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Modeling the competitive sorption and transport of Ni(II) and Zn(II) in soils: Comparing two multicomponent approaches

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ABSTRACT

The mobility of contaminants in soil is controlled by sorption reactions which can be affected by the presence of other solutes that compete for sorption sites. The ability to model such effects is necessary for evaluating the environmental risk of a given contaminant. In this study, the competitive sorption and transport of nickel (Ni) and zinc (Zn) in Olivier and Windsor soils was investigated using batch equilibration and miscible displacement experiments. During batch experiments, the sorption of Ni and Zn was mutually reduced in multicomponent systems, indicating that the metal cations compete for sorption sites. When applied concurrently, the retardation of both ions decreased and peak effluent concentrations increased relative to single ion experiments, demonstrating that competition increased the mobility of both ions during miscible displacement experiments. A novel Freundlich-type multicomponent isotherm (CDI) and its kinetic analog (CDIT) were developed and compared to the commonly used SRS isotherm and SRS-based kinetic approach (SRST) in describing the experimental data. The CDI provided a superior description of the competitive batch data, especially at low surface coverage, and may therefore be more applicable to multicomponent sorption than the SRS. The Olivier and Windsor transport data were best described by the CDIT and SRST, respectively, however, both models generally described the data well. Since both approaches gave comparable descriptions of the transport data while the CDI outperformed the SRS in describing the batch data, the CDI/CDIT may be more generally applicable to multicomponent systems and warrants further study.

1. Introduction

Understanding of the mobility of contaminants in soil is necessary for determining their environmental risk. The composition of the soil solution, namely the presence of multiple species that compete for sorption sites, can greatly affect the behavior of a contaminant in the subsurface. This is an important consideration as heavy metal contamination of soils often involves multiple species (Dermond et al., 2010; Liao et al., 2016), which can increase contaminant mobility. For example, the simultaneous presence of Ni and Zn was shown to decrease the sorption of both cations by soil, although Ni was more affected than Zn (Antoniadis and Tsadilas, 2007). Competition for sites has also been demonstrated to reduce Ni and Zn sorption by Fe, Mn, and Al oxides (Trivedi et al., 2001; Guo et al., 2018; Choi et al., 2020), which have been shown to be dominant materials that control metal behavior in soils (Bradli, 2004;

Covelo et al., 2007a). Increased mobility due to competition has been well demonstrated for a wide range of transition and post transition metals, as reviewed by Selim (2013b) and Violante (2013). Moreover, designer sorbents such as modified biochars are commonly used to remove multiple chemicals from contaminated soils and water (Lu et al., 2022; Liu et al., 2022), and as such, it is important to consider competitive interactions in engineered systems.

The ability to model the transport of heavy metals in soil is essential for predicting their fate in the environment. Tsang and Lo (2006) demonstrated that a transport model considering sorption kinetics outperformed an approach assuming linear equilibrium sorption in describing competitive Cd and Cu transport in soil. Similarly, Chotpantarat et al. (2012) compared a linear equilibrium model to nonlinear Langmuir-type equilibrium and kinetic models to describe the competitive transport of Pb and several other metal cations in binary systems

Abbreviations: BTCs, Breakthrough curves; CDE, Convection-dispersion equation; CDI, Competitive Distribution Coefficient isotherm; CDIT, Competitive Distribution Coefficient Transport model; SRST, SRS Kinetic Transport model.

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through a lateritic soil. [Elbana et al. \(2014\)](#) used a two-site, equilibrium-kinetic Langmuir-type model to describe the competitive transport of Sn and Pb through two soils. However, in all cases, these studies employed models that do not account for competitive interactions between metal ions, resulting in separate sets of parameters for each experiment, greatly reducing their utility. Conversely, others have attempted to incorporate terms into the convection-dispersion equation (CDE) to account for competition. [Hinz and Selim \(1994\)](#) described the competitive transport of Zn and Cd by assuming that the sorption of both occurs exclusively via cation exchange, and incorporated exchange isotherms into the CDE. [Selim et al. \(1992\)](#) incorporated ion exchange to account for competition between Cd and Ca as well as a specific Langmuir-type kinetic site to describe Cd transport in soils. A similar approach was presented by [Voegelin et al. \(2001\)](#) with the addition of pH-dependent exchange coefficients and cation exchange capacities, and successfully described the transport of a variety of metal cations.

More recently, [Serrano et al. \(2013\)](#) employed a non-electrostatic surface complexation model where competitive sorption on Fe oxide and phyllosilicate sites was assumed and provided reasonable descriptions of Pb and Cd transport. However, [Kretzschmar and Voegelin \(2001\)](#) argued that applying surface complexation models to soils is rarely appropriate due to their inherent heterogeneity, and that such approaches should be considered as empirical. In such cases, the extension of simpler empirical approaches with as few parameters as possible is preferable ([Kretzschmar and Voegelin, 2001](#)). In this regard, [Zhang and Selim \(2007\)](#) extended the competitive SRS isotherm ([Sheindorf et al., 1981](#)) into a kinetic formulation and successfully described competitive transport of phosphate and As in soils. The same model was used to describe the competitive transport of Mo and phosphate ([Sun and Selim, 2017](#)), further demonstrating its utility. Besides the approach of [Zhang and Selim \(2007\)](#), multicomponent kinetic transport models are lacking.

The goals of this study were to 1) investigate the competitive sorption and transport of Ni and Zn in two contrasting soils as well as to 2) compare the descriptive capability of a novel Freundlich-type multicomponent model to the proven approach of [Sheindorf et al. \(1981\)](#) and [Zhang and Selim \(2007\)](#).

