments and modeling. *J. Colloid Interface Sci.* 282:270–282. doi:10.1016/j.jcis.2004.08.019
- Hiemstra, T., and W.H. Van Riemsdijk. 1999. Surface structural ion adsorption modeling of competitive binding of oxyanions by metal (hydr)oxides. *J. Colloid Interface Sci.* 210:182–193. doi:10.1006/jcis.1998.5904
- Hinz, C., and H.M. Selim. 1994. Transport of zinc and cadmium in soils: Experimental evidence and modeling approaches. *Soil Sci. Soc. Am. J.* 58:1316–1327. doi:10.2136/sssaj1994.03615995005800050006x
- Janetti, E.B., I. Dror, M. Riva, A. Guadagnini, and B. Berkowitz. 2012. Estimation of single-metal and competitive sorption isotherms through maximum likelihood and model quality criteria. *Soil Sci. Soc. Am. J.* 76:1229–1245. doi:10.2136/sssaj2012.0010
- Jardine, P.M., and D.L. Sparks. 1984. Potassium–calcium exchange in a multireactive soil system: I. Kinetics. *Soil Sci. Soc. Am. J.* 48:39–45.
- Jeong, C.Y., S.D. Young, and S.J. Marshall. 2007. Competitive adsorption of heavy metals in humic substances by a simple ligand model. *Soil Sci. Soc. Am. J.* 71:515–528. doi:10.2136/sssaj2005.0281
- Kinniburgh, D.G. 1986. General purpose adsorption isotherms. *Environ. Sci. Technol.* 20: 895–904. doi:10.1021/es00151a008
- Kinniburgh, D.G., C.J. Milne, M.F. Benedetti, J.P. Pinheiro, J. Filius, L.K. Koopal, and W.H. Van Riemsdijk. 1996. Metal ion binding by humic acid: Application of the NICA–Donnan model. *Environ. Sci. Technol.* 30:1687–1698. doi:10.1021/es950695h
- Kretzschmar, R., and A. Voegelin. 2001. Modeling competitive sorption and release of heavy metals in soils. In: H.M. Selim and D.L. Sparks, editors, *Heavy metals release in soils*. Lewis Publ., Boca Raton, FL. p. 55–88.
- Lapidus, L., and N.L. Amundson. 1952. Mathematics for adsorption in beds: VI. The effect of longitudinal diffusion in ion exchange and chromatographic columns. *J. Phys. Chem.* 56:984–988. doi:10.1021/j150500a014
- Liao, L., and H.M. Selim. 2009. Competitive sorption of nickel and cadmium in different soils. *Soil Sci.* 174:549–555. doi:10.1097/SS.0b013e3181bbdb27
- Liao, L., and H.M. Selim. 2010. Reactivity of nickel in soils: Evidence of retention kinetics. *J. Environ. Qual.* 39:1290–1297. doi:10.2134/jeq2010.0004
- Mansell, R.S., S.A. Bloom, H.M. Selim, and R.D. Rhue. 1988. Simulated transport of multiple cations in soil using variable selectivity coefficients. *Soil Sci. Soc. Am. J.* 52:1533–1540. doi:10.2136/sssaj1988.03615995005200060003x
- Mesquita, M.E., and J.M. Vieira e Silva. 2002. Preliminary study of pH effect in the application of Langmuir and Freundlich isotherms to Cu–Zn competitive adsorption. *Geoderma* 106:219–234. doi:10.1016/S0016-7061(01)00125-2
- Milne, C.J., D.G. Kinniburgh, W.H. Van Riemsdijk, and E. Tipping. 2003. Generic NICA–Donnan model parameters for metal-ion binding by humic substances. *Environ. Sci. Technol.* 37:958–971. doi:10.1021/es0258879
- Murali, V., and L.A.G. Aylmore. 1983. Competitive adsorption during solute transport in soils: 3. A review of experimental evidence of competitive adsorption and an evaluation of simple competition models. *Soil Sci.* 136:279–290. doi:10.1097/00010694-198311000-00002
- Parker, J.C., and P.M. Jardine. 1986. Effect of heterogeneous adsorption behavior on ion transport. *Water Resour. Res.* 22:1334–1340. doi:10.1029/WR022i008p01334
- Parkhurst, D.L., and C.A.J. Appelo. 1999. User's guide to PHREEQC Version 2: A computer program for speciation, batch reaction, one-dimensional transport and inverse geochemical calculations. *Water Resour. Invest. Rep.* 99-4259. USGS, Lakewood, CO.
