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Bioavailability of Micronutrients and Other Trace Elements in Soils

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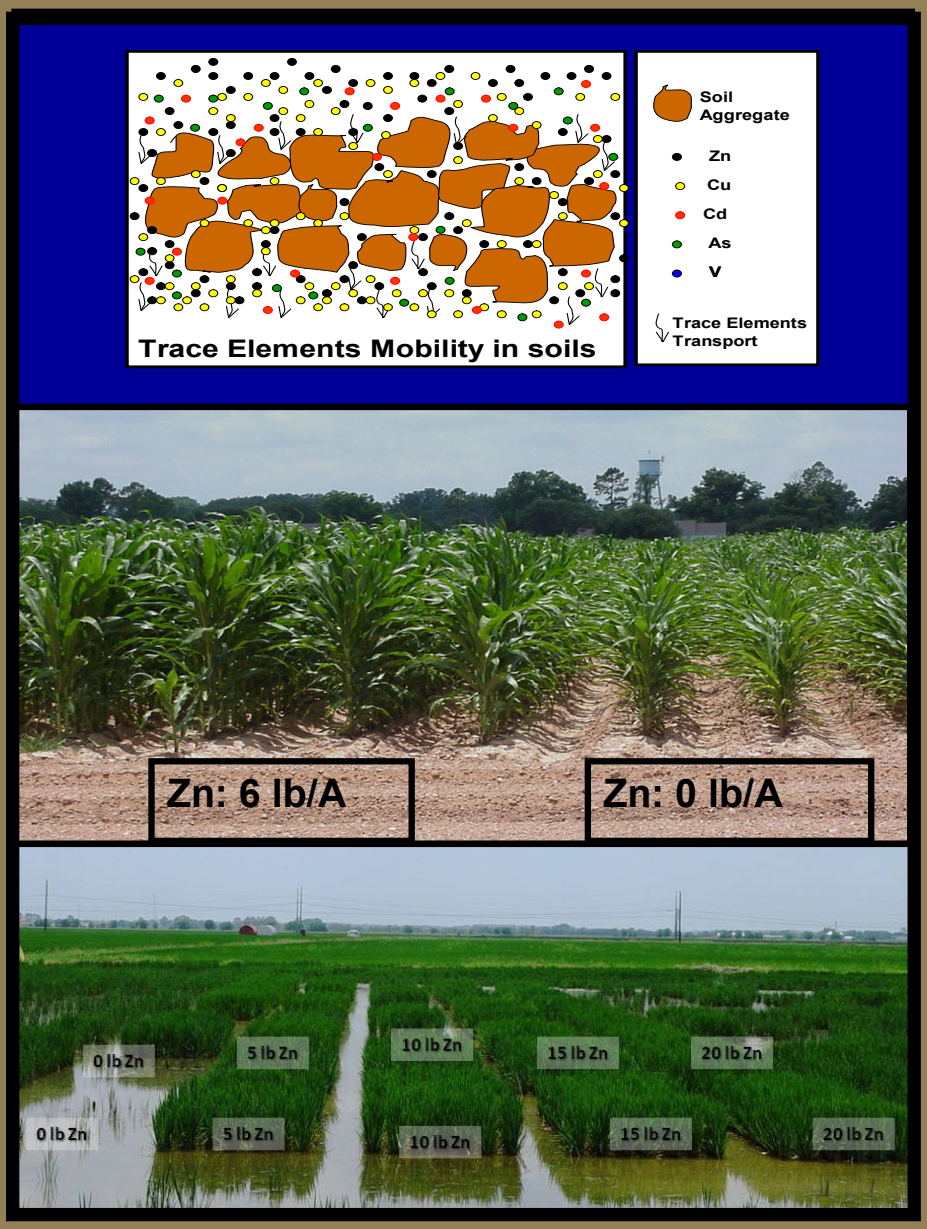

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INTRODUCTION

Understanding trace element interactions in the soil-water environment is essential in assessing their bioavailability and potential toxicity. Trace elements include several heavy metals, such as zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd) and vanadium (V), among others. Several heavy metals such as Zn and Cu are essential micronutrients required in the growth of both plants and animals. Micronutrients are often applied in the form of fertilizers or as supplements in animal feed. Heavy metals are extensively used as fungicides and as bactericides in numerous pharmaceuticals. The bioavailability of trace elements in the soil-water environment depends on an array of soil properties, including soil pH, organic matter (OM) content, amount and type of dominant clay and carbonates, among others. In addition, the counter ions present in the soil system greatly influence the fate of trace metals in soils. In fact, several studies suggested varied interactions of heavy metals with phosphates in soils.

The adsorption of trace elements by clay minerals, metal oxides and organic materials has generally been explained with two types of reaction mechanisms: (1) ion exchange in the diffuse layer as a result of electrostatic force and (2) surface complexation through the formation of strong covalent bonds between heavy metal ions and specific reaction sites on surfaces of minerals or organic matters. The ion exchange reaction is also referred to as nonspecific sorption and the surface complexation is referred as specific sorption.

Adsorption isotherms or, more accurately, sorption isotherms, are a convenient way to graphically represent the amount of an adsorbed compound, or adsorbate, in relation to its concentration in the equilibrium solution. In other words, an adsorption isotherm is a relationship relating the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid phase at a constant temperature. Freundlich and Langmuir sorption equations are extensively used to describe sorption isotherms for a wide range of chemicals. Knowledge of sorption isotherms and adsorption phenomena is essential for understanding heavy solute retention and transport in soils and geological media. It is crucial for assessing the environmental risk of contamination or pollution caused by these elements. Studies on solute adsorption in soils are often conducted as a one component system, where the ions or molecules are treated individually, or they can be conducted as a multicomponent system, where the ions are subjected to competition among them.

Freundlich Isotherm

The Freundlich isotherm is one of the simplest approaches for quantifying the behavior of retention of reactive solute with the matrix surfaces. It is one of the oldest nonlinear sorption equations and was based on quantifying the solute adsorbed by unit mass of soil with increasing concentration which was described as

$$S = K_f C^b \quad (1)$$

where S is the amount of solute retained by the soil in (mg Kg^{-1}), C is the solute concentration in solution (mg L^{-1}), K_f is the partitioning coefficient (L kg^{-1}) and the exponent b is dimensionless parameter. A major advantage of the Freundlich approach is that it is capable of describing successfully sorption for most trace elements, pesticides and other organics. The parameter K_f represents 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.

This partitioning coefficient K_f is a measure of the affinity of a heavy metal to a soil and is widely reported in the literature for various chemicals. The parameter b is a measure of the extent of the heterogeneity of sorption sites on the soil having different affinities for solute retention by matrix surfaces. In a heterogeneous system, sorption by the highest energy sites takes place preferentially at the lowest solution concentrations, and as the sorbed concentration increases, successively lower energy sites become occupied. This leads to a concentration-dependent sorption equilibrium behavior, i.e., a nonlinear isotherm (Selim 2015). When b equals unity, the Freundlich equation takes on the form of the linear equation.

$$S = K_d C \quad (2)$$

where K_d is the distribution coefficient (L/Kg). As K_d is used, this implies a linear, zero-intercept relationship between sorbed and solution concentration, which is a convenient assumption but certainly not universally true. This linear model is often referred to as constant partition model and the parameter K_d value is a universally accepted environment parameter that reflects the affinity of matrix surfaces for solute species. The Kd parameter provides an estimate for potential adsorption of dissolved contaminants in contact with soil and is typically used in fate and contaminant transport calculations. According to the USEPA (1999), Kd is defined as the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium.

Langmuir Isotherm

The Langmuir isotherm was developed to describe the adsorption of gases by solids in which a finite number of adsorption sites in planer surfaces is assumed. The major assumptions include that ions are adsorbed as a monolayer on the surface, and the maximum adsorption occurs when the surface is completely covered. Other assumptions are that the surface considered is homogeneous, the sites are of identical adsorption energy or affinity over the entire surface and that equilibrium is attained. As a result, a major advantage of the Langmuir equation over the linear and Freundlich equations is that a maximum sorption capacity is incorporated into the formulation of the model, which may be regarded as a measure of the amount of available retention sites on the solid phase. The standard form of the Langmuir equation is

$$\frac{S}{S_{\max}} = \frac{\omega C}{1 + \omega C} \qquad (3)$$

where ω and S_{max} are adjustable parameters. Here ω (ml µg-1) is a measure of the bond strength of molecules on the matrix surface, and S_{max} (µg g-1 of soil) is the maximum sorption capacity or total amount of available sites per unit soil mass.

GENERAL TYPE ISOTHERMS

Giles et al. (1974) proposed four general types of isotherms (C, L, H and S) which are illustrated in Fig. 1. The C-type isotherms indicate partitioning of ions or molecules between the solution and sorbed phase as in the linear model, equation (2). The L-type isotherm is characterized by decreasing slopes as the vacant sites become occupied by the sorbed ion or molecule. Freundlich and Langmuir isotherm are commonly referred to as

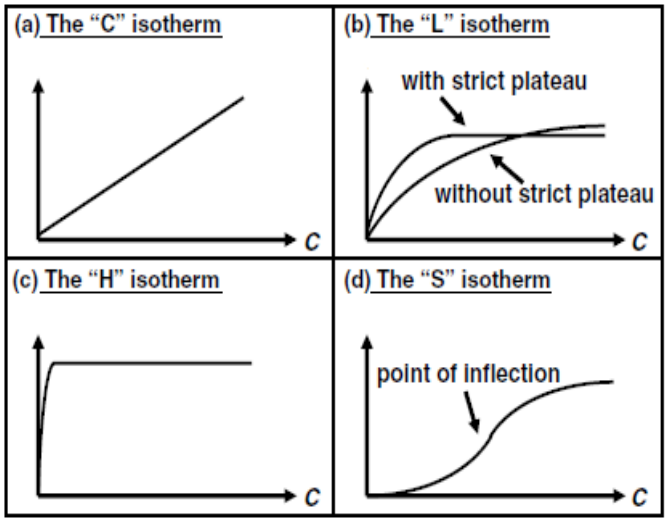


Fig. 1. The four main types of isotherms (after Giles et al., 1974).

L-curve isotherms. In L-type isotherms, at low solution concentrations, high-energy sites are occupied first. Subsequently, as the concentration in solution increases, sites of moderate and those of low affinities become occupied. The H-type isotherms are best characterized by extremely high sorption possibly due to irreversible reactions. The S-type isotherms indicate low affinity for sorption at low solution concentrations followed by a gradual sorption increase. At a higher concentration, sorption decreases, and sorption maxima are perhaps attained.

In the literature, L-type isotherms are frequently encountered for most trace elements and heavy metals. Specifically, Freundlich isotherms and Langmuir are adopted for a wide range of solutes. C-type is often observed for pesticides (herbicides and insecticides) where linear isotherms are often observed.

Empirical versus Mechanistic Models

Fontes (2012) argued that the adsorption phenomenon can be represented by two main conceptual models: (1) the empirical, the ones initially derived from experiments, and (2) the semiempirical or mechanistic, the ones that are based on reaction mechanisms. The main difference between these two models is the lack of an electrostatic term in the empirical models whereas its presence is integral to mechanistic models. Mechanistic type models, also known as chemical models, are expected to provide "a close representation of the real adsorption phenomenon in the soil system" (Sparks 2003). Nevertheless, due to the complexity of chemical models, empirical models are usually used in most solute studies with soils and geological media. Moreover, empirical models have been widely used in soil science and environmental studies related to metals and anions adsorption and pesticide retention in soils. A listing of such models is presented in Table 1. These models do not take into consideration the electrostatic influence of the electrically charged surfaces in the solution or the influence of changes in surface charges due to the composition of soil solution. In the empirical model, the model form is chosen a *posteriori* from the observed adsorption data and to enable a satisfying fit of the experimental data the mathematical form and the number of parameters are chosen to be as simple as possible (Bradl, 2004).