2. Modeling

2.1. Sheindorf-Rebhun-Sheintuch isotherm and kinetic model

The Freundlich isotherm can be derived based on the assumptions of an exponential distribution of binding site energies and that Langmuir-type adsorption occurs at each energy level ([Sips, 1948](#); [Sheindorf et al., 1981](#)). Furthermore, if competing solutes exhibit Freundlich-type sorption individually, then their sorption in a multicomponent system at each energy level can be described according to the competitive Langmuir isotherm ([Sheindorf et al., 1981](#)). Based on this, [Sheindorf et al. \(1981\)](#) derived a competitive Freundlich-type isotherm, commonly referred to as the SRS isotherm. For a two-component system comprised of cation i and j , the sorption of both species can be described according to the system of Eqs. (1) and (2):

$$S_i = K_i C_i (C_i + \alpha_i C_j)^{n_i-1} \quad (1)$$

$$S_j = K_j C_j (C_j + \alpha_j C_i)^{n_j-1} \quad (2)$$

where S is the sorbed concentration (mmol kg^{-1}), C is the solution concentration (mmol L^{-1}), K is a distribution coefficient (L kg^{-1}), n is a dimensionless nonlinearity parameter, and the subscripts i and j refer to cation i and j , respectively. The parameters α_i and α_j are dimensionless competitive coefficients describing the effect of cation j on the sorption of cation i , and vice versa, respectively. [Zhang and Selim \(2007\)](#) incorporated the SRS into a kinetic formulation giving Eqs. (3) and (4) that describe the change in sorbed concentration with respect to time for

cations i and j , respectively:

$$\rho \frac{\partial S_i}{\partial t} = \theta k_1 C_i (C_i + \alpha_i C_j)^{n_i-1} - \rho k_2 S_i \quad (3)$$

$$\rho \frac{\partial S_j}{\partial t} = \theta k_3 C_j (C_j + \alpha_j C_i)^{n_j-1} - \rho k_4 S_j \quad (4)$$

where ρ is the bulk density (g cm^{-3}), θ is the volumetric water content, and k_1 - k_4 are rate coefficients (hr^{-1}).

2.2. Competitive distribution coefficient isotherm and kinetic model

The change in the sorbed concentration of metal cation i with respect to time can be expressed according to [Selim \(2014\)](#):

$$\rho \frac{\partial S_i}{\partial t} = \theta k_1 C_i^{n_i} - \rho k_2 S_i \quad (5)$$

The sorption rate of a given ion has been shown to decrease in the presence of a competing ion ([Qin et al., 2006](#); [Zhang and Selim, 2007](#)). This can be accounted for in Eq. (5) by either decreasing or increasing the forward or backward rate coefficient, respectively. With the former, the resulting expression would result in longer equilibration times while the latter would result in shorter equilibration times. Others demonstrated that competition between sorbates tends to reduce equilibration times ([Zhao et al., 2001](#); [Tinnacher et al., 2013](#); [Padilla et al., 2022](#)), consistent with expectations of increasing the backward rate coefficient in multicomponent systems. As such, it was assumed that the overall backward rate coefficient for cation i is proportional to the sorbed concentration of cation j . Furthermore, if Freundlich-type sorption for cation j is assumed, sorbed j is proportional to its solution concentration raised to a fractional power. Applying the same approach to cation j , the change in sorbed concentrations of both cations with respect to time can be given as the system of Eqs. (6) and (7):

$$\rho \frac{\partial S_i}{\partial t} = \theta k_1 C_i^{n_i} - \rho (k_2 + k_5 C_j^{n_j}) S_i \quad (6)$$

$$\rho \frac{\partial S_j}{\partial t} = \theta k_3 C_j^{n_j} - \rho (k_4 + k_6 C_i^{n_i}) S_j \quad (7)$$

where k_1 - k_4 are rate coefficients (hr^{-1}) and k_5 and k_6 are empirical constants ($\text{L hr}^{-1} \text{mmol}^{-1}$) that scale the effect of cation j on cation i sorption and vice versa. At equilibrium, the differential terms are equal to zero. Rearranging, competitive sorption isotherms for both species are obtained, referred to here as the Competitive Distribution Coefficient isotherm (CDI):

$$S_i = \left(\frac{1}{A_i + B_i C_j^{n_j}} \right) C_i^{n_i} \quad (8)$$

$$S_j = \left(\frac{1}{A_j + B_j C_i^{n_i}} \right) C_j^{n_j} \quad (9)$$

where A and B parameters are defined as

$$A_i = \frac{\rho k_2}{\theta k_1}, B_i = \frac{\rho k_5}{\theta k_1} \quad (10)$$

$$A_j = \frac{\rho k_4}{\theta k_3}, B_j = \frac{\rho k_6}{\theta k_3} \quad (11)$$

It is important to note that Eqs. (8) and (9) are empirical and do not imply specific surface mechanisms, and therefore, should be assessed on their ability to describe measured data ([Sposito, 1989](#)).