- Plazinski, W., W. Rudzinski, and A. Plazinska. 2009. Theoretical models of sorption kinetics including a surface reaction mechanism: A review. *Adv. Colloid Interface Sci.* 152:2–13. doi:10.1016/j.cis.2009.07.009
- Raven, K.P., A. Jain, and R.H. Loeppert. 1998. Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. *Environ. Sci. Technol.* 32:344–349. doi:10.1021/es970421p
- Roy, W.R., J.J. Hassett, and R.A. Griffin. 1986. Competitive coefficient for the adsorption of arsenate, molybdate, and phosphate mixtures by soils. *Soil Sci. Soc. Am. J.* 50:1176–1182. doi:10.2136/sssaj1986.03615995005000050017x
- Sauvé, S.W., Hendershot, and H.E. Allen. 2000. Solid–solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. *Environ. Sci. Technol.* 34:1125–1131. doi:10.1021/es9907764
- Selim, H.M. 1992. Modeling the transport and retention of inorganics in soils. *Adv. Agron.* 47:331–384. doi:10.1016/S0065-2113(08)60493-9
- Selim, H.M., and M.C. Amacher. 1997. Reactivity and transport of heavy metals in soils. CRC Press, Boca Raton, FL.
- Selim, H.M., B. Buchter, C. Hinz, and L. Ma. 1992. Modeling the transport and retention of cadmium in soils: Multireaction and multicomponent approaches. *Soil Sci. Soc. Am. J.* 56:1004–1015. doi:10.2136/sssaj1992.03615995005600040002x
- Selim, H.M., and L. Ma. 2001. Modeling nonlinear kinetic behavior of copper adsorption–desorption in soil. In: H.M. Selim and D.L. Sparks, editors, *Physical and chemical processes of water and solute transport/retention in soil*. SSSA Spec. Publ. 56. SSSA, Madison, WI. p. 189–212.
- Serrano, S., F. Garrido, C.G. Campbell, and M.T. Garcia-Gonzalez. 2005. Competitive sorption of cadmium and lead in acid soils of central Spain. *Geoderma* 124:91–104. doi:10.1016/j.geoderma.2004.04.002
- Serrano, S., P.A. O'Day, D. Vlassopoulos, M.T. Garcia-Gonzalez, and F. Garrido. 2009. A surface complexation and ion exchange model of Pb and Cd competitive sorption on natural soils. *Geochim. Cosmochim. Acta* 73:543–558. doi:10.1016/j.gca.2008.11.018
- Sheindorf, C., M. Rebhun, and M. Sheintuch. 1981. A Freundlich-type multicomponent isotherm. *J. Colloid Interface Sci.* 79:136–142. doi:10.1016/0021-9797(81)90056-4
- Shi, Z.Q., D.M. Di Toro, H.E. Allen, and A.A. Ponizovsky. 2005. Modeling kinetics of Cu and Zn release from soils. *Environ. Sci. Technol.* 39:4562–4568. doi:10.1021/es048554f
- Shi, Z.Q., D.M. Di Toro, H.E. Allen, and D.L. Sparks. 2008. A WHAM-based kinetics model for Zn adsorption and desorption to soils. *Environ. Sci. Technol.* 42:5630–5636. doi:10.1021/es800454y
- Smith, S.L., and P.R. Jaffé. 1998. Modeling the transport and reaction of trace metals in water-saturated soils and sediments. *Water Resour. Res.* 34:3135–3147. doi:10.1029/98WR02227
- Sparks, D.L. 1989. Kinetics of soil chemical processes. Academic Press, San Diego.
- Sparks, D.L. 1998. Soil physical chemistry. 2nd ed. CRC Press, Boca Raton, FL.
- Sparks, D.L. 2003. Environmental soil chemistry. 2nd ed. Academic Press, San Diego.
- Sposito, G. 1994. Chemical equilibria and kinetics in soils. Oxford Univ. Press, New York.