EFFECT OF SOIL PROPERTIES

Buchter et al. (1989) studied the retention of 15 elements by 11 soils from 10 soil orders to determine the effects of element and soil properties on the magnitude of the Freundlich parameters K_f and b. They also explored the

Table 1. Selected equilibrium and kinetic type models for heavy metal retention in soils.	
Model	Formulation '
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)	$\partial S / \partial t = k_s (\theta / \rho) \left(C - C_p\right)$
Second-order irreversible	$\partial S / \partial t = k_s (\theta / \rho) C \left(S_{max} - S\right)$
Langmuir Kinetic	$\partial S / \partial t = k_f (\theta / \rho) C \left(S_{max} - S\right) - k_b S$
Elovich	$\partial S / \partial t = A \exp(-BS)$
Power	$\partial S / \partial t = K (\theta / \rho) C^n S^m$
Mass Transfer	$\partial S / \partial t = K (\theta / \rho) \left(C - C^*\right)$

'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 bulk density, Θ is volumetric soil water content, C_T is total solute concentration and S_T is total amount sorbed of all competing species.

Table 2. Taxonomic classification and selected chemical and physical properties of the soils used by Buchter et al. (1989)

Soil**	Horizon	Taxanomic Classification	pH	TOC	sum of cations CEC	exch. OH	MnO_2	amor. Fe_2O_3	free Fe_2O_3	Al_2O_3	$CaCO_3$	sand	silt	clay
				%	--cmol$_c$/kg--	----------%----------			%	---------%---------				
Alligator	Ap	very-fine, m orillonitic, acid, thermic Vertic Haplaquept	4.8	1.54	30.2	3.5	0.028	0.33	0.74	0.15	----	5.9	39.4	54.7
unnamed	Ap	Calcíorthid	8.5	0.44	14.7	33.8	0.015	0.050	0.25	0.000	7.39	70.0	19.3	10.7
Cecil	Ap	clayey, kaolinitic, thermic Typic Hapludult	5.7	0.61	2.0	0.011	0.099	1.76	0.27	----	----	67.7	12.8	7,3
Cecil	B	clayey, kaolinitic, thermic Typic Hapludult	5.4	0.26	2.4	6.6	0.002	0.082	7.48	0.94	----	30.0	18.8	51.2
Kula	Ap1	medial, isothermic Typic Euthandept	5.9	6.62	22.5	82.4	0.093	1.68	5.85	3.51	----	73.7	25.4	0.9
Kula	Ap2	medial, isothermic Typic Euthandept	6.2	6.98	27.0	58.5	0.13	1.64	6.95	3.67	----	66.6	32.9	0.5
Lafitte	Ap	euic, thermic Typic Medisaprist	3.9	11.6	26.9	4.7	0.009	1.19	1.16	0.28	----	60.7	21.7	17.6
Molokai	Ap	clayey, kaolinitic, isohyper-thermic Typic Torrox	6.0	1.67	11.0	7.2	0.76	0.19	12.4	0.91	----	25.7	46.2	28.2
Norwood	Ap	fine-silty, mixed (calc.), thermic Typic Udifluvent	6.9	0.21	4.1	0.0	0.008	0.061	0.30	0.016	----	79.2	18.1	2.8
Olivier	Ap	fine-silty, mixed, thermic Aquic Fragiudalf	6.6	0.83	8.6	1.9	0.27	0.30	0.71	0.071	----	4.4	89.4	6.2
unnamed	B21h	Spodosol	4.3	1.98	2.7	5.2	0.0000	0.009	0.008	0.22	----	90.2	6.0	3.8
Webster	Ap	fine-loamy, mixed, mesic Typic Haplaquoll	7.6	4.39	48.1	14.1	0.063	0.19	0.55	0.10	3.14	27.5	48.6	23.9

** The states from which the soil samples originated are Louisiana (Alligator, Lafitte, Norwood and Olivier soils); South Carolina (Cecil soil); Hawaii (Kula and Molokai soils); Iowa (Webster soil); New Hampshire (Windsor soil); New Mexico (Calciorthid); and Florida (Spodosol).

Table 3. Freundlich model parameters K_f and *b* for of the soils used by Buchter et al. (1989)

Element	Initial species	Soil											mean*
		Alligator	Calciorthid	Cecil	Kula	Lafitte	Molakai	Norwood	Olivier	Oldsmar	Webster	Windsor	
		K_f (mL/g)											
Co	Co^{2+}	3.57E+01	2.51E+02	6.56E+00	1.05E+02	3.39E+01	9.25E+01	2.74E+01	6.70E+01	2.55E+00	3.63E+02	6.28E+00	3.75E+01
Ni	Ni^{2+}	3.78E+01	2.06E+02	6.84E+00	1.10E+02	5.01E+01	4.49E+01	2.09E+01	5.05E+01	3.44E+00	3.37E+02	8.43E+00	3.61E+01
Cu	Cu^{2+}	2.58E+02	2.62E+03	5.37E+01	2.05E+03	2.21E+02	3.68E+02	8.91E+01	2.18E+02	5.62E+01	6.35E+03	7.71E+01	3.17E+03
Zn	Zn^{2+}	2.81E+01	4.20E+02	1.12E+01	2.38E+02	2.01E+01	8.04E+01	4.21E+01	8.91E+01	2.12E+00	7.74E+02	9.68E+00	4.79E+01
Cd	Cd^{2+}	5.25E+01	2.88E+02	1.39E+01	1.87E+02	5.27E+01	9.12E+01	2.88E+01	9.79E+01	5.47E+00	7.55E+02	1.44E+01	5.93E+01
Hg	Hg^{2+}	1.08E+02	1.96E+01	8.13E+01	2.49E+02	1.90E+02	1.20E+02	1.13E+02	1.29E+02	8.63E+01	2.99E+02	1.30E+02	1.15E+02
Pb	Pb^{2+}	1.81E+03		2.36E+02	4.32E+07	9.18E+02	8.17E+03	3.85E+02	1.64E+04	1.36E+02		4.72E+02	3.37E+02
V	VO^{-3}	1.42E+02	1.08E+01	3.97E+01	2.22E+03	1.03E+02	5.05E+02	1.86E+01	9.12E+01	9.08E+01	8.07E+01	1.53E+01	1.03E+02
Cr	CrO^{2-}_4	3.41E+00			6.28E+01	3.03E+01	6.41E+00			5.47E+00		8.47E+00	1.12E+01
Mo	$Mo_7O^{6-}_{24}$	5.75E+01	1.80E+01	4.11E+02	8.15E+01	1.18E+02			2.56E+01		4.38E+01	6.44E+01	
As	AsO^{3-}_4	4.78E+01	8.87E+00	1.98E+01	1.50E+03	7.10E+01	1.56E+02	8.53E+00	4.60E+01	1.87E+01	2.36E+01	1.05E+02	4.71E+01
		b											
Co	Co^{2+}	0.953	0.546	0.745	0.878	1.009	0.621	0.627	0.584	0.811	0.782	0.741	0.754
Ni	Ni^{2+}	0.939	0.504	0.688	0.738	0.903	0.720	0.661	0.646	0.836	0.748	0.741	0.739
Cu	Cu^{2+}	0.544	1.140	0.546	1.016	0.987	0.516	0.471	0.495	0.602	1.420	0.567	0.755
Zn	Zn^{2+}	1.011	0.510	0.724	0.724	0.891	0.675	0.515	0.625	0.962	0.697	0.792	0.739
Cd	Cd^{2+}	0.902	0.568	0.768	0.721	0.850	0.773	0.668	0.658	0.840	0.569	0.782	0.736
Hg	Hg^{2+}	0.741	0.313	0.564	1.700	0.751	0.960	0.582	1.122	0.513	2.158	0.681	1.008
Pb	Pb^{2+}	0.853		0.662	5.385	0.558	1.678	0.741	0.998	0.743		0.743	1.485
V	VO^{-}_3	0.592	0.857	0.629	1.402	0.679	0.847	0.877	0.607	0.483	0.762	0.647	0.762
Cr	CrO^{2-}_4	0.504			0.609	0.374	0.607			0.394		0.521	0.501
Mo	$Mo_7O^{6-}_{24}$	0.882		0.617	1.031	0.607	0.664			0.451		0.544	0.685
As	AsO^{3-}_4	0.636	0.554	0.618	1.462	0.747	0.561	0.510	0.548	0.797	0.648	0.601	0.698

correlation of the Freundlich parameters with selected soil properties and found that pH, cation-exchange capacity (CEC) and iron/aluminum oxide contents were the most important factors for correlation with the partitioning coefficients. The names, taxonomic classification and selected properties of the 11 soils used in their study are listed in Table 2, and estimated values for K_f and *b* for selected heavy metals are given in Table 3. A wide range of K_f values from 0.0419 to 4.32×10^7 ml g^{-1} were obtained, which illustrates the extent of heavy metals affinity among various soil types. Such a wide range of values was not obtained for the exponent parameter *b*, however. The magnitude of K_f and *b* was related to both soil and element properties. Strongly retained elements such as copper (Cu), mercury (Hg), lead (Pb) and vanadium (V) had the highest K_f values. The transition metal cations cobalt (Co) and nickel (Ni) had similar K_f and *b* values as did the group IIB elements Zn and Cd. Oxyanion species tended to have lower *b* values than did cation species. Soil pH and CEC were significantly correlated to log K_f values for cation species. High pH and high CEC soils retained greater quantities of the cation species than did low pH and low CEC soils. A significant negative correlation between soil pH and the Freundlich parameter *b* was obtained for cation species whereas a significant positive correlation between soil pH and *b* for Cr(VI) was found (Buchter et al., 1989). Greater quantities of anion species were retained by soils with high amounts of amorphous iron oxides, aluminum oxides and amorphous material than were retained by soils with low amounts of these minerals. Several anion species were not retained by high pH soils. Despite the facts that element retention by soils is the result of many interacting processes and that many factors influence retention, significant relationships among retention parameters and soil and element properties exist even among soils with greatly different characteristics. Buchter et al. (1989) made the following conclusions:

1. pH is the most important soil property that affects K_f and b.
2. CEC influences K_f for cation species.
3. The amounts of amorphous iron oxides, aluminum oxides and amorphous material in soils influence both cation and anion retention parameters.
4. Except for Cu and Hg, transition metals (Co and Ni) and group lIB cations (Zn and Cd) have similar K_f and b values for a given soil.
5. Significant relationships between soil properties and retention parameters exist even in a group of soils with greatly different characteristics.

The relationships between soil properties and retention parameters (e.g., Fig. 2) can be used to estimate retention parameters when the data for a particular element and soil type are lacking but soil property data are available. For example, the retention characteristics of Co, Ni, Zn and Cd are sufficiently similar that these elements can be grouped together, and an estimated b value for anyone of them could be estimated from soil pH data using the regression equation for curve A in Fig. 2. For many purposes such an estimate would be useful, at least as a first approximation, in describing the retention characteristics of a soil.

Curve A: $b = 1.24 - 0.0831\ pH \quad (r = 0.83)$ (4)

Curve B: $b = -0.0846 + 0.116\ pH \quad (r = 0.98)$ (5)

A literature search revealed that sorption parameters as affected by reaction time for a wide range of soils is lacking. In this bulletin, we presented results of trace elements retention of five trace elements by ten different soils. The soils varied extensively, and the trace elements were Cu, Zn, Pb, Ni and Cd. The selection of these heavy metals was made based on EPA Code of Federal Regulation CFR 40 Part 503 for land-applied sewage sludges (USEPA, 1993, 1994a, 1994b, 1995). The specific objectives were twofold: first, to quantify heavy metal affinity for the different soils, and second, to quantify the effect of time of reaction or kinetics on heavy metals affinities. A third objective was to assess the capability of Buchter et al. (1989) models in predicting measured data.