2.3. Sensitivity analysis

To compare the SRS and CDI isotherms, a sensitivity analysis was

conducted with results displayed in Supplemental Figs. S1 and S2. Specifically, focus was given to the effect of α and B on modeled isotherms given by the SRS and CDI, respectively. Values of K and A were taken as unity and the nonlinearity parameters were varied to simulate highly nonlinear to approximately linear sorption of either cation. Initial concentrations of cation i and j were 1.0 and 0.5 mM, respectively. Final concentrations of either cation were iteratively solved for using Newton-Raphson. For SRS, the value of α_j was taken as $1/\alpha_i$ (Sheindorf et al., 1981), while values of B_j were taken as zero for the CDI. Both isotherms appear reasonably flexible to describe a wide range of competitive sorption scenarios. The value of n_j appears to have little effect on SRS modeled S_i , whereas values of n_j closer to unity result in higher concentrations of S_i for the CDI. However, this is a result of final concentrations of $C_j < 1$; for $C_j > 1$, the opposite would be expected. To determine the effect of the competitive coefficient of cation j on the sorption of i , values of α_j or B_j were varied with resulting isotherms for cation i shown in Supplemental Fig. S3. As expected, increasing values of α_j resulted in higher sorbed concentrations of cation i due to the $\alpha_i = 1/\alpha_j$ relationship. For CDI, the effect of B_j was low when $A_j \geq 1$ or $B_i \leq 0.5$. As such, results in Supplemental Fig. S3 were obtained with A_j set to 0.1 and B_i set to 1. Increasing values of B_j resulted in reductions of S_i , due to increased C_j leading to greater values of the denominator in Eq. (8). A major distinction between the isotherms is that the SRS estimates reduced sorption at low surface coverage even when the effect of competition is low ($\alpha_i = 0.1$) whereas the CDI does so to a much lesser extent. To illustrate this further, estimated values of the partitioning coefficient ($K_D = S/C$) for each isotherm are shown in Supplemental Fig. S4. Others have shown that competition between species is lower at low surface coverage due to an abundance of sites and/or high energy associations between the surface and sorbed species (Serrano et al., 2005; Flogeac et al., 2007; Violante, 2013). The CDI consistently estimates higher K_D values at low solution concentration than the SRS and may therefore have an advantage in describing low sorbed concentrations in multicomponent systems.

2.4. Transport

The one-dimensional, simultaneous transport of two metal cations can be described by a system of convection-dispersion equations, given by Eqs. (12) and (13).

$$\theta \frac{\partial C_i}{\partial t} + \rho \frac{\partial S_i}{\partial t} = \theta D \frac{\partial^2 C_i}{\partial x^2} - q \frac{\partial C_i}{\partial x} \quad (12)$$

$$\theta \frac{\partial C_j}{\partial t} + \rho \frac{\partial S_j}{\partial t} = \theta D \frac{\partial^2 C_j}{\partial x^2} - q \frac{\partial C_j}{\partial x} \quad (13)$$

where D is the hydrodynamic dispersion coefficient ($\text{cm}^2 \text{hr}^{-1}$) and q is the Darcy flux in the x direction (cm hr^{-1}). Eqs. (12) and (13) are subject to the initial and boundary conditions given by Zhang and Selim (2007). The incorporation of Eqs. (3) and (4) on the left-hand side of Eqs. (12) and (13), respectively, yields the SRS Kinetic Transport Model (SRST), while that of Eqs. (6) and (7) gives the Competitive Distribution Coefficient Transport Model (CDIT). Eqs. (12) and (13) were solved simultaneously using Crank-Nicolson and Eqs. (3) and (4) or Eqs. (6) and (7) were solved for each depth and time using 4th Order Runge-Kutta.

3. Methods

3.1. Soils

Two soils were used for all experiments. Surface horizon (0–10 cm) Olivier silt loam (fine-silty, mixed, active, thermic Aquic Fraglossudalf) and Windsor sandy loam (mixed, mesic Typic Udipsamment) were sampled from Louisiana and New Hampshire, respectively. Soils were air-dried and passed through a 2 mm sieve prior to experiments. Selected

physiochemical properties of both soils are included in Table 1.

3.2. Sorption

Sorption isotherms for Ni and Zn were obtained in triplicate. Three g of air-dried soil were weighed into 40 mL polypropylene centrifuge tubes, whereupon 30 mL of solution containing 0.10–5.00 mM Ni or Zn were added. Solutions were prepared in a background of 10 mM Ca (NO_3)₂ and 5 mM MES (2-(N-morpholino) ethane sulfonic acid) adjusted to the pH of the soil (5.80 for Olivier, 6.11 for Windsor) using NaOH. MES has been used as a buffer in transition metal sorption experiments previously and does not form any complexes with metal cations in solution (Peng et al., 2018; Shi et al., 2013; Ferreira et al., 2015). Soil/solution mixtures were then vortexed, transferred to a platform shaker, and shaken at 21 ± 1 °C. Following 24 h of reaction time, mixtures were centrifuged at 11,000g for 10 min and a 3 mL aliquot of supernatant was analyzed via inductively coupled plasma optical emission spectrophotometry (ICP-OES) for solution concentrations of Ni and Zn. Prior to analyses, all samples were acidified using HCl. To determine the effect of competition on the sorption of either metal cation, batch experiments were repeated with the inclusion of either 0.50 or 1.00 mM Ni or Zn in the background solution. For SRS, values of K_{Ni} and n , or K_{Zn} and m were obtained by fitting Freundlich isotherms to single ion sorption data using the PROC NLN procedure in SAS 9.4. Values of α_{Ni} and α_{Zn} were obtained by using Excel Solver to fit Eqs. (1) and (2) to all soil specific sorption data simultaneously (while holding K_{Ni} , K_{Zn} , n , and m constant) according to the iterative approach of Barrow et al. (2005) via general Newton-Raphson. To obtain CDI isotherms, Eqs. (7) and (8) were fit to all sorption data simultaneously using the PROC MODEL procedure in SAS 9.4.