- Tipping, E. 1993. Modeling the competition between alkaline-earth cations and trace-metal species for binding by humic substances. *Environ. Sci. Technol.* 27:520–529. doi:10.1021/es00040a011
- Tipping, E. 1994. WHAM: A chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Comput. Geosci.* 20:973–1023. doi:10.1016/0098-3004(94)90038-8
- Tye, A.M., S.D. Young, N.M.J. Crout, H. Zhang, S. Preston, V.L. Barbosa-Jefferson, et al. 2003. Predicting the activity of Cd²⁺ and Zn²⁺ in soil pore water from the radiolabile metal fraction. *Geochim. Cosmochim. Acta* 67:375–385. doi:10.1016/S0016-7037(02)01138-9
- Vidal, M., M.J. Santos, T. Abrao, J. Rodriguez, and A. Rigol. 2009. Modeling competitive metal sorption in a mineral soil. *Geoderma* 149:189–198. doi:10.1016/j.geoderma.2008.11.040
- Voegelin, A., and R. Kretzschmar. 2005. Formation and dissolution of single and mixed Zn and Ni precipitates in soil: Evidence from column experiments and extended x-ray absorption fine structure spectroscopy. *Environ. Sci. Technol.* 39:5311–5318. doi:10.1021/es0500097
- Voegelin, A., V.M. Vulava, and R. Kretzschmar. 2001. Reaction-based model describing competitive sorption and transport of Cd, Zn, and Ni in an acidic soil. *Environ. Sci. Technol.* 35:1651–1657. doi:10.1021/es0001106
- Waltham, C.A., and M.J. Eick. 2002. Kinetics of arsenic adsorption on goethite in the presence of sorbed silicic acid. *Soil Sci. Soc. Am. J.* 66:818–825. doi:10.2136/sssaj2002.0818
- Weng, L.P., E.J.M. Temminghoff, S. Lofts, E. Tipping, and W.H. Van Riemsdijk. 2002. Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil. *Environ. Sci. Technol.* 36:4804–4810. doi:10.1021/es0200084
- Weng, L.P., E.J.M. Temminghoff, and W.H. Van Riemsdijk. 2001. Contribution of individual sorbents to the control of heavy metal activity in sandy soil. *Environ. Sci. Technol.* 35:4436–4443. doi:10.1021/es010085j
- Wu, C.-H., C.-Y. Kuo, C.-F. Lin, and S.-L. Lo. 2002. Modeling competitive adsorption of molybdate, sulfate, selenate, and selenite using a Freundlich-type multi-component isotherm. *Chemosphere* 47:283–292. doi:10.1016/S0045-6535(01)00217-X
- Zhang, H. 2011. Non-equilibrium transport of heavy metals in soils: Physical and chemical processes. In: H.M. Selim, editor, *Dynamics and bioavailability of heavy metals in the rootzone*. CRC Press, Boca Raton, FL. p. 37–63.
- Zhang, H., and H.M. Selim. 2005. Kinetics of arsenate adsorption–desorption in soils. *Environ. Sci. Technol.* 39:6101–6108. doi:10.1021/es050334u
- Zhang, H., and H.M. Selim. 2007. Modeling competitive arsenate–phosphate retention and transport in soils: A multi-component multi-reaction approach. *Soil Sci. Soc. Am. J.* 71:1267–1277. doi:10.2136/sssaj2006.0422
- Zhang, H., and H.M. Selim. 2008. Competitive sorption–desorption kinetics of arsenate and phosphate in soils. *Soil Sci.* 173:3–12. doi:10.1097/ss.0b013e31815ce750
- Zhang, H., and H.M. Selim. 2012. Equilibrium and kinetic modeling of competitive heavy metal sorption and transport in soils. In: H.M. Selim, editor, *Competitive sorption and transport of trace elements in soils and geological media*. CRC Press, Boca Raton, FL. p. 42–74.
- Zhu, J., M. Pigna, V. Cozzolino, A.G. Caporale, and A. Violante. 2010. Competitive sorption of copper(II), chromium(III) and lead(II) on ferrihydrite and two organomineral complexes. *Geoderma* 159:409–416. doi:10.1016/j.geoderma.2010.09.006