Soils and Experimental Methods

The names, taxonomic classifications and selected properties of the 10 soils used in this study are listed in Table 4. The Ap horizons of all soils were used in this retention study. The only exception is that for the sandy candor subsurface sample which was sampled at a depth of 90 cm. Physical and chemical properties of the 10 soils are given in Table 5. Soil pH was measured using a one-to-one soil/water suspension, and the NH_4OAc at pH 7 method was used to determine cation exchange capacity (CEC). Total carbon was measured using a dry combustion method (Elementar Americans Inc., Mount Laurel, NJ). The carbonate content of soil was determined according to the pressure calcimeter method. For the batch experiments, a 5-mL aliquot was sampled and the total Cd, Cu, Ni, Pb

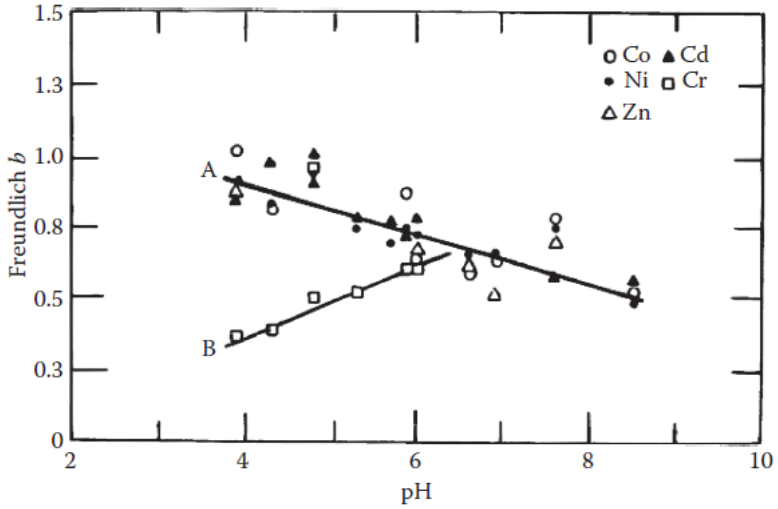


Fig. 2. Correlation between soil *pH* and Freundlich parameter *b* (after Buchter et al. 1989). Curve A is a regression line for Co, Ni, Zn, and Cd (b = 1.24 - 0.0831 pH, r = 0.83). Curve B is for Cr(VI) (b = -0.0846 + 0.116 pH, r = 0.98).

Table 4. Selected soil properties of the 10 soils used in the study.

Soil Series	State	Texture	pH	%C	CEC	Sand %	Silt %	Clay %	Carbonates (%)
Arapahoe	NC	FSL	5.02	10.22	30.10	64.7	25.2	10.1	
Candor - Surface	NC	LCoS	4.39	2.24	5.30	84.1	6.6	9.3	
Candor - Subsurface	NC	CoS	4.05	0.56	1.70	91.0	4.1	4.9	
Olney	CO	FSL	8.12	1.14	10.10	71.1	11.6	17.3	3.32
Lincoln	OK	VFSL	7.54	1.27	3.00	59.5	29.7	10.8	3.6
Nada	TX	FSL	6.61	0.76	6.30	56.8	33.6	9.6	
Morey	TX	L	7.74	1.05	27.80	29.4	46.5	24.1	
Crowley	LA	SiL	5.22	1.16	16.50	8.3	77.3	14.4	
Sharkey	LA	SiC	5.49	2.76	39.70	6.4	48.6	45.0	
Houston	TX	SiC	7.78	4.26	47.70	9.6	41.2	49.2	26.0

Table 5. Taxonomic classification of the 10 soils used in this study.

Soil Series	State	Taxonomic Classification
Arapahoe	NC	Coarse-loamy, mixed, semiactive, nonacid, thermic Typic Humaquepts
Candor - Surface	NC	Sandy, kaolinitic, thermic Grossarenic Kandiudults
Candor - Subsurface	NC	Sandy, kaolinitic, thermic Grossarenic Kandiudults
Olney	CO	Fine-loamy, mixed, superactive, mesic Ustic Haplargids
Lincoln	OK	Sandy, mixed, thermic Typic Ustifluvents
Nada	TX	Fine-loamy, siliceous, active, hyperthermic Albaquic Hapludalfs
Morey	TX	Fine-silty, siliceous, superactive, hyperthermic Oxyaquic Argiudolls
Crowley	LA	Fine, smectitic, thermic Typic Albaqualfs
Sharkey	LA	Fine-silty, mixed, active, thermic Typic Glossaqualfs
Houston	TX	Fine, smectitic, thermic Udic Haplusterts

and Zn concentration in the supernatant solution were analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Spectro Citros CCD, Spectro Analytical Instruments, Kleve, Germany).

Adsorption Isotherms

To assess the retention capability of the different soils used in this study to retain heavy metals, adsorption isotherms were measured. The batch equilibration technique was with four different initial concentrations of the heavy metals. Due to the anticipated differences in the affinity of the heavy metals to soils, the range of initial concentrations used varied based on the heavy metal. For lead (Pb) maximum input concentration used was 400 mg/L whereas for all other heavy metals the maximum concentration used varied from 100-150 mg/L. All solutions were prepared in 0.005 *M* $Ca(NO_3)_2$ as a background solution. Adsorption was performed in duplicates where 3-g sample of each soil were placed in Teflon centrifuge tubes and mixed with 30 mL solution of known heavy metal concentrations described above. The tubes were sealed, and the mixtures were continuously shaken for 24 hours and then centrifuged for 10 minutes. A 5-mL aliquot was sampled, and the concentration of the heavy metal in the supernatant at reaction times of 1 and 7 days was measured. The mixtures were subsequently returned to the shaker after each sampling. The collected samples were analyzed using ICP–AES. The detection limits of ICP-AES were 2.3, 3.6, 10.0, 28.0 and 1.2 for Cd, Cu, Ni, Pb and Zn µg/L (ppb) respectively. The amount of a heavy metal retained (sorbed) by the soil matrix was determined by the difference between the concentrations of the supernatant and that of the initial solutions.

Data Analysis

The linear and Freundlich models, equations (1) and (2), were fit to the isotherm data using a nonlinear, least-squares curve-fitting method. The curve-fitting method is basically the maximum neighborhood method and is based on an optimum interpolation between the Taylor series method and the method of steepest descent. Criteria used for estimating goodness-of-fit of the model to the data were the coefficient of determination (r^2) and the root mean square statistics (RMSE),

$$RMSE = \sqrt{\frac{rss}{N_d - P}} \qquad (5)$$

where *rss* is the residual sum of squares, N_d is the number of data points and *P* is the number of fitted parameters.

RESULTS AND DISCUSSION

Results of the retention of the five heavy metals by the different soils are presented as adsorption isotherms. This is a convenient way to graphically represent the amount of an adsorbed element in relation to its concentration in solution. There are several ways to present the different isotherms. In this study, for each heavy metal, we present isotherms for all soils. An alternative way is to present, for each soil, isotherms for the five heavy metals. Although we selected to present isotherms for each heavy metal separately, common features among the different soils are highlighted throughout the discussion. As clearly illustrated in the following sections, retention of all five heavy metals was significantly influenced by soil pH, CEC, organic matter and carbonate content. Generally, soils with lowest pH and CEC exhibited lowest retention. In contrast, soils with high CEC and high pH due to the presence of carbonates showed high affinity for all heavy metals.

Cadmium

Cadmium adsorption isotherms for all 10 soils are presented in Fig. 3. The results shown illustrate the differences in the amount of Cd retained by the different soils. This is indicated by Cd concentration in the soil solution that did not exceed 18 mg/L for Sharkey, Arapahoe and Houston black clay. In contrast, for Lincoln, Nada and the Candor sand, Cd concentrations in soil solution exceeded 50 mg/L. Lower concentration indicates stronger retention by the soil. Soils high in clay content and organic matter soils exhibited highest retention for Cd. In contrast, Candor sands and high pH soils Lincoln and Nada showed least retention for Cd.

All Cd isotherms in Fig. 3 are strongly nonlinear with varying degree of sorption among soils. The solid and dashed curves shown represent calculations based on the Freundlich, equation (1). Parameter values for K_d of the linear model and K_f and b for the Freundlich model along with their r^2 and *RMSE* statistics are given in Table 6. Based on these statistics, the use of a linear model is not recommended. In Table 7, Freundlich parameter K_f and b estimates for all 10 soils are presented. The range of *b* values was 0.35 to 1.0 where highest values of 0.84, 0.94 and 1.0 were for Candor surface and subsurface sands and the high pH Lincoln soil. Krishnamurti and Naidu (2003) reported nonlinear sorption for two soils having pH > 8. Buchter et al. (1989) reported a range of 0.56 to 0.96, which is consistent with the results presented here. Recently, Elbana and Selim (2010) estimated b values of 0.28 for a calcareous soil and 0.46 for an acidic soil.

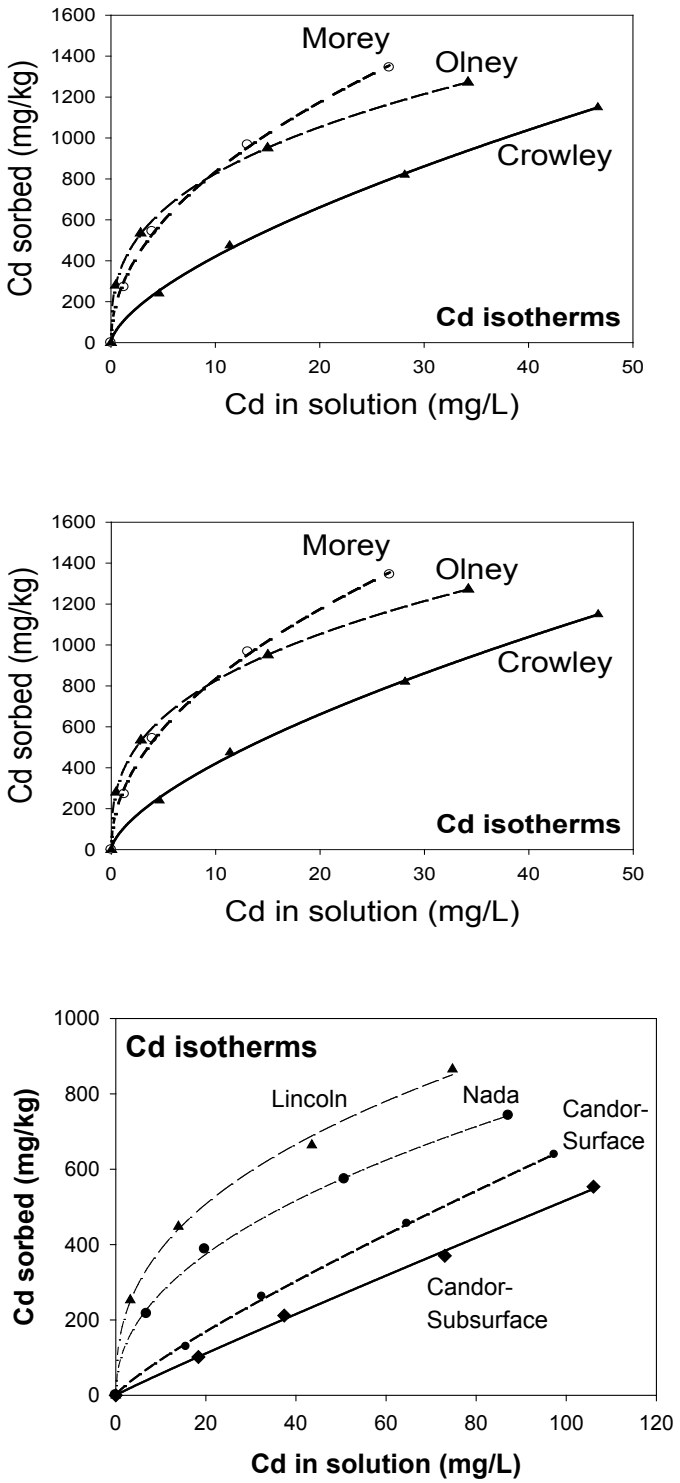


Fig. 3. Cadmium isotherms for several soils after 1 day of reaction. Solid and dashed curves are simulations using the Freundlich model.

The nonlinearity of Cd isotherms shown in Fig. 3 have significant implications. First, a wide range of concentrations is critical to obtain accurate information on the affinity of Cd at different concentration levels. Specifically, the use of a single point isotherm, which is often reported in the literature, assumes a linear isotherm and leads to erroneous values of the affinity coefficient. Second, the concentration level chosen may result in overestimation of the affinity coefficient. At low concentrations, high affinities are encountered, which results in high affinity coefficients. The use of such affinity coefficients would result in erroneous estimated and should not be used at higher concentrations. It should also be pointed out that the due to the nonlinearity of sorption isotherms, Cd affinity decreases as the concentration increased and thus is more susceptible to greater mobility in the soil.