3.3. Transport

The mobility of Ni or Zn in both soils under saturated steady-state flow conditions was determined using miscible displacement column experiments. Air-dried soil was uniformly packed into Kapton film columns to a depth of 4.0 cm. Columns were saturated by slowly applying ~ 10 pore volumes (PV) of the background solution described above via upward flow supplied by a piston displacement pump (Fluid Metering Inc., Syosset, NY, USA), after which flow was increased to achieve a Darcy flux of 0.5 cm hr^{-1} and columns were allowed to equilibrate for an additional 10 PV. Following this, ~ 2 PV pulse of tritiated water ($^3\text{H}_2\text{O}$) was applied to the column and leached with several PV of background solution. Column effluent was collected in fractions every 45 min using an ISCO Retriever II fraction collector (Teledyne Isco Inc., Lincoln, NE, USA). One mL samples of the fractionated effluent were mixed with 4 mL scintillation cocktail (Packard Ultima Gold) in a 7 mL borosilicate glass scintillation vial and concentrations of tritiated water were determined on a scintillation counter (Perkin Elmer TriCarb 4810 TR, Waltham, MA, USA). Count times were 5 min and no quench correction was made. Best estimates of the hydrodynamic dispersion coefficient, D , were obtained by modeling breakthrough curves (BTCs) of $^3\text{H}_2\text{O}$ using the CXTFIT module within the STANMOD software package in an inverse mode (Simunek et al., 1999). Observed and modeled tritium BTCs are shown in Supplemental Fig. S5 and best-fit values of D are given in Supplemental Table S1.

The transport of Ni and Zn in either soil was evaluated under both single ion and multicomponent systems. In single ion experiments, 25 PV of either 1.0 mM Ni or Zn in background solution was applied to soil columns and then subsequently leached with background solution until effluent concentrations were $\sim 1\%$ of those in the influent. To determine whether nonequilibrium conditions were present in the soil column during transport, flow was interrupted for 24 h at various times depending on the specific column. Competitive transport was evaluated using both consecutive and concurrent pulse applications (Zhang and Selim, 2007; Elbana et al., 2014). In concurrent pulse experiments, a 25

Table 1
Physiochemical properties of Olivier and Windsor soils.

Soil	pH	¹ OC (g kg ⁻¹)	² CEC (cmol kg ⁻¹)	Sand (%)	Silt	Clay	³ Al _{OX} (mmol kg ⁻¹)	³ Fe _{OX}	⁴ Al _{CBD}	⁴ Fe _{CBD}
Olivier	5.80	21.28	8.6	5	89	6	3.0	5.7	48	73
Windsor	6.11	2.03	2.0	77	20	3	25.6	6.4	135	66

¹ Organic Carbon (Nelson and Sommers, 1982).

² Cation Exchange Capacity (Soil Survey Laboratory Methods Manual, 1996).

³ Oxalate Extractable (Chao and Zhou, 1983).

⁴ Citrate-bicarbonate-dithionate Extractable (Mehra and Jackson, 1960).

PV pulse of 1.0 mM Ni and Zn was applied to columns followed by the application of background solution. For consecutive pulse experiments, a 25 PV pulse of 1.0 mM Ni was applied to the column followed by 25 PV of 1.0 mM Zn, after which background solution was applied to the column. Experiments were then repeated in reverse (25 PV of Zn followed by 25 PV of Ni). Effluent concentrations of Ni and Zn were determined via ICP-OES, as above.

Descriptions of BTC data by the SRST and CDIT models were obtained as follows. Values of k_1 - k_4 were obtained by fitting either model to the single ion experiments (k_1 and k_2 for Ni, k_3 and k_4 for Zn). Values of α_{Ni} and α_{Zn} , or k_5 and k_6 , for the SRST and CDIT models, respectively, were then obtained by fitting the models to the competitive transport (concurrent pulse) data while holding the values of k_1 - k_4 constant. Model descriptions by the SRST were obtained using the publicly available Chem_Transport software package (http://www.speess.lsu.edu/chem_transport) while the simulation and fitting modules of the CDIT were written in Fortran 95. Both the SRST and CDIT models utilize the Levenberg-Marquardt nonlinear least squares procedure to acquire estimates of parameter values. Goodness of fit was evaluated using r^2 and the sum of the squared errors.

4. Results and discussion

4.1. Sorption

Isotherms for the sorption of Ni and Zn by Olivier and Windsor soils

are displayed in Fig. 1. Olivier had a higher affinity than Windsor for both metal cations with consistently higher sorbed concentrations across the range of solution concentrations. The sorption of both Ni and Zn has been positively correlated with CEC and organic matter content (Shaheen et al., 2013; Covelo et al., 2007b), both of which are greater for Olivier and likely account for its higher affinity. Both soils had a greater affinity for Zn than for Ni, consistent with results reported previously for a variety of soils (Elbana et al., 2018). Differences in the affinities of cations for soil have been explained according to the hard-soft acid principle, namely, that softer acids tend to preferentially form covalent bonds with surface functional groups and are thus of higher affinity (Shaheen et al., 2012). However, the Misono softness parameter for Ni is greater than that of Zn (2.82 vs 2.34, Misono et al., 1967), and is inconsistent with the current results. Others have related the relative affinities of cations to their first hydrolysis constant (Antoniadis and Tsadilas, 2007; Usman, 2008; Du et al., 2011), which can be taken as a measure of the tendency of a cation to form a complex with surface coordinated hydroxyls. The hydrolysis constant of Zn is greater than that of Ni (pK_H of 9.0 vs 9.9, respectively) and is consistent with the sorption results.

