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V.1

Modeling reactive metal transport in soils

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V.1.1. Introduction

Models that can accurately predict the retention and movement of heavy metals in soils can be useful in helping to select the most cost-effective technology for mitigating contaminated soil sites. Furthermore, such models are useful in assessing the degree of cleanup required. For example, if a model predicts that a particular metal is relatively mobile in a particular soil environment, then extraction of the metal from the soil may be the best treatment choice. If on the other hand, a model predicts that a particular metal is relatively immobile in a particular soil environment, then a method that further immobilizes or fixes the metal in place might be the most suitable choice.

In this chapter, models that govern retention reactions and transport of heavy metals in the soil are presented. Models of the equilibrium type are first discussed then followed by models of the kinetic type. Retention models of the multiple reaction type including the two-site equilibrium–kinetic models, the concurrent- and consecutive multireaction models (MRMs), and the second-order approach will be derived. In addition, competitive type models where ion exchange is assumed to be the dominant retention mechanism are presented. Selected experimental retention and breakthrough results for Cu, Pb, Cr, Cd, and Zn are illustrated for the purpose of model evaluation and validation.

V.1.2. Equilibrium models

Over the last three decades, numerous models for describing reactive solute retention in soils have been developed (Selim, 1992, 1999; Selim and Amacher, 1997, 2001; Kretzschmar and Voegelin, 2001). Table V.1.1 provides a summary of several equilibrium and kinetic type retention approaches. Below we describe major retention approaches of the equilibrium type followed by selected kinetic type approaches. The Langmuir isotherm is perhaps the most commonly used equilibrium type isotherm, which may be expressed as

$$\frac{S}{S_{\max}} = \frac{\omega C}{1 + \omega C} \qquad \text{(V.1.1)}$$

where S is the amount of solute retained by the soil (μg/g soil), C is the solute concentration in solution (μg/ml), and ω and $S_{\max}$ are adjustable parameters. Here ω (cm^3/μg) is

Table V.1.1. Selected equilibrium and kinetic type models for heavy metal retention in soils.

Model	Formulation[a]
Equilibrium type	
Linear	$S = K_d C$
Freundlich	$S = K_f C^b$
General Freundlich	$S/S_{max} = [\omega C/(1 + \omega C)]^{\beta}$
Rothmund–Kornfeld ion exchange	$S_i/S_T = K_{RK}(C_i/C_T)^n$
Langmuir	$S/S_{max} = \omega C/[1 + \omega C]$
General Langmuir Freundlich	$S/S_{max} = (\omega C)^{\beta}/[1 + (\omega C)^{\beta}]$
Langmuir with sigmoidicity	$S/S_{max} = \omega C/[1 + \omega C + \sigma/C]$
Kinetic type	
First order	$\partial S/\partial t = k_f(\Theta/\rho)C - k_b S$
*n*th order	$\partial S/\partial t = k_f(\Theta/\rho)C^n - k_b S$
Irreversible (sink/source)	$\partial S/\partial t = k_s(\Theta/\rho)(C - C_p)$
Second-order irreversible	$\partial S/\partial t = k_s(\Theta/\rho)C(S_{max} - S)$
Langmuir kinetic	$\partial S/\partial t = k_f(\Theta/\rho)C(S_{max} - S) - k_b S$
Elovich	$\partial S/\partial t = A \exp(-BS)$
Power	$\partial S/\partial t = K(\Theta/\rho)C^n S^m$
Mass transfer	$\partial S/\partial t = K(\Theta/\rho)(C - C^*)$

[a] A, B, b, C^*, C_p, K, K_d, K_{RK}, k_b, k_f, k_s, n, m, S_{max}, ω, β, and σ are adjustable model parameters, ρ is the bulk density, Θ is the volumetric soil water content, C_T is the total solute concentration, and S_T is the total amount sorbed of all competing species.

a measure of the bond strength of molecules on the matrix surface and S_{max} (μg/g soil) is the maximum sorption capacity or total amount of available sites per unit soil mass. The Langmuir sorption isotherm has been used extensively by scientists for several decades. Moreover, Langmuir isotherms were used successfully to describe Cd, Cu, Pb, and Zn retention in soils. Figure V.1.1 shows experimental and fitted isotherm examples of use of the Langmuir equation to describe Cu retention in McLaren and Cecil soils (Selim and Amacher, 1997).

Several modifications of the Langmuir approach have been developed by a number of scientists. The presence of two types of surface sites responsible for sorption was postulated and an adaptation of the original equation was proposed. This adaptation was successfully used to describe Cr(VI) and Zn for a wide range of soils. Figure V.1.2 shows experimental and fitted isotherms illustrating the use of the two-site Langmuir approach for Cr(VI) retention for three soils (Selim and Amacher, 1988). A more recent adaptation of the two-surface Langmuir approach is the incorporation of a sigmoidicity which proved desirable in describing sorption isotherms at extremely low concentrations for Pb, Cd, and Cu in a surface Luvisol (Schmidt and Sticher, 1986).