Cadmium exhibited kinetic behavior for all soils where increased Cd sorption was measured over time. This is illustrated by the selected isotherms in Fig. 4 for Houston and Arapaho. Strong time-dependent sorption was observed for Houston soil, whereas Arapaho exhibited limited kinetic behavior. High pH soils such as Lincoln and Olney exhibited moderate kinetic behavior, whereas limited kinetics was observed for the remaining soils. Increases in Kf due to time of reaction are given in Table 7. In addition, the parameter b did not change with time for all soils. This is an important finding in predictions of retention and mobility of Cd in soils where only b is considered time invariant. Evidence of time-dependent sorption in soils has been observed by numerous investigations (e.g., Aringhieri et al., 1985; Selim et al. 1992). Hinz and Selim (1994) observed limited Cd kinetic behavior for acidic soils.

Copper

Copper isotherms for the selected soils are shown in Fig. 5. The isotherms are highly nonlinear with varying degrees of sorption among soils. Parameter values for K_d of the linear model and K_f and b for the linear and Freundlich models are given in Table 6. Copper affinity for Arapaho soil with high OM exceeded that for all soils shown in Fig. 5. The only exception was for Houston black clay where Cu was retained entirely (>99%) with measured Cu concentrations in soil solution less < 0.1 mg/L (figure not shown). Such strong Cu sorption is indicative of irreversible retention and possibly precipitation. In contrast, Candor sands exhibited least amount of retention of Cu (figure not shown). Based on Table 6, the Freundlich parameter *b* ranged from 0.29 to 1.32 with b > 1 only for the alkaline pH soils, namely, Houston Black clay and Morey and Lincoln soils. Elbana and Selim (2011) estimates *b* values of 0.23 for an acidic soil and 1.25 for a calcareous soil. They also reported their calcareous soil exhibited an order of magnitude greater Cu sorption when

Table 6. Linear and Freundlich adsorption parameters for cadmium (Cd) after a 1-day reaction time for all soils.

Soil Series	K_d	r^2	K_f	b	r^2
	(mL/g)		(mL/g)		
Arapahoe	144.680	0.920	313.180	0.650	0.998
Candor-surface	6.820	0.989	13.620	0.840	0.999
Candor-subsurface	5.210	0.998	6.304	0.957	0.999
Olney	42.343	0.645	367.210	0.352	1.000
Lincoln	13.091	0.703	157.040	0.392	0.998
Nada	9.691	0.878	92.939	0.465	0.999
Morey	56.666	0.809	267.606	0.494	0.999
Crowley	26.684	0.932	93.422	0.653	0.999
Sharkey	87.844	0.927	220.879	0.651	0.999
Houston	380.021	0.810	738.244	0.499	0.998

Table 7. Freundlich model K*f* and *b* parameter values for 10 soils and five heavy metals.

Element	Arapahoe	Candor-Surface	Candor-Subsurface	Olney	Lincoln	Nada	Morey	Crowley	Sharkey	Houston
					K_f - 1 day					
Cu	1004.91	64.51	16.15	5027.78	512.40	235.45	833.78	213.88	501.73	66205.54
Zn	150.51	CS	0.0038	552.83	181.27	60.29	323.29	37.21	91.07	988.81
Cd	313.18	13.62	6.30	367.21	157.04	92.94	267.61	93.42	220.88	738.24
Ni	78.51	CS	0.0008	169.79	64.04	16.65	159.24	17.72	65.92	373.10
Pb	3792.51	93.99	7.09	5169.46	1679.58	1360.44	4224.09	1280.45	2825.04	C S*
					K_f - 7 day					
Cu	1305.73	103.12	72.88	2209492.85	3993.56	350.52	4842.30	283.91	630.16	29606459.71
Zn	22.37	0.51	1.53	847.56	243.53	50.98	387.64	45.00	96.24	1258.36
Cd	323.09	16.68	7.94	514.97	0.39	93.58	301.51	103.19	224.12	935.35
Ni	89.39	CS	0.0006	261.10	134.28	28.04	130.48	23.51	70.94	467.14
Pb	4705.95	174.11	33.53	6889.88	3863.83	1497.59	5296.20	1452.22	3275.69	C S*
					b - 1 day					
Cu	0.54	0.40	0.54	1.32	0.29	0.30	0.41	0.41	0.46	1.16
Zn	0.43	2.85	2.50	0.31	0.32	0.51	0.37	0.66	0.70	0.33
Cd	0.65	0.84	0.96	0.35	1.00	0.47	0.49	0.65	0.65	0.50
Ni	0.73	CS	2.74	0.56	0.56	0.85	0.60	0.90	0.84	0.54
Pb	0.62	0.65	0.95	0.16	0.18	0.18	0.08	0.28	0.27	C S
					b - 7 day					
Cu	0.58	0.39	0.34	3.96	1.10	0.22	0.96	0.35	0.44	3.48
Zn	0.83	1.32	1.14	0.37	0.33	0.56	0.34	0.62	0.69	0.28
Cd	0.66	0.80	0.92	0.30	0.33	0.48	0.46	0.63	0.65	0.54
Ni	0.74	CS	2.83	0.62	0.57	0.73	0.65	0.83	0.84	0.64
Pb	0.69	0.56	0.70	0.24	0.36	0.18	0.12	0.26	0.29	C S

* CS = Complete sorption.

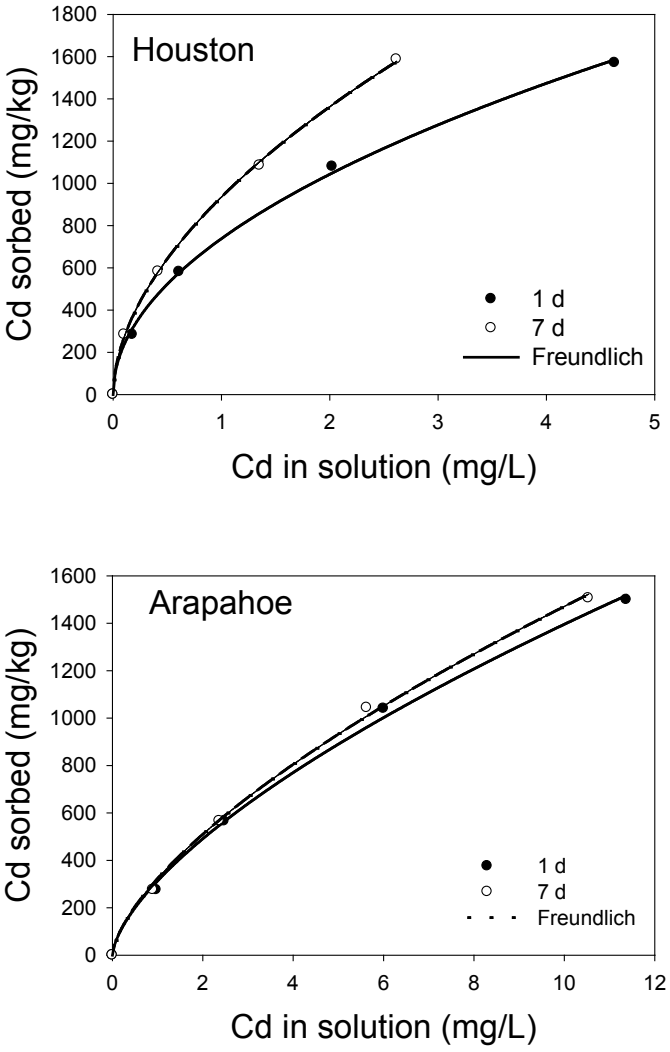


Fig. 4. Cadmium isotherms for Morey and Lincoln soils after 1 and 7 days of reaction. Curves are simulations using the Freundlich model.

compared to an acidic soil. Nonlinear isotherms having b > 1 are not commonly encountered for acidic soils, however. Moreover, such nonlinearity (b>1) is often indicative of precipitation as the dominant retention mechanism (Selim, 2014).

Several scientists, including Florido et al. (2010), Wang et al. (2009) and Lopez-Periago et al. (2008) reported time-dependent retention of Cu in several soils. Lopez-Periago et al. (2008) studied adsorption and release kinetics by several acidic soils where hysteretic behavior was dominant for several soils. In this study, Cu exhibited kinetic behavior for all soils where Cu sorption increased from 1 to 7 days. This is illustrated by the selected isotherms in figs. 6 and 7 for Houston and Crowley soils. Our results indicated the acidic soils such as Sharkey, Arapaho, Candor sands and Nada exhibited least kinetics. In contrast, high pH soils, e.g., Morey, Lincoln and Houston Black clay extensive time-dependent sorption was observed. In Table 6, the respective values of K_f and b for 1-day sorption are presented. In addition, the parameter b did not change with time for acidic soils, whereas for high pH soils (>6.6) increased values for b was observed. Selim and Ma (2001) reported no change of b over time for one acidic soil.

The observed increase of Cu sorption over time illustrated in figs. 6 and 7 has significant implications. Most significant is that K_f and K_d parameters based on 1- and 7-day reaction time represent an underestimation of the extent of sorption of heavy metals in soils. Therefore, prediction of the extent of affinity and potential mobility of a heavy metal, based on 1-day sorption data, is likely to provide erroneous results and thus is not recommended.

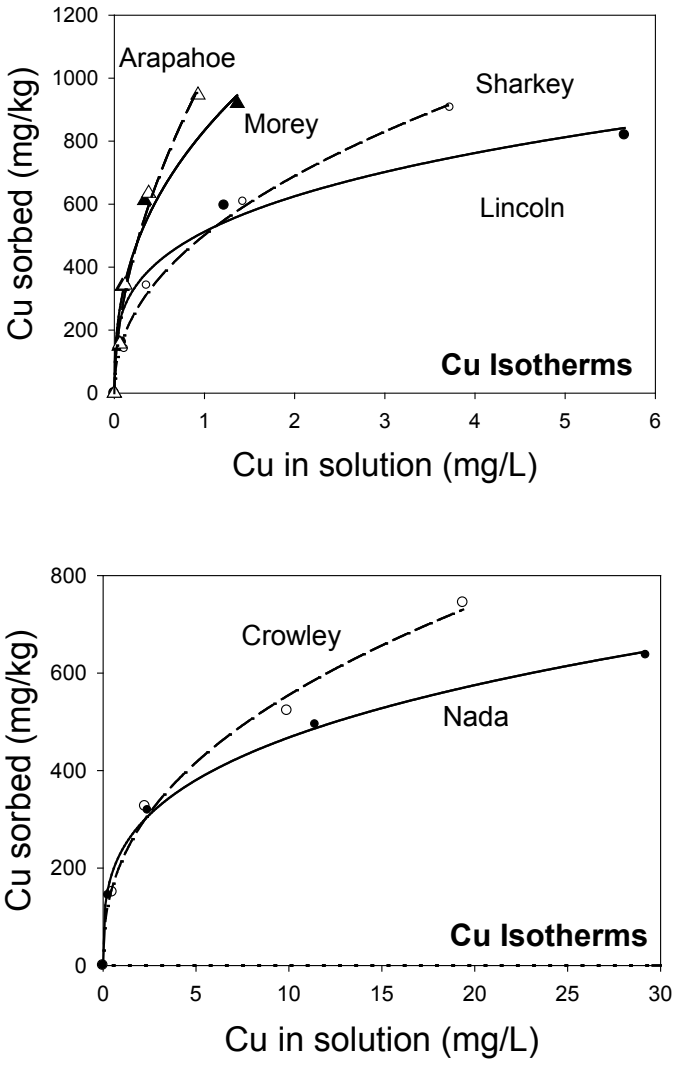
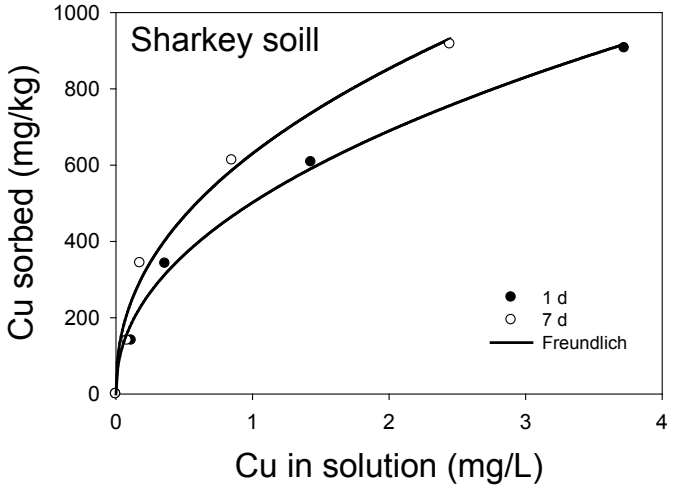


Fig. 5. Copper isotherms for different soils after 1 day of reaction. Solid curves are simulations using the Freundlich model.