In general, the presence of Zn reduced the sorption of Ni, and vice versa, in both soils. This was expected as reduced sorption of both Ni and Zn while simultaneously present has been demonstrated previously (Trivedi et al., 2001; Antoniadis and Tsadilas, 2007; Choi et al., 2020; Padilla and Selim, 2021). To determine the effect of input concentrations of both cations on subsequent sorbed concentrations, a Tukey

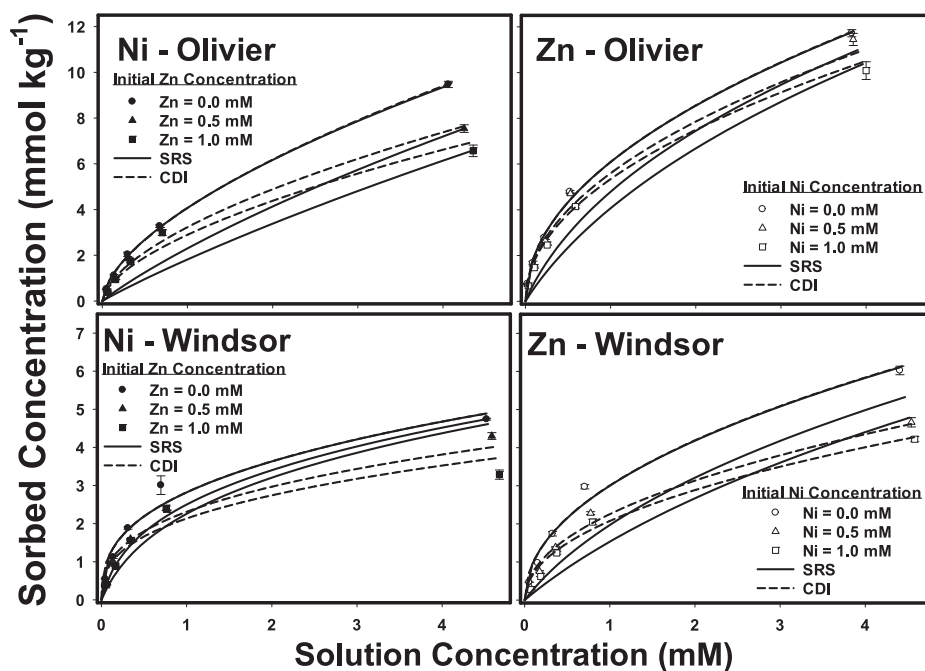


Fig. 1. Isotherms for Ni (left, closed symbols) and Zn (right, open symbols) sorption by Olivier and Windsor soils. Error bars are the 95% confidence interval. Solid and dashed curves are descriptions of the observed data using the SRS and CDI isotherms, respectively.

pairwise comparison was conducted for each input concentration of Ni and Zn at the $\alpha = 0.05$ level, with results displayed in Fig. 2. The sorption of Ni by Olivier was continually decreased for each input concentration of Zn when Ni was added at 0.10, 0.25, and 5.00 mM, although only 1.0 mM Zn reduced Ni sorption when Ni was added at 1.0 and 0.5 mM. The presence of 0.5 mM Ni had no effect on Zn sorption relative to single cation experiments for all input Zn concentrations, however, Ni added at 1.0 mM did significantly decrease Zn sorption in all cases. This indicates that Ni sorption by Olivier was more affected than that of Zn in the two-component system. Moreover, the sorbed concentration of Ni decreased relative to non-competitive experiments by an average of 11 and 19% in the presence of 0.50 and 1.00 mM Zn, respectively, while Zn sorption decreased only by an average of 4 and 13% in the presence of 0.50 and 1.00 mM Ni, respectively, emphasizing the dominance of Zn sorption over Ni. Such dominance was demonstrated previously for Zn and Ni sorption by soil (Antoniadis and Tsadilas, 2007) and Fe and Mn oxides (Trivedi et al., 2001; Choi et al., 2020). Competition between metal cations has been shown to be minimal at low surface coverage (Serrano et al., 2005; Flogeac et al., 2007; Violante, 2013). This appears true for Zn where only Ni added at 1.0 mM decreased Zn sorption when added at its lowest input concentration (0.10 mM). However, the sorption of Ni when added at 0.10 mM was significantly decreased in the presence of both levels of Zn, indicating that the relationship between competition and surface coverage is ion-specific.

For Windsor, each increase in initial Ni concentration resulted in significant decreases of Zn sorption across the range of Zn input concentrations. This contrasts with what was observed for Olivier and was likely due to the lower affinity of Windsor; fewer total available sites resulted in greater competition. Initial Zn concentrations of 1.00 mM significantly decreased Ni sorption in all cases whereas 0.50 mM Zn decreased Ni sorption in limited cases. Furthermore, the average decrease in Ni sorption relative to non-competitive experiments was 17 and 24% in the presence of 0.50 and 1.00 mM Zn, respectively, while Zn sorption decreased an average of 24 and 34% in the presence of 0.50 and 1.00 mM Ni, respectively. This indicates a dominance of Ni sorption over that of Zn, and contrasts with the trend observed in Olivier as well as with previous results (Trivedi et al., 2001; Antoniadis and Tsadilas,

2007; Choi et al., 2020). As such, the preference of a sorbent for a metal cation over another should be considered specific to the sorbent rather than the cation pair, in contrast to what has been suggested by others (Shaheen et al., 2013).

Descriptions of the experimental data using the SRS and CDI isotherms are shown as solid and dashed curves in Fig. 1, respectively, with optimized parameter values given in Table 2. For the single ion case, SRS and CDI descriptions are nearly identical. This is expected as the isotherms reduce to the same form where $A = 1/K$. Indeed, values of K estimated by the CDI were not significantly different than best-fit values for the SRS ($\alpha = 0.05$) in all cases. For Olivier, the SRS correctly captured the highest sorbed concentrations of Ni and Zn during competitive experiments, however, descriptions of lower sorbed concentrations were poor. For both cations, the SRS overestimated the effect of competition at low surface coverage, resulting in an underestimation of sorbed concentrations of both cations in multicomponent systems. On the other hand, the CDI provided much better descriptions of lower sorbed concentrations in the multicomponent case while maintaining good descriptions of higher sorbed concentrations. SRS descriptions of the Windsor sorption data were generally poor. In multicomponent systems, lower sorbed concentrations were underestimated while highest sorbed concentrations were overestimated for both Ni and Zn. Considerable discrepancies between measured data and SRS descriptions were also reported for bicomponent systems involving Ni and Zn (Antoniadis and Tsadilas, 2007) as well as Ni and Cd (Liao and Selim, 2010). Vidal et al. (2009) did achieve very good descriptions of competitive sorption using the SRS, however, separate sets of parameters were obtained for each dataset, negating any benefit of using a multicomponent isotherm. Conversely, the CDI described Zn sorption data well, correctly capturing both low and high sorbed concentrations. CDI descriptions of the Ni data were worse, where the highest sorbed concentrations were poorly described. However, descriptions of lower sorbed concentrations were better than those of the SRS. For both soils, the CDI descriptions were superior; the CDI SSE was about $\frac{1}{4}$ and $\frac{1}{2}$ of that of the SRS for Olivier and Windsor, respectively.