Another commonly used equilibrium approach is the Freundlich isotherm,

$$S = K_f C^b \qquad \text{(V.1.2)}$$

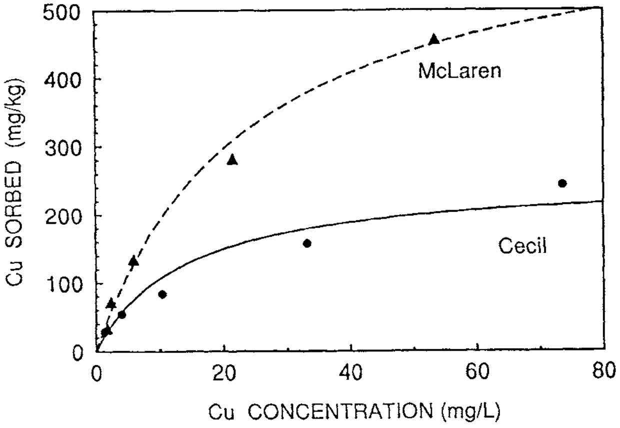

Figure V.1.1. Retention isotherms for Cu after 8 days of reactions for Cecil and McLaren soils. Solid curves are calculated isotherms using equilibrium Langmuir model.

where K_f is the distribution coefficient (cm^3/g) and the parameter b is dimensionless and typically has a value of $b < 1$. The distribution coefficient describes the partitioning of a solute species between solid and liquid phases over the concentration range of interest and is analogous to the equilibrium constant for a chemical reaction. For b equals unity, the Freundlich equation is often referred to as the linear retention equation (see Table V.1.1).

There are numerous examples for solute retention, which were described successfully by use of the Freundlich equation (Sposito, 1984; Buchter et al., 1989; Sparks, 1989).

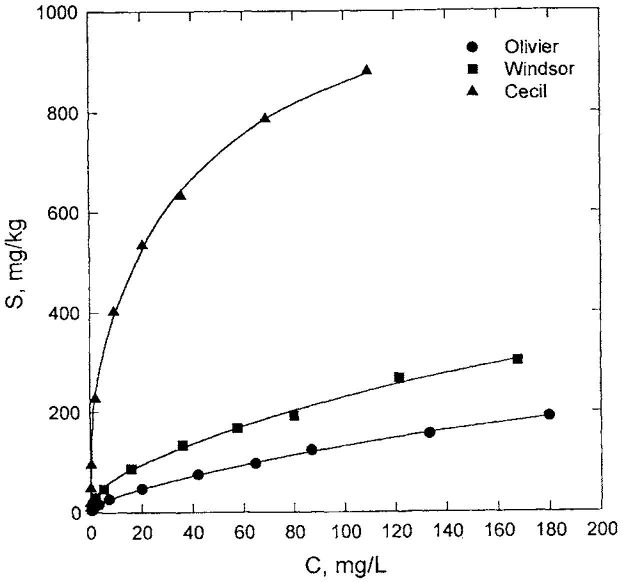

Figure V.1.2. Two-site Langmuir sorption curves for Cr(VI) retention by Olivier, Windsor, and Cecil soils after 336 h of reaction.

Logarithmic representation of the Freundlich equation is frequently used to represent the data as illustrated in Figure V.1.3. Here the slope of the best-fit curve provides the nonlinear parameter b and the intercept as K_f according to ($\log(S) = K_f + b\log(C)$) as long as a linear representation of the data in the log form is achieved. In Figure V.1.3, we illustrate the use of the Freundlich equation for Pb isotherms for several soils (Buchter et al., 1989).

Another type of equilibrium retention approaches is that based on competitive ion exchange processes. Such mechanisms describe interactions of multiple species present in the soil solution and that on exchange surfaces of the soil matrix (Sposito, 1981). For the simplest case of binary homovalent exchange, and assuming similar ion activities in the solution phase, results in the following ion exchange isotherm equation,

$$K_{ij} = [{}^{\nu}K_{ij}]^{1/\nu} = \frac{(s_i/c_i)}{(s_j/c_j)} \tag{V.1.3}$$

where ν is the ion valency, K_{ij} is a generic selectivity coefficient of ions i over j (Rubin and James, 1973) or a separation factor for the affinity of ions on exchange sites. In addition, c_i and c_j are the relative ion concentrations (dimensionless) such that $c_i = C_i/C_T$ and $c_j = C_j/C_T$, where C_i, C_j, and C_T (mmol(+)/ml) are the concentrations in the soil solution of ions i and j, and the total concentration, respectively. Also s_i and s_j are amounts retained on the solid matrix surfaces (dimensionless) and are expressed as equivalent fractions where $s_i = S_i/\Omega$ and $s_j = S_j/\Omega$. Here, S_i and S_j are the amounts adsorbed (mmol(+)/g soil) and Ω is the cation exchange (or adsorption) capacity of the soil (mmol(+)/g soil).

Based on Equation (V.1.3), for $K_{12} = 1$, a linear isotherm relation is produced, represented by the solid line in Figure V.1.4. This clearly illustrates a 1:1 relationship between relative concentration in solution and that on the adsorbed phase. This also implies that the two ions 1 and 2 each have equal affinity for the exchange sites. In contrast, for $K_{12} < 1$, we have nonlinear sorption isotherms. Specifically, for $K_{12} > 1$, sorption of ion 1 is preferred and the isotherms are convex. For $K_{12} < 1$, sorption affinity is apposite and the isotherms are concave. Examples of homovalent ion exchange isotherms are illustrated in Figure V.1.4 (Cd–Ca in two soils) (Selim et al., 1992).