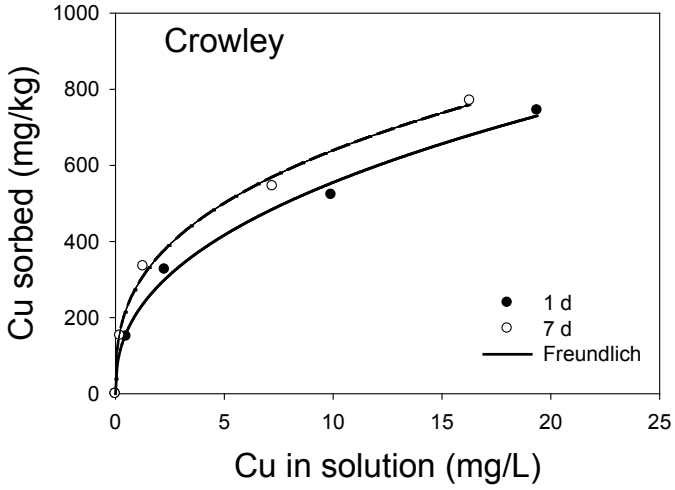
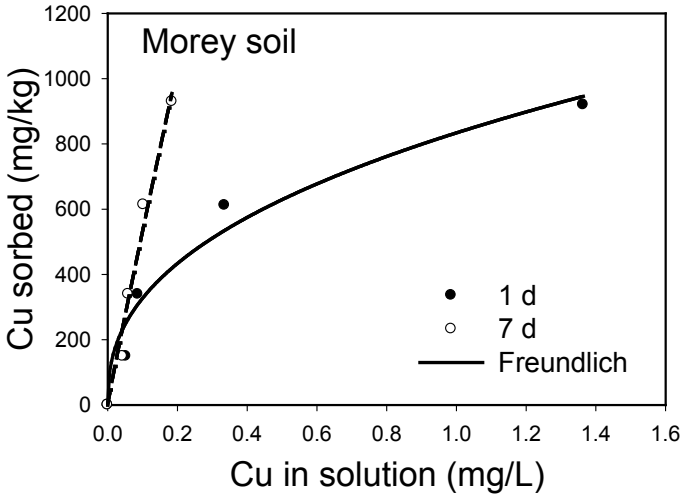


Fig. 6. Copper isotherms for Sharkey and Crowley soils after 1 and 7 days of reaction. Curves are simulations using the Freundlich model.



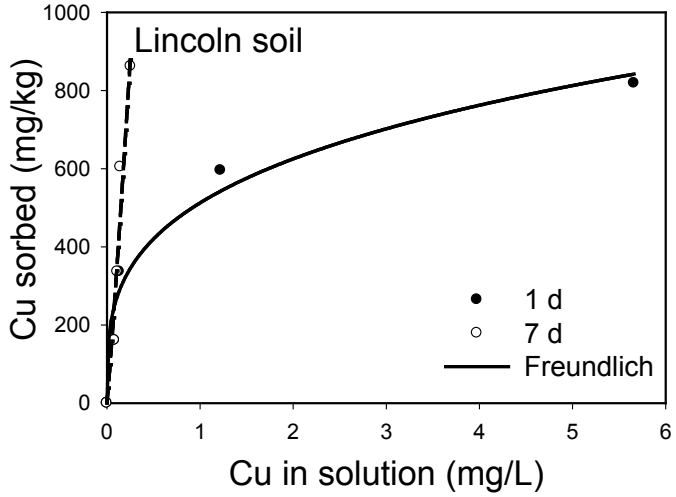
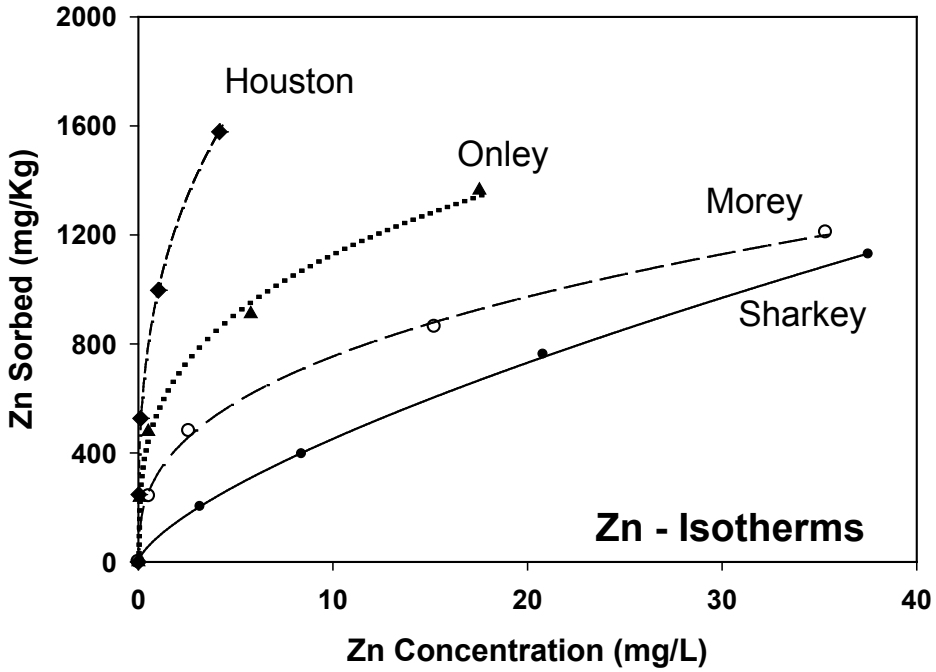


Fig. 7. Copper isotherms for Morey and Lincoln soils after 1 and 7 days of reaction. Curves are simulations using the Freundlich models.



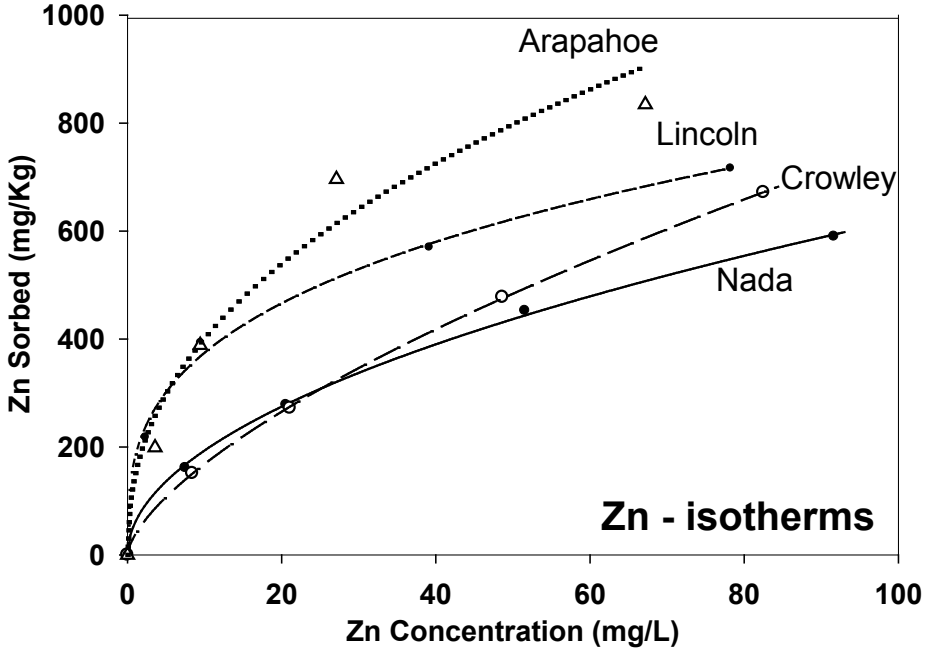


Fig. 8. Zinc isotherms for four soils after 1 day of reaction. Solid and dashed curves are simulations using the Freundlich model.

Zinc

Zinc isotherms for selected soils are shown in Fig. 8. These results indicate much less affinity for Zn by all 10 soils when compared to copper. Houston soil exhibited highest sorption, whereas most loamy soils indicated moderate sorption for zinc. For Candor sand soils, extremely low sorption for Zn was observed (figure not shown). For all soils, Zn isotherms were nonlinear, and the Freundlich, equation (1), provided good description of the results. The parameter *b* is a measure of the heterogeneity of sorption sites, where sorption by the highest energy sites takes place preferentially at the lowest solution concentrations, and as the sorbed concentration increases, successively lower energy sites become occupied. This leads to a concentration-dependent sorption equilibrium behavior, i.e. nonlinear isotherm (Selim, 2014). The results for the Freundlich parameter *b* values given in Table 7 indicate a wide range of values from 0.31-0.70. The only exception was Candor surface and subsurface sands with *b* values > 2.5 where least affinity for Zn was observed. Zhao and Selim (2010) reported a range of *b* values for Zn from 0.40-0.50 for one neutral and two acidic soils. Buchter et al. (1989) reported a range of *b* values of 0.51 to 1.01 with the highest *b* for a calcareous soil.

A comparison of various isotherms indicate that Cu is adsorbed more strongly than Zn as well as Cd. In recent years, some authors have examined metal competition in various types of soils. Based on their results, copper is adsorbed more strongly than Zn and Cd in calcareous soils (Mesquita and Vieira e Silva, 1996); acid soils (Agbenin and Olojo, 2004; Arias et al., 2006); clay minerals; and isolated organic soil components (Saha et al., 2002).

Zinc isotherms for selected soils after 1- and 7-day adsorption are shown in Fig. 9. These isotherms show the influence of time of adsorption varied extensively among soils. In fact, for soils that exhibited strong sorption, increased sorption from 1-7 days was much greater than all other soils. This is illustrated by the lack of time-dependent behavior for sorption by Sharkey when compared to Houston soil. In addition, the parameter *b* did not change with time for all soils. The observed limited kinetics for Sharkey soil is an indication of fast sorption processes possibly dominated by ion exchange. On the other hand, it is likely that irreversible sorption due to the presence of carbonates resulted in the observed strong kinetic behavior for Houston soil. Kinetic retention behavior of Zn has been observed by several investigators (Dang et al.,1994; Perez-Novo; 2011). Kinetic behavior also may be deduced from the slow release during Zn transport as exhibited by extensive tailing of breakthrough curves (Voegelin et al., 2001; Voegelin et al., 2005). Recent evidence of Zn kinetics during Zn release or desorption in acidic and neutral soils was reported by Perez-Novo et al. (2011b) and Zhao and Selim (2010).