Estimated values of the SRS competitive coefficients α_{Ni} and α_{Zn} were 9.21 and 1.40, respectively, for Olivier, while CDI values for B_{Ni} and B_{Zn}

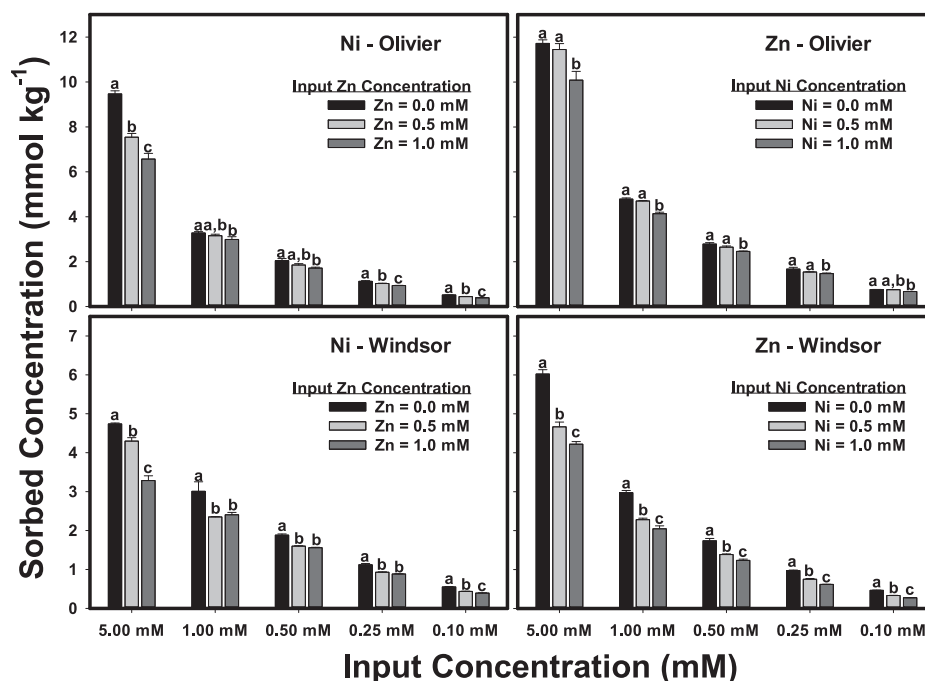


Fig. 2. Sorbed concentrations of Ni (left) in the presence of various input concentrations of Zn and sorbed concentrations of Zn (right) in the presence of various input concentrations of Ni. Error bars are the 95% confidence interval. Different letters indicate significant differences at the $\alpha = 0.05$ level.

Table 2
Optimized parameters for the SRS and CDI isotherms.

SRS								
Soil	$K_{Ni} \pm 95\% \text{ CI}$ (L kg ⁻¹)	$n_{Ni} \pm 95\% \text{ CI}$	$K_{Zn} \pm 95\% \text{ CI}$ (L kg ⁻¹)	$n_{Zn} \pm 95\% \text{ CI}$	α_{Ni}	α_{Zn}	SSE	r ²
Olivier	4.07 ± 0.25	0.60 ± 0.05	6.09 ± 0.53	0.49 ± 0.06	9.21	1.40	10.61	0.97
Windsor	2.82 ± 0.68	0.36 ± 0.17	3.01 ± 0.60	0.48 ± 0.14	0.48	3.26	5.20	0.93
CDI								
Soil	$A_{Ni} \pm 95\% \text{ CI}$ (kg L ⁻¹)	$B_{Ni} \pm 95\% \text{ CI}$ (kg mmol ⁻¹)	$n_{Ni} \pm 95\% \text{ CI}$	$A_{Zn} \pm 95\% \text{ CI}$ (kg L ⁻¹)	$B_{Zn} \pm 95\% \text{ CI}$ (kg mmol ⁻¹)	$n_{Zn} \pm 95\% \text{ CI}$	SSE	r ²
Olivier	0.25 ± 0.02	0.13 ± 0.03	0.60 ± 0.05	0.16 ± 0.01	0.03 ± 0.01	0.49 ± 0.06	2.63	0.99
Windsor	0.35 ± 0.07	0.13 ± 0.06	0.36 ± 0.17	0.33 ± 0.01	0.16 ± 0.04	0.48 ± 0.14	2.31	0.97

were 0.13 and 0.03, respectively. Smaller values of α_{Zn} and B_{Zn} are indicative of the dominance of Zn sorption over that of Ni and were consistent with the measured results. For Windsor, the competitive parameters for Ni sorption were less than those for Zn for both the SRS and CDI, indicating that Ni was dominant over Zn, also consistent with the measured data. The SRS was rigorously derived based on mechanistic assumptions (exponential distribution of binding site energies coupled with Langmuir-type sorption at each energy level; Sheindorf et al., 1981) and may therefore be preferable to the purely empirical CDI. However, the SRS in this case can be considered as a purely empirical description. Specifically, $\alpha_{Ni} = 1/\alpha_{Zn}$ by definition, yet this was not the case for either soil. As such, the SRS and CDI should be compared based on their ability to describe the observed data (Sposito, 1989), where the CDI was superior. Furthermore, it is very common that the $\alpha_N = 1/\alpha_{Zn}$ relationship is not realized (Roy et al., 1986; Zhang and Selim, 2007; Antoniadis and Tsadilas, 2007; Liao and Selim, 2010; Vidal et al., 2009; Sun and Selim, 2017). Therefore, the CDI may provide superior descriptions of competitive sorption for other solutes as well.