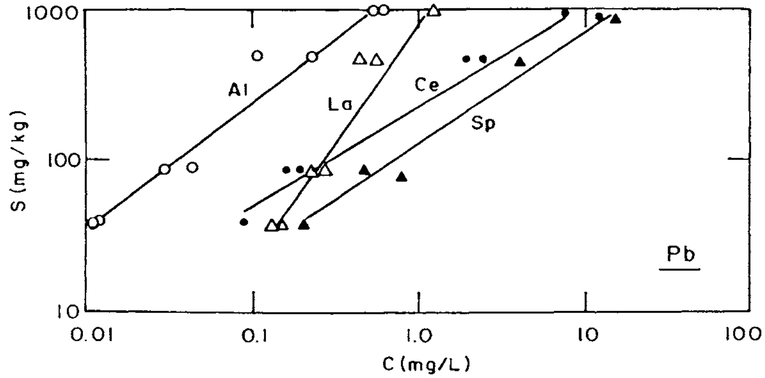

Figure V.1.3. Retention isotherms for Pb on selected soils. Solid curves are calculated isotherms using equilibrium Freundlich. The soils are represented by: Alligator (Al), Cecil (Ce), Lafitte (La), and Spodosol (Sp).

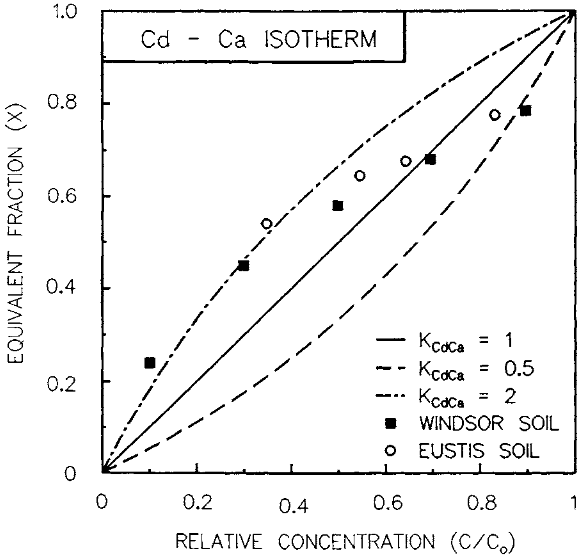

Figure V.1.4. Cadmium–calcium exchange isotherm for Windsor and Eustis soils. Solid and dashed curves are simulations using different selectivities (K_{CdCa}).

The capability of the ion exchange approach in describing multiple pulse applications is illustrated in Figures V.1.5 and V.1.6 (for Windsor soil). Here Cd input pulses were 10 and 100 mg/l, respectively (Selim et al., 1992). The ion exchange model well predicted the position of the BTC peaks and the assumption of equilibrium ion exchange adequately predicted the observed snow plow effect where effluent concentration exceeds that of the input pulse ($C/C_0 > 1$) for the two Windsor data sets.

The Rothmund–Kornfeld binary exchange is another equilibrium approach, which incorporates variable selectivity based on the amount of adsorbed (s_i) or exchanger composition. The approach is empirical and provides a simple equation that incorporated the characteristic shape of binary exchange isotherms as a function of equivalent fraction

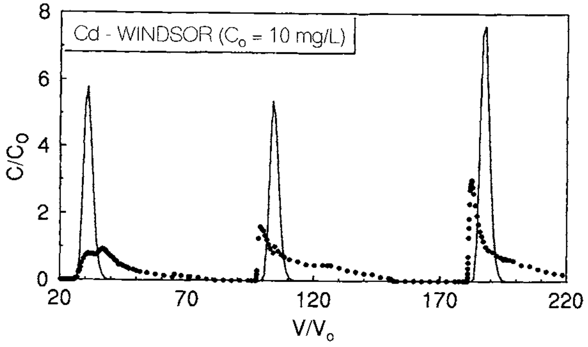

Figure V.1.5. Measured (closed circles) and predicted breakthrough curves in Windsor soil column for three Cd pulses of $C_0 = 10$ mg/l. Curves are predictions using equilibrium ion exchange model.

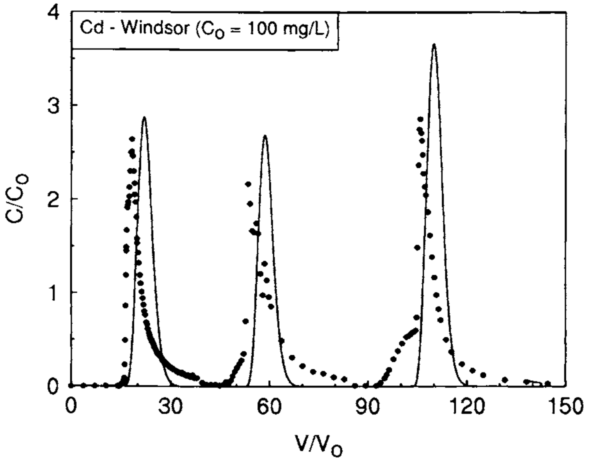

Figure V.1.6. Measured (closed circles) and predicted breakthrough curves in Windsor soil column for three Cd pulses of $C_0 = 100$ mg/l. Curves are predictions using equilibrium and ion exchange model.