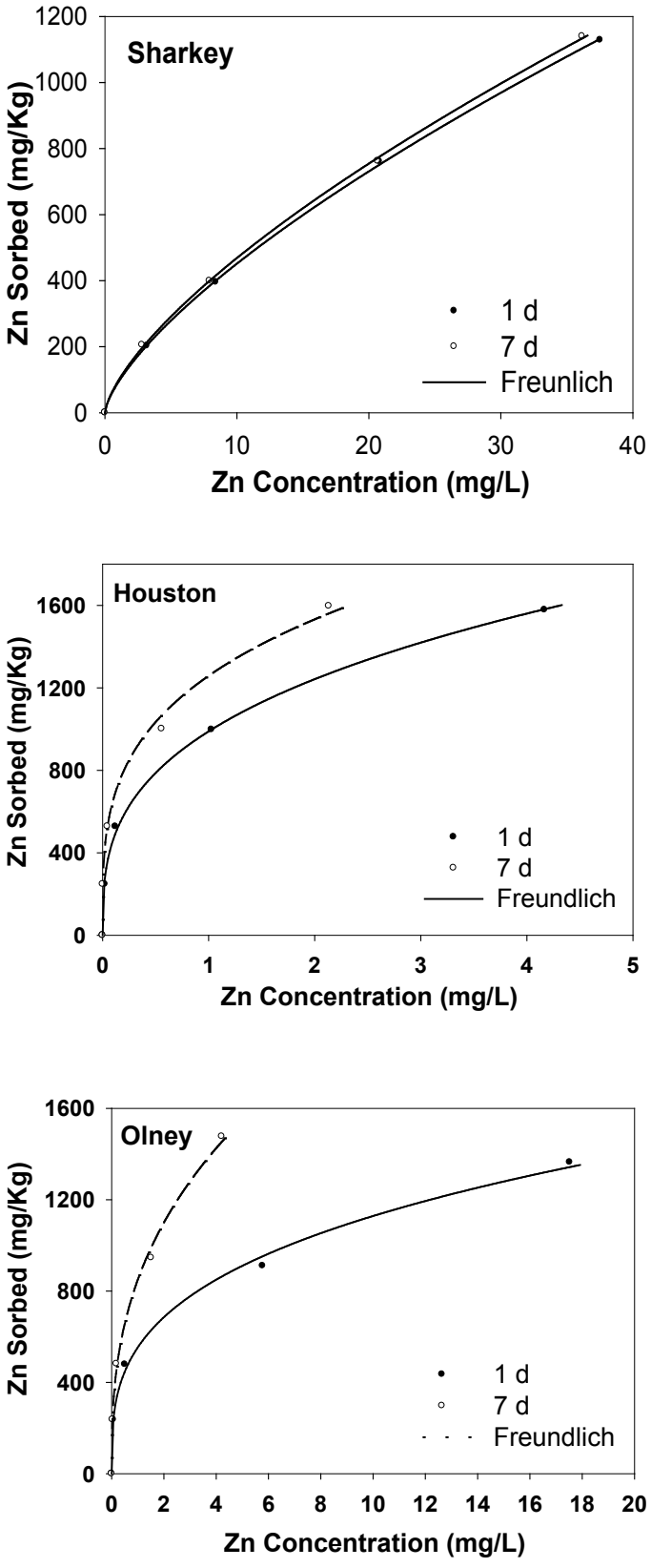


Fig. 9. Zinc isotherms for Sharkey, Houston and Olney soils after 1 and 7 days of reaction. Curves are simulations using the Freundlich model.

Nickel

Nickel isotherms for selected soils are shown in Fig. 10. Results from this study indicate that Houston soil exhibited highest sorption, whereas most loamy soils indicated less Ni sorption. Among all soils, Candor sands exhibited the lowest affinity for nickel (data not shown). The Freundlich parameter *b* given in Table 7 ranged from 0.54 to 0.90 except for Candor surface and subsurface sands with b >1. Buchter et al. (1989) reported a range of 0.51 to 0.90 including that for a calcareous soil. Lixia and Selim (2010) reported a range of *b* values from 0.49-0.59 for one neutral and two acidic soils.

A number of studies suggested that Ni may be considered as a weakly sorbed heavy metal when compared to others such as Pb, Cu and Zn (Tiller et. al, 1984; Atanassova, 1999). Specifically, Ni was observed to have low affinity for reactive phases in acidic soils. This finding is consistent with our results, and Ni can thus be considered mobile and susceptible to transport. In fact, Atanassova (1999) argues that Ni and Cd are two cations that have low affinities for soil colloids and are generally considered to be weakly bonded metals. Our results are consistent with the above findings, and Ni has the least affinity to soils among all five heavy metals investigated.

Time-dependent Ni sorption is illustrated by the isotherms shown in figs. 11 and 12. The extent of kinetics is manifested by the increased amount of sorption after 7 days compared to 1 day. The influence of kinetics was greatest for Houston and Olney (Fig. 11) and least for Arapahoe and Sharkey soils (Fig. 12). The extent of kinetics varied among other soils where a limited increase in sorption over time was observed for acidic soils and consistent with our findings for Zn as discussed above. This is manifested by the K_f values for 1 and 7 days presented in Table 7. In addition, the parameter *b* did not change with time for all 10 soils. Lixia and Selim (2010) reported that for one neutral and two acidic soils there was no change of *b* with time of reaction up to 22 days.

Information on the rate of sorption of Ni on soils is limited, where in most studies equilibrium conditions are assumed. A limited number of studies, however, have investigated release or desorption of Ni from minerals and soils (Atanassova, 1999, Scheckel and Sparks, 2001, Barrow et al., 1989). Antnassova (1999) reported that most Ni sorbed by a Dutch soil in a 24-hour equilibrium batch experiment could be released by excess of calcium and only a small proportion of Ni was specifically sorbed. Vega et al. (2006) reported that no significant amount of heavy metals (Pb, Zn, Cu and Ni) was desorbed from mine soils.

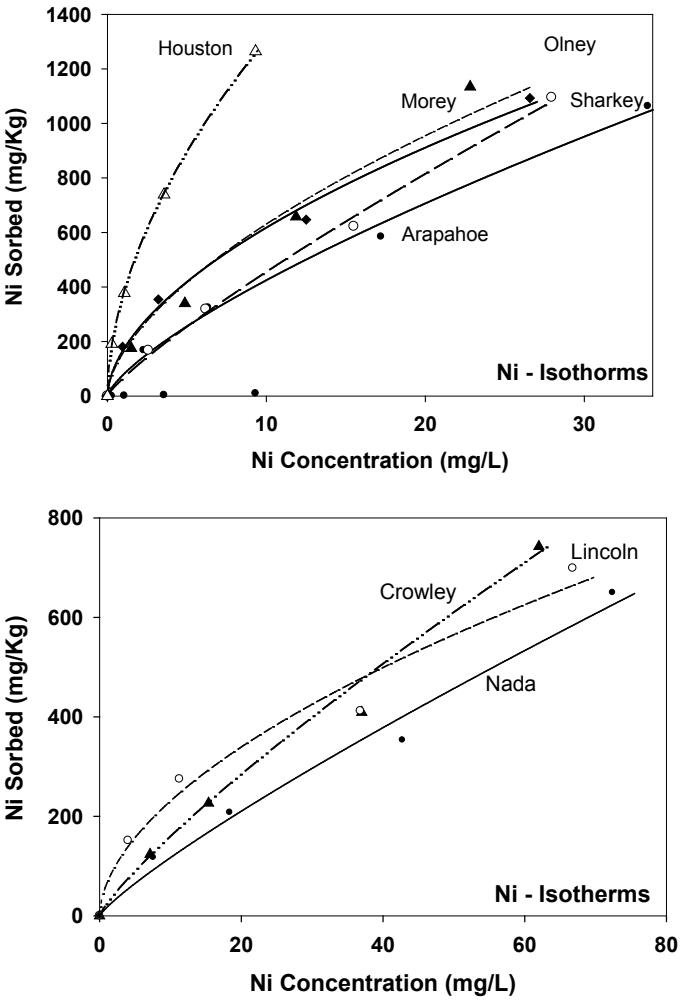


Fig. 10. Nickel isotherms for several soils after 1 day of reaction. Solid and dashed curves are simulations using the Freundlich model.

Lead

It is well accepted that Pb is one of the heavy metals with a strong affinity to soils. In fact, Pb is often regarded as immobile due to its high sorption and slow release from soils (Kabata-Pendias and Sadueski, 2007). The extent of Pb mobility in soils is controlled by soil characteristics and environmental conditions. Soil pH, CEC, clay content, CaCO3 and OM were positively correlated with Pb sorption in soil (Hooda and Alloway, 1998). This is supported with various studies; for example, Martínez-Villegas et al. (2004) that showed that Pb sorption isotherms were strongly nonlinear, and the sorption capacity increased with increasing pH. Strawn and Sparks (2000) found that removing OM decreased Pb sorption by 40% compared with untreated soil. Moreover, McKenzie (1980) found that Pb sorption by Mn oxides was up to 40 times greater than that by Fe oxides, and no evidence for oxidation of Pb or the formation of specific Pb–Mn

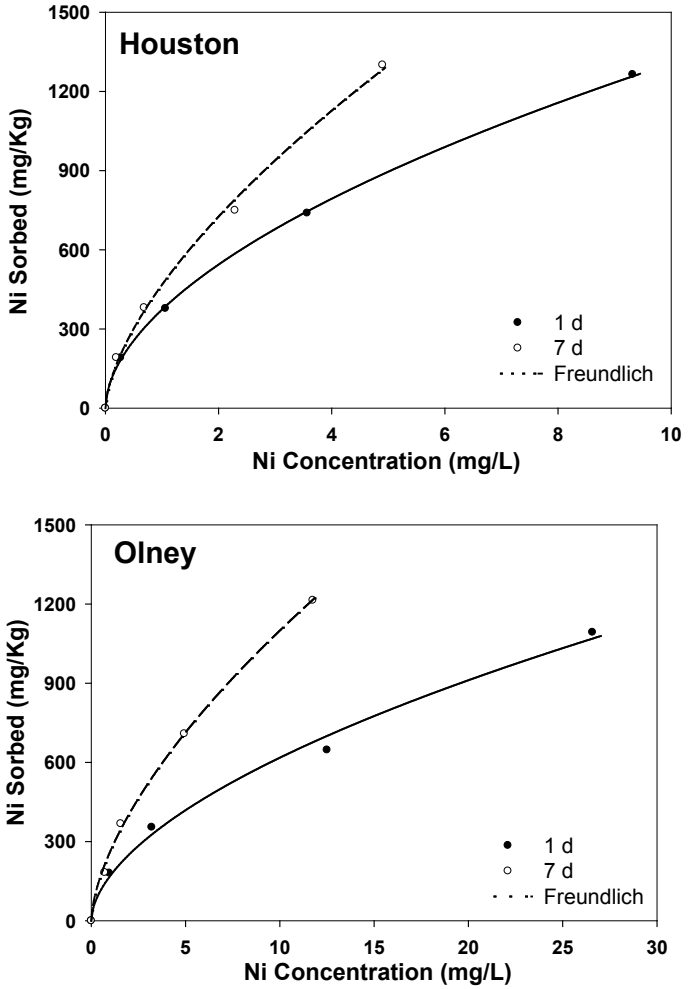


Fig. 11. Nickel isotherms for Houston and Olney soils after 1 and 7 days of reaction. Curves are simulations using the Freundlich models.