4.2. Transport

Breakthrough curves of Ni and Zn from both soils during single ion experiments are displayed in Fig. 3. As expected from batch data, the

mobility of Ni was greater than Zn in both soils. Specifically, Ni breakthrough from Olivier was retarded by 4 PV, the maximum concentration in the effluent reached 80% of that in the influent solution, and 96% of the applied Ni was recovered in the effluent. Conversely, Zn breakthrough was retarded by nearly 11 PV, the maximum concentration in the effluent was 49% of the influent solution, and only 84% of the mass applied was recovered in the effluent. For Windsor, Ni breakthrough was retarded by 8 PV and the maximum effluent concentration was 78% of the influent, compared to a retardation of Zn breakthrough of about 10 PV and a maximum effluent concentration of 60% of the influent. Recovered Ni and Zn in the effluent was 87 and 74% of that applied, respectively. All four BTCs were asymmetric with extensive tailing. While some have suggested this is a result of nonequilibrium conditions within the column (Elbana and Selim, 2010; Elbana et al., 2014), tailing can also be a result of nonlinear equilibrium sorption (Serrano et al., 2013).

To determine whether nonequilibrium conditions were present in the soil columns, flow was interrupted during each single cation experiment, as indicated by the arrows in Fig. 3. Perturbations in the effluent concentration were observed in all cases, indicating sorption nonequilibrium (Brusseau et al., 1989). Sorption nonequilibrium has been reported previously for both Ni and Zn sorption by Olivier and Windsor soils (Zhao and Selim, 2010; Liao and Selim, 2010; Selim et al., 2013). Such

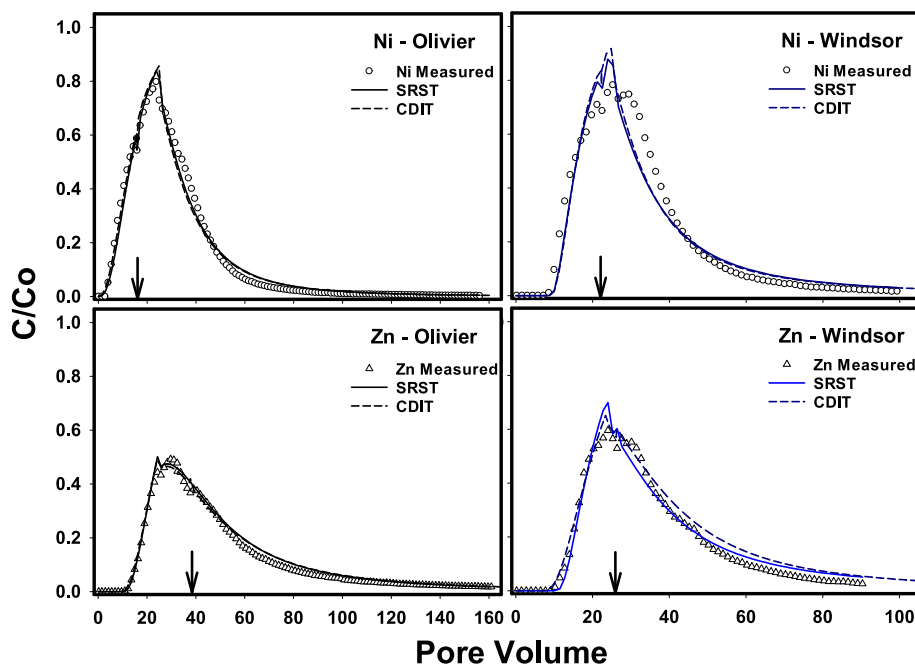


Fig. 3. Breakthrough curves of Ni (circles) and Zn (triangles) from single cation experiments. Solid and dashed curves are descriptions of the data by the SRST and CDIT models, respectively. Arrows indicate flow interruption.

nonequilibrium could be attributable to both physical and/or chemical processes, however, the data presented in Fig. 3 cannot distinguish between the two. Effluent concentration perturbations following flow interruption during the transport of a conservative tracer are indicative of physical nonequilibrium (Reedy et al., 1996; Jardine et al., 1998). Zhang (2007) performed flow interruption experiments during the transport of $^3\text{H}_2\text{O}$ through Windsor and Olivier columns. No perturbation was observed in the Windsor soil, indicating that the nonequilibrium during Ni and Zn transport experiments was due to chemical nonequilibrium. However, a significant decrease in $^3\text{H}_2\text{O}$ concentration was observed following flow interruption in the Olivier column. As such, physical nonequilibrium as the cause of effluent concentration perturbations of Ni and Zn could not be ruled out. To investigate this further, $^3\text{H}_2\text{O}$ BTCs from Olivier soil were fit using the CFITIM module included in the STANMOD software package. The CFITIM module is a nonreactive, physical nonequilibrium model that considers both a mobile and immobile region corresponding to inter and intraparticle space, respectively (van Genuchten et al., 2012). Comparisons between model fits were made using an F test at the $\alpha = 0.05$ level. The two-region CFITIM provided a superior description of the Olivier data in three of the five cases, however, in no case were all parameters significantly different than zero ($\alpha = 0.05$). Therefore, for practical purposes, a single flow domain was assumed for reactive transport modeling discussed below.