of the amount sorbed (s_i) as well as the total solution concentration in solution (C_T). The Rothmund–Kornfeld formulation can be expressed as,

$$\frac{(s_i)^{\nu j}}{(s_j)^{\nu i}} = {}^{R}K_{ij}\left[\frac{(c_i)^{\nu j}}{(c_j)^{\nu i}}\right]^n \tag{V.1.4}$$

where n is a dimensionless empirical parameter associated with the ion pair i–j and ${}^{R}K_{ij}$ is the Rothmund–Kornfeld selectivity coefficient. The above 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

$$s_i = {}^{R}K_{ij}(c_i)^n \tag{V.1.5}$$

The ion exchange isotherms in Figure V.1.7 show the relative amount of Zn and Cd adsorbed as a function of relative solution concentration along with best-fit isotherms based on the Rothmund–Kornfeld equation for two acidic soils (Hinz and Selim, 1994). The diagonal line represents a non-preference isotherm (${}^{R}K_{ij} = 1$, $n = 1$) where competing ions (Ca–Zn or Ca–Cd) have equal affinity for exchange sites. The sigmoidal shapes of the isotherms reveal that Zn and Cd sorption exhibits high affinity at low concentrations, whereas Ca exhibits high affinity at high heavy metal concentrations. This behavior is well described by the Rothmund–Kornfeld isotherm with n less than one. An example of transport behavior of Zn in a Windsor soil column is presented in Figure V.1.8 (Hinz and Selim, 1994). Since the total concentration of the Zn and Cd input pulse solutions was much lower than that of the displacing Ca solution, chromatographic peaks were observed. Early appearance of Zn was well described by the predicted BTC (dashed curves) where equal Ca–Zn exchange affinity was assumed. In fact, the chromatographic effect for Ca and Zn was adequately described by the equal affinity BTCs. However, the tailing was not well predicted.

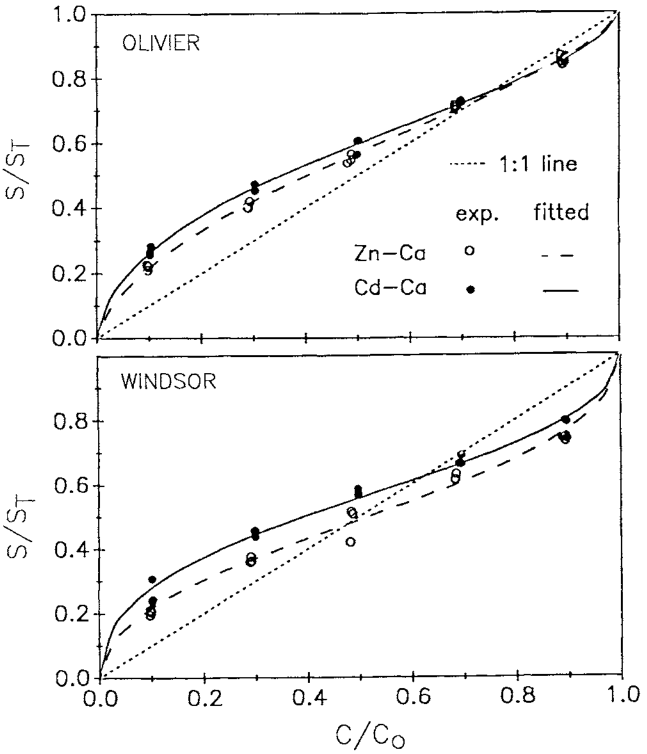

Figure V.1.7. Ion exchange isotherms of Cd–Ca and Zn–Ca for Olivier and Windsor soils (relative concentration (C/C_0) versus the sorbed fraction (S/S_T). Solid and dashed curves are fitted using the Rothmund–Kornfeld equation.

V.1.3. Kinetic models

The failure of equilibrium type models to adequately describe the retention of several heavy metals during transport in soils led Amacher et al. (1988) to propose a general purpose (equilibrium–kinetic) multireaction approach. Amacher et al. (1988, 1990) used an MRM to describe the time-dependent retention of Cr(VI), Cd, and Hg in a group of soils. Subsequent development of a two-site second-order kinetic model (SOTS) and incorporation of the nonlinear and second-order models into the convective–dispersive transport equation demonstrated that these models could also be used to describe Cr(VI) retention during transport through soil columns under steady water flow (Selim and Amacher, 1988; Selim et al., 1989). A schematic representation of the MRM is shown in Figure V.1.9.