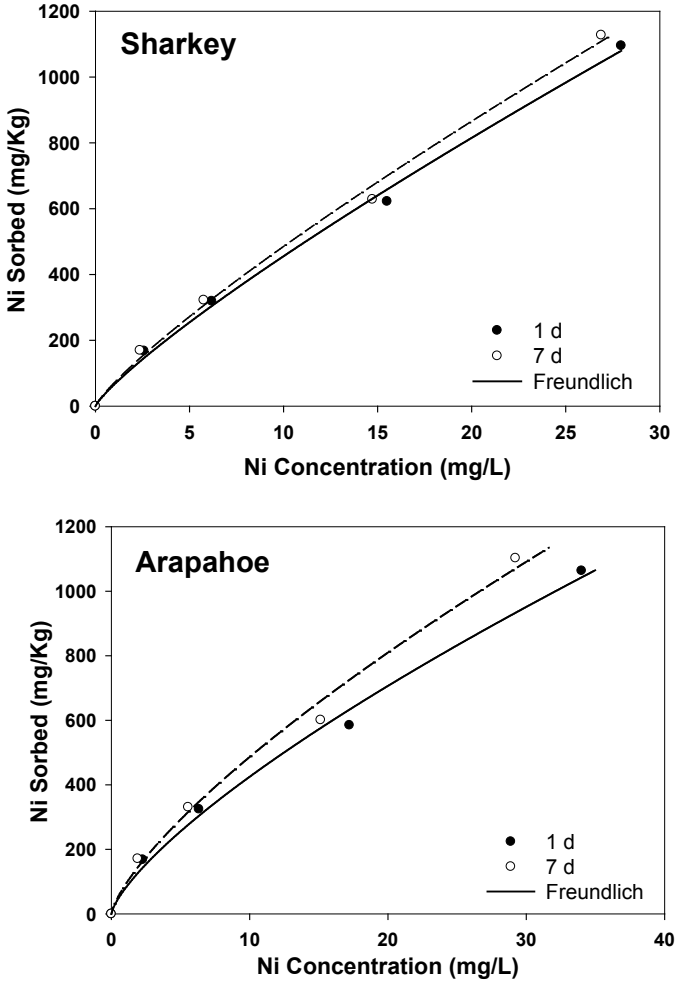
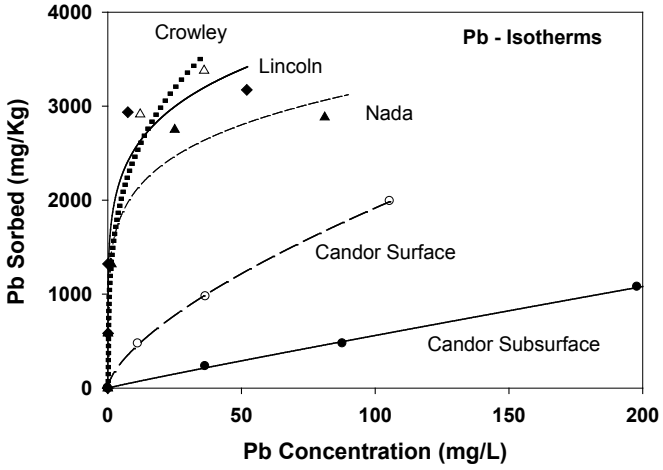
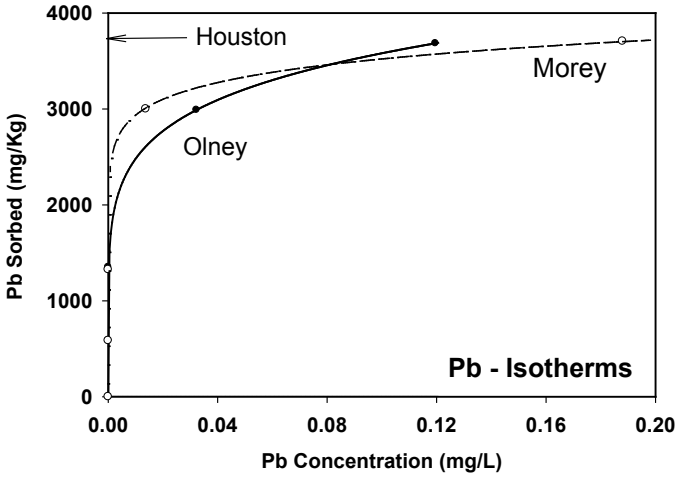


Fig. 12. Nickel isotherms for Sharkey and Arapahoe soils after 1 and 7 days of reaction. Curves are simulations using the Freundlich modes.

minerals was found. Lead isotherms for all soils are shown in Fig. 13. Isotherm results indicate a wide range of affinities for Pb in these soils. Houston soil exhibited highest sorption in which lead concentration in the soil solution was below detection (28 µg/L) for the entire range of input concentrations. All other soils exhibited different degrees of affinities for lead as illustrated in Fig. 13. Soils with high OM content, such as Arapahoe, as well as soils with high clay contents, such as Sharkey, exhibited high sorption in which Pb concentration was less than 3.1 mg/L. As expected, Pb retention was lowest in Candor sands with increasing Pb sorption for Nada, Lincoln and Crowley soils. It should also be emphasized that Olney soil with high pH and carbonate content exhibited high sorption for lead.

Due to the high affinity of Pb to soils, sorption was rapid with little additional sorption of 1 day of reaction. The isotherms shown in Fig. 14 illustrate the extent of retention over 7 days for Morey and Candor surface sand. With the exception of Lincoln soil, all others exhibited less kinetics than those presented in Fig. 14. Therefore, the rate of Pb sorption is fast in which quasi equilibrium is likely reached in a few hours or days. Moreover, the parameter *b* did not change with time for all 10 soils.





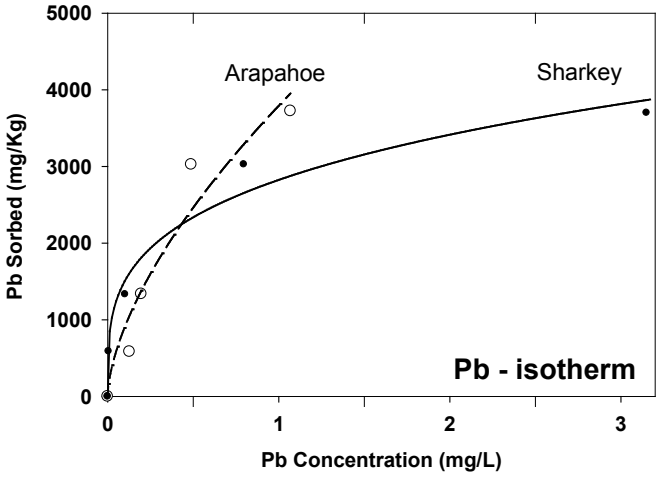
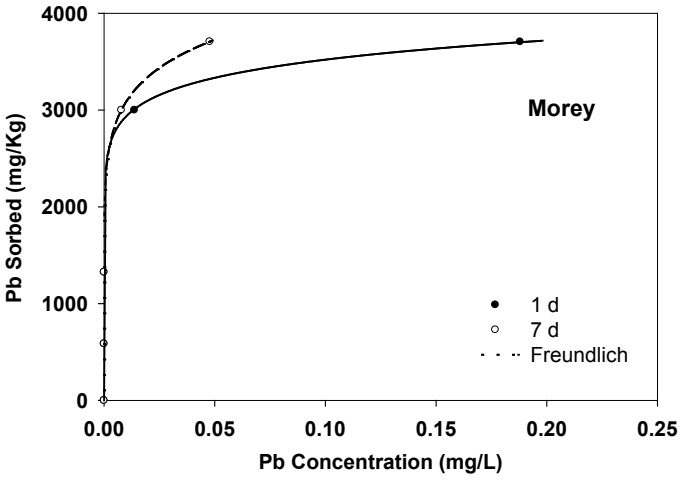


Fig. 13. Lead isotherms for several soils after 1 day of reaction. Curves are simulations using the Freundlich models.



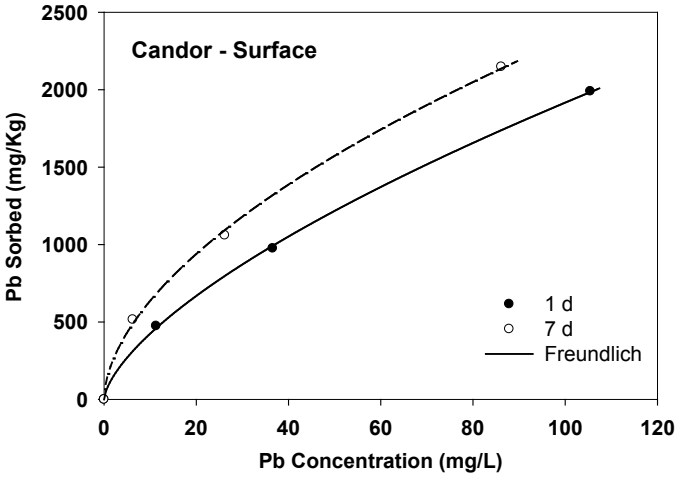


Fig. 14. Lead isotherms for Morey and Candor-surface soils after 1 and 7 days of reaction. Curves are simulations using the Freundlich models.

PREDICTIONS

A correlation of Kf and b values with soil properties was carried out for all heavy metals in a similar manner to that of Buchter et al. (1989). Here we used parameter values obtained after a 1-day reaction. We found highest correlation with pH followed by organic matter. As indicated in Fig. 15, considerable scatter with and a general trend for a decreasing b as pH increased was observed.

Linear regression of b versus pH for individual heavy metals and found that Cd and Pb best coefficients of correlation (r = 0.809 and 0.774, respectively). In the meantime, values of *b* for Cd did not display specific patter with increasing pH and was thus excluded from further analysis. As a result, the regression (solid) line shown in Fig. 15 represents overall regression for the four heavy metals (zinc, lead, cadmium and nickel). The following regression equation was obtained for a 1-day reaction

$$b = 1.087 - 0.0900\ pH \quad R = 0.503 \qquad (6)$$

The dashed line shown in the Fig. 15 is based on equation (4) of Buchter et al. (1989). Although the dashed overestimated most *b* values, the slope of the dashed and solid lines were similar, i.e., parallel. We should emphasis here that *b* values for all soil were included in the regression analysis except for the two sandy Candor soils. In the soils, due to possible precipitation, *b* values for most heavy metals were > 1 and were thus excluded.

We also performed regression analysis based on parameters after 7 days of reaction in find out whether *b* values from 1 day was significantly different from 7-day results (Fig. 16). The regression equation for 7 days is

$$b = 1.115 - 0.0908\ pH \quad R = 0.537 \qquad (7)$$

A comparison of the two regression equations (6) and (7) for 1 and 7 days indicates different intercepts. Values for the slope, however, were almost identical (0.0900 and 0.908) for 1 and 7 days. Additionally, a paired t-test for the significance between *b* parameter values based on 1 and 7 days revealed no significance between the two data sets (p = 0.773, t = - 0.290). This finding, that b is time invariant, has a significant implication since it simplifies predictive capability predictive capabilities of affinity for sorption of heavy metals with time. Such information is important in estimation of the bioavailability and risk assessments of the potential mobility of these trace elements for a wide range of soils.

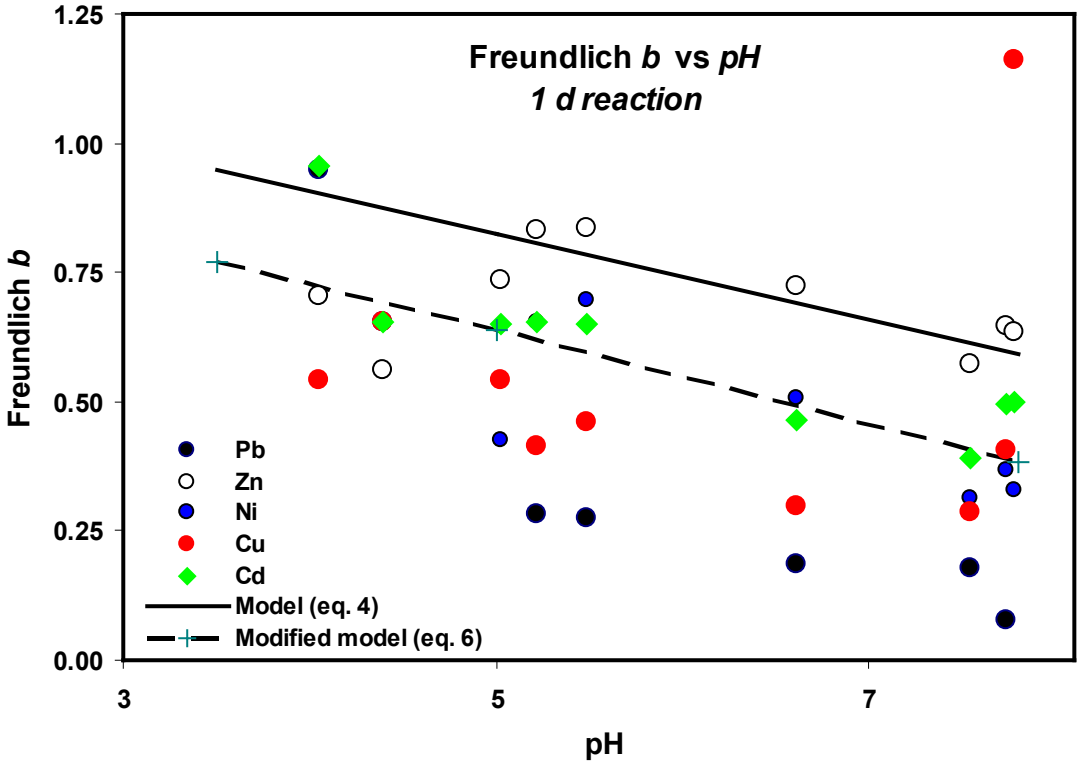


Fig. 15. Measured 1-day Freundlich *b* parameter values for all five heavy metals. The solid and dashed lines were calculated using equations (4) and (6), respectively.

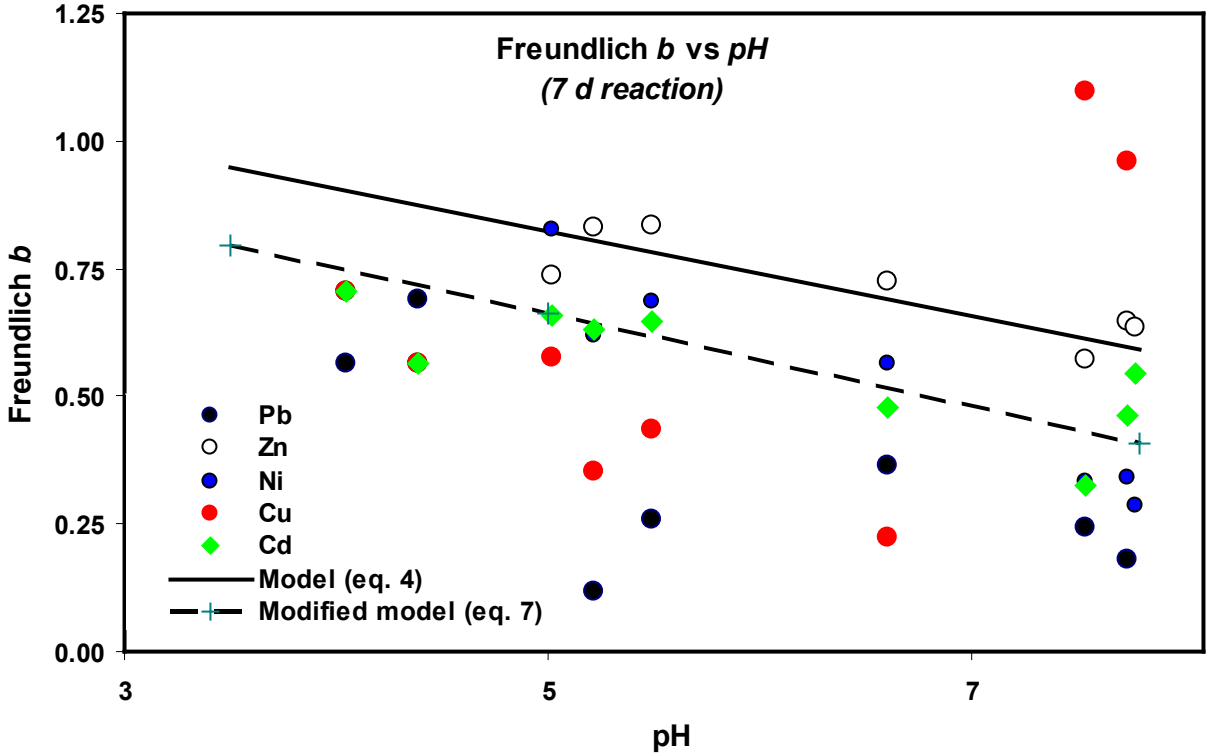


Fig. 16. Measured 7-day Freundlich *b* parameter values for all five heavy metals. The solid and dashed lines were calculated using equations (4) and (7), respectively.

SUMMARY AND CONCLUSIONS

The retention of five heavy elements by 10 soils from 10 soil orders was quantified to determine the effects of soil properties on the magnitude of soil retention in the different soils. We also investigated the influence of time of reaction on sorption for all soils and heavy metals. A major finding of this study is that adsorption isotherms for all heavy elements and soils were nonlinear. Moreover, soil properties affecting sorption were pH, CEC, organic matter, clay content and the presence of carbonates. Additional findings are:

1. Soils with high organic matter and soils with high CEC and pH from the presence of carbonates exhibited strong sorption for all five heavy metals. Sandy soils having low CEC showed lowest sorption for all metals.
2. For all 10 soils used in this study, adsorption of heavy elements followed the order Pb > Cu > Cd > Zn > Ni. In the presence of carbonates, adsorption followed the order Pb > Cu > Zn > Cd > Ni.
3. The influence of time of reaction in increased sorption varied among soils and heavy metals.
4. A modified regression equation was suitable to predict the Freundlich parameter *b* vs. pH for a 1-day reaction time. The modified equations were similar to that proposed by Buchter (1989) with significantly different intercept.
5. With the exception of Cu, the Freundlich parameter *b* did not change significantly with time.
6. This finding, that *b* is time invariant, has a significant implication since it simplifies predictive capabilities of affinity for sorption of heavy metals with time.

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LITERATURE CITED

Agbenin, J.O., Olojo, L.A., 2004. Competitive adsorption of copper and zinc by a Bt horizon of a savanna alfisol as affected by pH and selective removal of hydrous oxides and organic matter. Geoderma 119, 257–265.

Arias, M., Pérez-Novo, C., López, E., Soto, B., 2006. Competitive adsorption and desorption of copper and zinc in acid soils. Geoderma 133, 151–159.

Aringhieri, R., P. Carrai, and G. Petruzzelli. Kinetics of Cu^{2+} and Cd^{2+} adsorption by an Italian soil. Soil Sci. 139:197–204.

Atanassova, I. 1999. Competitive effect of copper, zinc, cadmium and nickel on ion adsorption and desorption by soil clays. Water Air & Soil Poll. 113: 115–125.

Barrow, N. J., J. Gerth and G. W. Brümmer. 1989. Reaction-kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. II. Modeling the extent and rate of reaction. J. Soil Sci. 40 (2): 437-450.

Bradl, H.B. 2004. Adsorption of heavy metal ions on soils and soil constituents. Journal of Colloid and Interface Science, 277: 1-18.

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

Dang Y.P., Dalal R.C. D. G. Edwards D.G., and K. G. Tiller. 1994. Kinetics of zinc desorption from vertisols. Soil Sci. Soc. Am. J. 58: 1392-1399.

USEPA, 1993. 40 CFR-Part 257 and 503, Standards for the Disposal of Sewage Sludge; Final Rule. Fed. Regist. 58:9248–9415. US EPA, Washington, DC, USA.

http://www.ecfr.gov/cgi-bin/text-idx?tpl=/ecfrbrowse/Title40/40cfr503_main_02.tpl

USEPA. 1994a. A plain English guide to EPA Part 503 Biosolids Rule EPA-832-R-93-003. USEPA Office of Wastewater Management, Washington, DC.

http://water.epa.gov/scitech/wastetech/biosolids/503pe_index.cfm

USEPA, 1994b. A Guide to the Biosolids Risk Assessments for the EPA Part 503 Rule. EPA 832-B-93-05. USEPA Office of Wastewater Management, Washington, DC.

http://water.epa.gov/polwaste/wastewater/treatment/biosolids/upload/2002_06_28_mtb_biosolids_sludge.pdf

USEPA.1995. Land application of sewage sludge and domestic seepage: Process design manual. EPA-625-R-95-001. USEPA, Washington, DC.

http://nepis.epa.gov/Adobe/PDF/30004O9U.pdf

USEPA. 1999. Understanding variation in partition coefficient, Kd, values. Report EPA 402-R-99-004A.

Elbana, Tamer A and H. M. Selim. 2010. Cadmium Transport in alkaline acidic soils: Miscible displacement experiments. Soil Science Society of America Journal 74: 1956–1966.

Elbana, T. A. and H M. Selim. 2011. Copper Mobility in Acidic and Alkaline Soils: Miscible Displacement Experiments. Soil Science Society of America Journal 75:2101–2110.

Florido, A., C. Valderrama, J. A. Arevalo, I. Casas, M. Martinez, and N. Miralles. 2010. Application of two sites non-equilibrium sorption model for the removal of Cu(II) onto grape stalk wastes in a fixed-bed column. Chem. Eng. J., 156: 298–304.

Fontes, M. 2012. Behavior of Heavy Metals in Soils: Individual and Multiple Competitive Adsorption. Chapter 3 in Selim (ed) "Competitive Sorption and Transport of Trace Elements in Soils and Geological Media", CRC, pages (77-117).

Giles, C.H., D'Silva, A.P. and Easton, I.AJ. 1974. A general classification of the solute adsorption isotherms II. J. Colloid Interface Sci., 47: 766-778.

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.

Hooda, P.S. and B.J. Alloway. 1998. Cadmium and lead sorption behaviour of selected English and Indian soils. Geoderma, 84:121-134

Kabata-Pendias, A. and W. Sadurski. 2007. Trace Elements in Soils and Plants. CRC, Boca Ratopn, FL.

Krishnamurti, G. S. R. and R. Naidu. 2003. Solid-solution equilibrium of cadmium in soils. Geoderma 113:17-30.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem Soc. 40:1361-1402.

Liao, Lixia and H. M. Selim. 2010. Reactivity of nickel in soils: Evidence of retention kinetics. J. Environ. Qual. 39:1290–1297.

Lopez-Periago, J.E., M. Arias-Estevez, J.C. Novoa-Munoz, D. Fernandez-Calvino, B. Soto, C. Perez-Novo, and J. Simal-Gandara. 2008. Copper retention kinetics in acid soils. Soil Sci. Soc. Am. J. 72:63–72.

Martínez-Villegas, N., L.Ma. Flores-Vélez, and O. Domínguez, 2004. Sorption of lead in soil as a function of pH: a study case in México. Chemosphere 57, 1537–1542.

Mesquita, M.E., Vieira e Silva, J.M., 1996. Zinc adsorption by a calcareous soil. Copper interaction. Geoderma 69, 137–146.

Pérez-Novo, C., A. Bermúdez-Couso, E. López-Periago, D. Fernández-Calviño, and M. Arias-Estévez. 2011a. Zinc adsorption in acid soils Influence of phosphate. Geoderma 162:358–364.

Saha, U.K., Taniguchi, S., Sakurai, K., 2002. Simultaneous adsorption of cadmium, zinc,and lead on hydroxyaluminium– and hydroxyaluminosilicate–montmorillonite complexes. Soil Science Society of America Journal 66, 117–128.

Scheckel, K. G. and D. L. Sparks. 2001. Dissolution kinetics of nickel surface precipitates on clay mineral and oxide surfaces. Soil Sci. Soc. Am. J. 65:685-694.

Selim, H. M. 2015. Chemical Transport and Fate in Soils: Principals and Applications. CRC/Taylor and Francis, Boca Raton, FL (352 p).

http://www.crcpress.com/product/isbn/9781466557949

Selim, H. M. 2014. On the nonlinearity of sorption of solutes in soil. Soil Sci. 179:237-241.

Selim, H. M. 2013. Transport and Retention of Heavy Metal in Soils: Competitive Sorption. Adv. Agron. 119: 275-308.

Selim, H. M., B. Buchter, C. Hinz and L. Ma. 1992. Modeling the Transport and Retention of Cadmium in Soils: Mulltireaction and multicomponent approaches. Soil Sci. Soc. Am. J. 56:1004-1015.

Selim, H. M. and L. Ma. 2001. Modeling nonlinear kinetic behavior of copper adsorption-desorption in soil. Soil Sci. Soc. Am. Spec. Publ. 56:189-212.

Sparks, D. L. 2003. Environmental Soil Chemistry. Elsevier, NY.

Strawn, D.G. and Sparks, D.L., 2000. Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soils. Soil Sci. Soc. Am. J. 64:144-156.

Tiller, K. G., V. K. Nayyar, and P. M. Clayton. 1984. Specific and nonspecific sorption of cadmium by soils clays as influenced by zinc and calcium. Aust. J. Soil Sci. 17:17-28.

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.

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.

Zhao, K. and H. M. Selim. 2010. Adsorption-Desorption Kinetics of Zn in soils: Influence of phosphate. Soil Sci. 2010:175: 145-153.

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