In this model we consider the solute to be present in the soil solution phase (C) and in four phases representing solute retained by the soil matrix as S_e, S_1, S_2, S_3, and S_{irr}. We further assume that S_e, S_1, and S_2 are in direct contact with the solution phase and are governed by concurrent type reactions. Here we assume S_e as the amount of solute that is sorbed reversibly and is in equilibrium with C at all times. The governing equilibrium retention/release mechanism was that of the nonlinear Freundlich type. The reactions

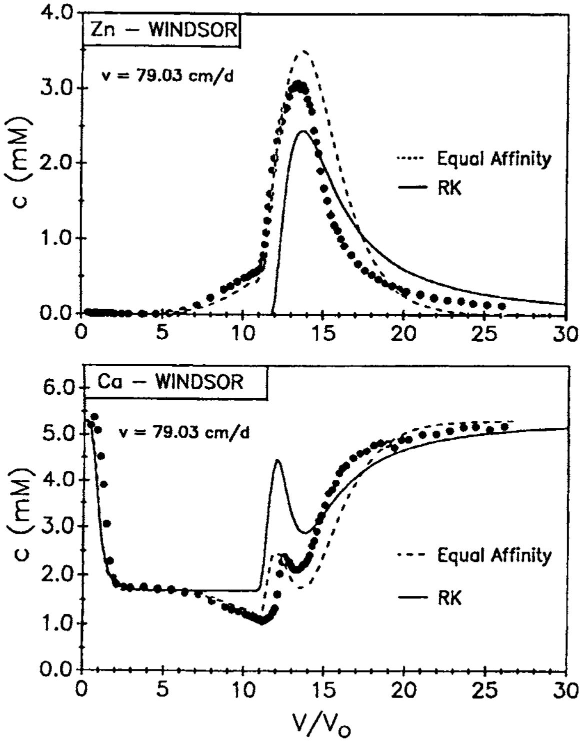

Figure V.1.8. Zn and Ca breakthrough curves in Windsor soil column at variable ionic strength. Predictions were based on equal affinity ($K_{12} = 1$) and the Rothmund–Kornfeld (RK) equation.

associated with S_1 and S_2 were considered to be reversible processes of the nonlinear kinetic type:

$$S_e = K_f C^b \tag{V.1.6}$$

$$\frac{\partial S_1}{\partial t} = k_1 \frac{\Theta}{\rho} C^n - k_2 S_1 \tag{V.1.7}$$

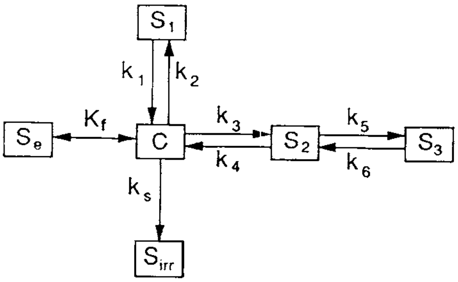

Figure V.1.9. A schematic representation of the MRM.

$$\frac{\partial S_2}{\partial t} = k_3 \frac{\Theta}{\rho} C^m - k_4 S_2 \tag{V.1.8}$$

where k_1 to k_4 are the associated rate coefficients (h^{-1}) and r and Q are the soil bulk density (g/cm^3) and soil moisture content (cm^3/cm^3), respectively. These two phases (S_1 and S_2) may be regarded as the amounts sorbed on surfaces of soil particles and chemically bound to Al and Fe oxide surfaces or other types of surfaces, although it is not necessary to have *a priori* knowledge of the exact retention mechanisms for these reactions to be applicable. Moreover, these phases may be characterized by their kinetic sorption and release behavior to the soil solution and thus are susceptible to leaching in the soil. In addition, the primary difference between these two phases not only lies in the difference in their kinetic behavior but also on the degree of nonlinearity as indicated by the parameters n and m. The MRM also considers irreversible solute removal via a retention sink term Q in order to account for irreversible reactions such as precipitation/dissolution, mineralization, and immobilization, among others. We expressed the sink term as a first-order kinetic process:

$$Q = \rho \frac{\partial S_{\mathrm{irr}}}{\partial t} = k_{\mathrm{irr}} \Theta C \tag{V.1.9}$$

where k_{irr} is the associated rate coefficient (h^{-1}).

The MRM also includes an additional retention phase (S_3), which is governed by a consecutive reaction with S_2. This phase represents the amount of solute strongly retained by the soil that reacts slowly and reversibly with S_2 and may be a result of further rearrangements of the solute retained on matrix surfaces. Thus, inclusion of S_3 in the model allows the description of the frequently observed very slow release of solute from the soil. The reaction between S_2 and S_3 was considered to be of the kinetic first-order type, i.e.

$$\frac{\partial S_3}{\partial t} = k_5 S_2 - k_6 S_3 \tag{V.1.10}$$

where k_5 and k_6 (h^{-1}) are the reaction rate coefficients. If a consecutive reaction is included in the model, then Equation (V.1.8) must be modified to incorporate the reversible reaction between S_2 and S_3. As a result, the following equation

$$\rho \frac{\partial S_2}{\partial t} = k_3\, \Theta C^n - \rho(k_4 + k_5)S_2 + \rho k_6 S_3 \tag{V.1.11}$$

must be used in place of Equation (V.1.8). The above reactions are nonlinear in nature and represent initial-value problems that were solved numerically using finite difference approximations (explicit–implicit).

Selected examples of experimental and MRM model predicted kinetic retention for Cd are given in Figure V.1.10. Here, the kinetic dependence of Cd retention, carried out in batch experiments, is shown for various soils (Selim, 1989). The amount of cadmium retained varied among soils with Cecil soil exhibiting the lowest retention, whereas Sharkey soil showed maximum Cd sorption from soil solution. The fast decrease in Cd concentration (with time) indicates a fast-type sorption reaction, which was followed by slower type reactions. It is also apparent that after 300 h of reaction time, quasi-equilibrium conditions were not attained. The capability of the MRM model to describe

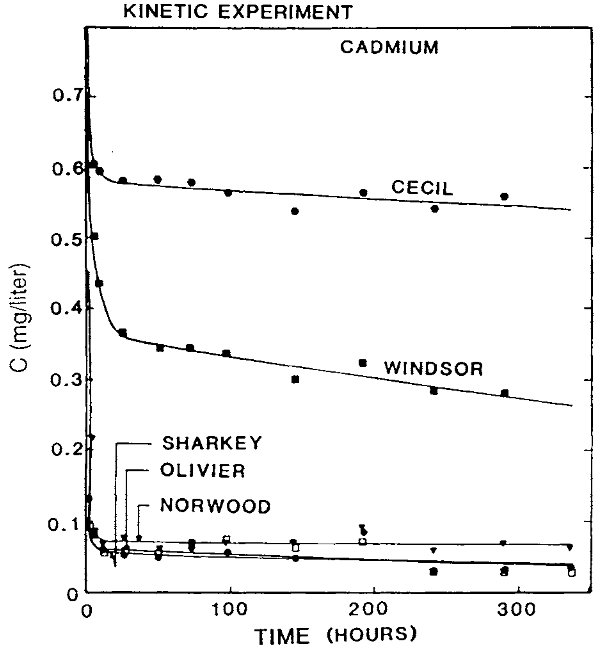

Figure V.1.10. Time-dependent retention of Cd by five soils at an initial Cd concentration (C_0).

the time-dependent characteristics for several soils is well demonstrated by the solid curves in Figure V.1.10.

For the second-order two-site approach (SOTS), one assumes that there exist two types of retention sites on soil matrix surfaces. In addition, the reactions associated with the two sites 1 and 2 were considered as kinetically controlled, heterogeneous chemical retention reactions. Therefore, one can assume that these processes are predominantly controlled by surface reactions of adsorption and exchange. We denote F as the fraction of type 1 sites to the total amount of sites S_T. We also denote ϕ as the amount of unfilled or vacant sites in the soil,

$$\phi_1 = S_{T1} - S_1 = FS_T - S_1 \tag{V.1.12}$$

$$\phi_2 = S_{T2} - S_2 = FS_T - S_2 \tag{V.1.13}$$

where ϕ_1 and ϕ_2 are amounts of vacant sites and S_1 and S_2 are amounts of solute retained on type 1 and type 2 sites, and S_{T1} and S_{T2} are the total amount of type 1 and type 2 sites, respectively. As the sites become occupied by the retained solute, the amount of vacant sites approaches zero $((\phi_1 + \phi_2) \rightarrow 0)$ and the amount of solute retained by the soil approaches that of the total capacity of sites $(S_1 + S_2) \rightarrow S_T$. As a result, the rate of retention may be expressed as,

$$\rho \frac{\partial S_1}{\partial t} = k_1\, \Theta \phi_1 C - k_2 \rho S_1 \quad \text{for type 1 sites} \tag{V.1.14}$$

$$\rho \frac{\partial S_2}{\partial t} = k_3\, \Theta \phi_2 C - k_4 \rho S_2 \qquad \text{for type 2 sites} \tag{V.1.15}$$

where k_1 to k_4 are the associated rate coefficients. It is convenient to regard type 1 sites as those where equilibrium is rapidly reached. In contrast, type 2 sites are highly kinetic and may require several days or months for apparent local equilibrium to be achieved. This SOTS model was also extended to the diffusion-controlled mobile–immobile (SOMIM) or two-region model where a fraction of the dynamic to the stagnant sites and a mass transfer between the mobile and immobile water regions were incorporated (see Selim and Amacher, 1997).

The time-dependent retention of Cr(VI) by several soils was well described using the second-order two-site (SOTS) model (Selim and Amacher, 1988). An example of experimental and SOTS predicted time-dependent adsorption for a Windsor soil is shown in Figure V.1.11. Moreover, to illustrate the versatility of SOTS, two model versions were examined, a three-parameter or a one-site version (k_1, k_2, and k_{irr}) in which S_T was not differentiated into type 1 and type 2 sites ($F = 1$) and a five-parameter or a two-site version (k_1, k_2, k_3, k_4, and k_{irr}) in which two types of reaction sites were considered. For most input concentrations (C_0's), either the three- or five-parameter versions described the data adequately with high r^2 values and low parameter standard errors (data not shown). For Windsor soil, the five-parameter model version provided the best description of the data at low C_0's, whereas the three-parameter model version was best for higher C_0's.

To further examine the capability of the SOTS model, Selim and Amacher (1988) utilized Cr(VI) transport data for three soils from miscible displacement experiments.

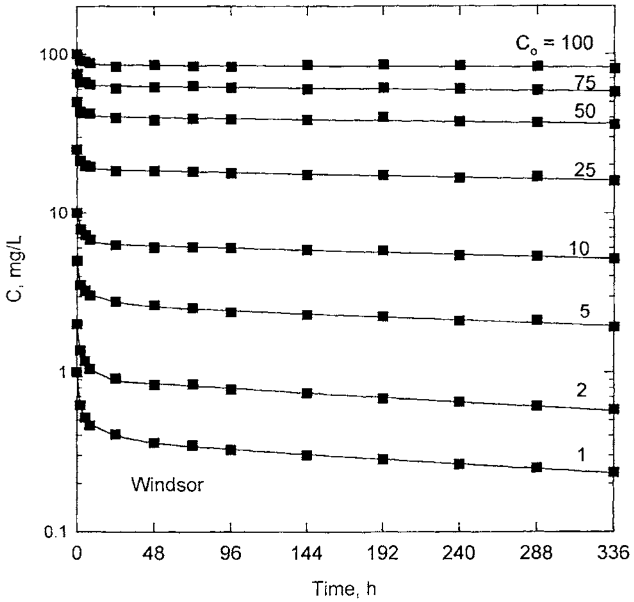

Figure V.1.11. Time-dependent retention of Cr(VI) by Windsor soil. Closed squares are the data points and solid lines are second-order two-site model predictions for different initial concentration curves ($C_0 = 1, 2, 5, 10, 25, 50, 75$, and 100 mg/l).

For Windsor soil, the predicted BTCs shown in Figure V.1.12 were obtained using different sets of model rate coefficients. This is because a unique set for the rate coefficients was not obtained from the batch data, rather a strong dependence of rate coefficients on input concentration was observed (Selim and Amacher, 1988). The use of batch rate coefficients at $C_0 = 100$ μg/ml, which is the concentration of Cr pulse inputs, grossly underestimated Cr retention by the predicted BTCs for the Windsor soils. Reasons for this failure are not fully understood with a most likely explanation is that the model is an apparent rather than mechanistic rate law which may not completely account for all reactions and reaction components. Closest predictions were realized using batch rate coefficients from C_0 of 10 or 25 μg/ml.

The capability of the second-order mobile–immobile (SOMIM) model to describe Cr miscible displacement results was also examined and predictions for Windsor soil are shown in Figure V.1.13. Predicted BTCs were obtained using different sets of model rate coefficients due to their strong dependence on input concentrations (C_0's). Closest predictions to experimental Cr measurements were obtained from batch rate coefficients at low C_0 values ($C_0 \leq 10$ μg/ml). Moreover, the use of rate coefficients at higher C_0's resulted in decreased tailing and reduced retardation of the BTCs. These observations are consistent with previous predictions using the SOTS model (Fig. V.1.12). Reasons for the observed less than adequate predictions of BTCs for the three soils using SOMIM are likely due to the poor estimates for the fraction immobile water content, the mass transfer and perhaps lack of nonequilibrium conditions between the mobile and immobile fractions. It is also conceivable that a set of applicable rate coefficients over

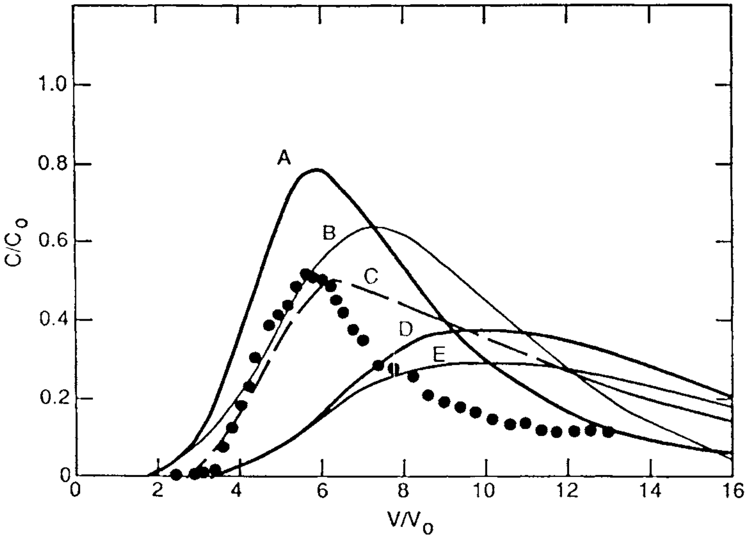

Figure V.1.12. Effluent concentration distributions for Cr(VI) in Windsor soil. Curves A, B, C, D, and E are predictions using the second-order two-site model with batch rate coefficients for C_0 of 25, 10, 5, 2, and 1 mg/l, respectively.

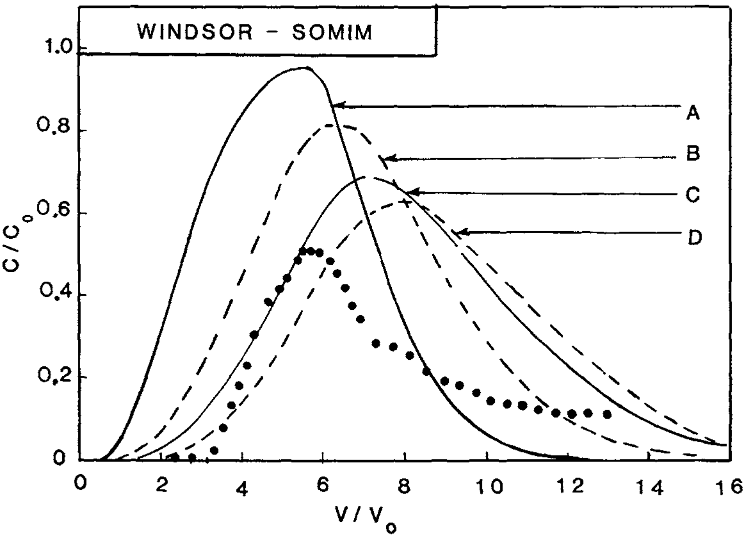

Figure V.1.13. Effluent concentration distributions for Cr in Windsor soil. Curves A, B, C, and D are predictions using the second-order mobile–immobile model with batch rate coefficients for $C/C_0 = 25$, 5, 2, and 1 mg/l, respectively.

the concentration range for Cr transport experiments cannot be obtained simply by use of the batch data sets.

The preceding examples illustrate various possibilities of using mass-action type equilibrium and kinetic approaches for describing reactive metal transport in heterogeneous porous media such as soils. In cases where specific reaction mechanisms are better understood, such as the interaction of a reactive oxyanion with a well-characterized mineral surface (see Scheidegger and Sparks, 1996 for some pertinent examples), more precise equilibrium and kinetic equations that describe the interaction of the reactive solute with the charged surface can be developed (e.g. Grossl et al., 1997). However, until sorption processes in heterogeneous media containing mixed assemblages of reactive mineral and organic surfaces (e.g. soil) are better understood and characterized, we will need to continue using more general and empirical mass-action type models such as those presented here to describe reactive metal transport in soils.

References

Amacher, M.C., Selim, H.M., Iskandar, I.K., 1988. Kinetics of chromium (VI) and cadmium retention in soils; a nonlinear multireaction model. Soil Sci. Soc. Am. J., 52, 398–408.

Amacher, M.C., Selim, H.M., Iskandar, I.K., 1990. Kinetics of mercuric chloride retention by soils. J. Environ. Qual., 19, 382–388.

Buchter, B., Davidoff, B., Amacher, M.C., Hinz, C., Iskandar, I.K., Selim, H.M., 1989. Correlation of Freundlich K_d and n retention parameters with soils and elements. Soil Sci., 148, 370–379.

Grossl, P.R., Eick, M., Sparks, D.L., Goldberg, S., Ainsworth, C.C., 1997. Arsenate and chromate retention mechanisms on goethite. 2. Kinetic evaluation using a pressure-jump relaxation technique. Environ. Sci. Technol., 31, 321–326.

Harmsen, K., 1977. Behavior of Heavy Metals in Soils. Centre for Agriculture Publishing and Documentation, Wageningen, The Netherlands.

Hinz, C., Selim, H.M., 1994. Transport of Zn and Cd in soils: experimental evidence and modeling approaches. Soil Sci. Soc. Am. J., 58, 1316–1327.

Kretzschmar, R., Voegelin, A., 2001. Modeling competitive sorption and release of heavy metals in soils. In: Selim, H.M., Sparks, D.L. (Eds), Heavy Metals Release in Soils, Lewis Publishers, Boca Raton, FL, pp. 55–88.

Rubin, J., James, R.V., 1973. Dispersion-affected transport of reacting solution in saturated porous media, Galerkin method applied to equilibrium-controlled exchange in unidirectional steady water flow. Water Resour. Res., 9, 1332–1356.

Scheidegger, A.M., Sparks, D.L., 1996. A critical assessment of sorption–desorption mechanisms at the soil mineral/water interface. Soil Sci., 161, 813–831.

Schmidt, H.W., Sticher, H., 1986. Long-term trend analysis of heavy metal content and translocation in soils. Geoderma, 38, 195–207.

Selim, H.M., 1989. Prediction of contaminant retention and transport in soils using kinetic multireaction models. Environ. Health Perspect., 83, 69–75.

Selim, H.M., 1992. Modeling the transport and retention of inorganics in soils. Adv. Agron., 47, 331–384.

Selim, H.M., 1999. Modeling the kinetics of heavy metals reactivity in soils. In: Selim, H.M., Iskandar, I.K. (Eds), Fate and Transport of Heavy Metals in the Vadose Zone, Lewis Publishers, Boca Raton, FL, pp. 91–106.

Selim, H.M., Amacher, M.C., 1988. A second-order kinetic approach for modeling solute retention and transport in soils. Water Resour. Res., 24, 2061–2075.

Selim, H.M., Amacher, M.C., 1997. Reactivity and Transport of Heavy Metals in Soils. CRC Press/Lewis Publishers, Boca Raton, FL, p. 201.

Selim, H.M., Amacher, M.C., 2001. Sorption and release of heavy metals in soils: nonlinear kinetics. In: Selim, H.M., Sparks, D.L. (Eds), Heavy Metals Release in Soils, Lewis Publishers, Boca Raton, FL, pp. 1–29.

Selim, H.M., Amacher, M.C., Iskandar, I.K., 1989. Modeling the transport of chromium (VI) in soil columns. Soil Sci. Soc. Am. J., 53, 996–1004.

Selim, H.M., Buchter, B., Hinz, C., Ma, L., 1992. Modeling the transport and retention of cadmium in soils: multireaction and multicomponent approaches. Soil Sci. Soc. Am. J., 56, 1004–1015.

Sparks, D.L., 1989. Kinetics of Soil Chemical Processes. Academic Press, San Diego, CA, p. 210.

Sposito, G., 1981. The Thermodynamics of Soil Solutions. Oxford University Press, New York, p. 223.

Sposito, G., 1984. The Surface Chemistry of Soils. Oxford University Press, New York, p. 234.