Breakthrough curves of Ni and Zn from each soil during concurrent pulse applications (1.0 mM Ni and Zn) are shown in Fig. 4. The mobility of both metal cations increased when applied simultaneously. Specifically, the retardation of Ni was substantially reduced in both soils, with breakthrough from Olivier and Windsor occurring after about 3 and 4 PV, respectively. Similarly, Zn breakthrough from Olivier and Windsor was reduced to about 8 and 4 PV, respectively. Earlier breakthrough of metal cations due to competition has been reported previously. For example, the simultaneous application of Sn and Pb substantially reduced Pb retardation in Windsor and Olivier soils, while Ni, Mn, and Zn were demonstrated to result in earlier breakthrough of Pb from a lateritic soil (Elbana et al., 2014; Chotpantarat et al., 2011, 2012). Earlier breakthrough of solutes during multicomponent transport was also demonstrated by several others (Tsang and Lo, 2006; Zhang and Selim, 2007; Fonseca et al., 2011; Selim, 2013a). Maximum effluent concentrations of Ni and Zn from both soils increased substantially relative to single cation experiments. Maximum concentrations of Ni were 100 and 93% of the influent concentration from Olivier and Windsor, respectively, while those of Zn were 62 and 91% of the influent. This further emphasizes the increased mobility of either cation when applied concurrently and has been demonstrated previously (Tsang and Lo, 2006; Chotpantarat et al., 2011, 2012; Selim, 2013a; Elbana et al., 2014). The fraction of the mass of Ni and Zn applied recovered in the effluent was very similar between single cation and

concurrent pulse application experiments for Olivier, and for Zn, may suggest the presence of sites for which Ni does not compete (Sun and Selim, 2017). For Windsor, substantially more Ni and Zn were recovered in the effluent relative to single cation experiments, consistent with enhanced mobility due to competition.

Results from consecutive pulse experiments (Ni followed by Zn, and vice versa) are shown in Fig. 5. In general, the metal cation that was applied first was mostly unaffected relative to single cation experiments, evidenced by similar retardation, maximum effluent concentrations, and mass recovery. However, the metal cation that was applied second exhibited increased mobility. For example, the breakthrough of Ni from Olivier when applied after Zn was earlier by 2 PV relative to single ion experiments. Likewise, Zn breakthrough was also about 2 PV earlier when applied after Ni, and its maximum concentration in the effluent was 68% of the influent (compared to 49% in the single cation experiment). Like concurrent pulse experiments, Zn recovery was mostly unaffected by Ni, suggesting the existence of sorption sites specific to Zn. In Windsor, maximum effluent concentrations of Ni were greater relative to single cation experiments when applied after Zn, however, its retardation unexpectedly increased by about 1.5 PV. Conversely, breakthrough of Zn was about 4 PV earlier when applied after Ni, its maximum relative concentration in the effluent was 81% of the influent (60% during single cation experiment) and 92% of the applied Zn was recovered in the effluent (compared to 74% during single cation experiments). Enhanced mobility of the second metal cation is due to some proportion of the available sites being occupied by the first metal cation, which in turn reduces the sites available for the second metal cation (Selim, 2013a). Like the current results, increased mobility of vanadate following the application of a phosphate pulse was reported by Selim (2013a), and increased mobility of Pb following the application of Sn was reported by Elbana et al. (2014).

Descriptions of the measured BTCs from each experiment using the SRST and CDIT models are included in Figs. 3–5 as solid and dashed curves respectively. Descriptions of Ni are shown as black curves while those of Zn are blue. Optimized parameters are provided in Supplemental Table S2 and goodness-of-fit statistics are given in Table 3. Consistency between the isotherm parameters obtained from batch and column experiments can be assessed based on the corresponding ratio of rate coefficients. Variances of the resulting estimates can be calculated according to the following:

$$\text{Var}\left(C^* \frac{k_N}{k_D}\right) = \left(C^* \frac{k_N}{k_D}\right)^2 \left[\frac{\sigma_{k_N}^2}{k_D^2} + \frac{\sigma_{k_D}^2}{k_N^2} \right] \quad (14)$$

where C is θ/ρ for SRS and ρ/θ for CDIT, and k_N/k_D is k_f/k_b for SRS and k_b/k_f for CDIT. From the variance, standard errors can be calculated for isotherm parameters estimated by the transport models and compared to those obtained from batch experiments. Two-tailed *t*-tests at the $\alpha =$

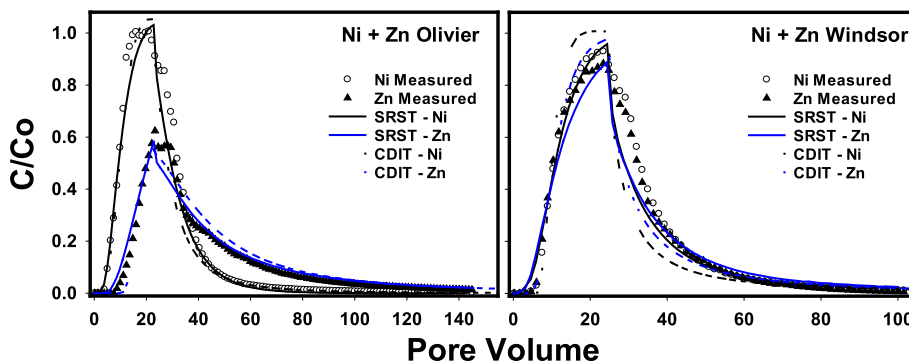


Fig. 4. Breakthrough curves of Ni (circles) and Zn (triangles) from Olivier and Windsor soils during concurrent pulse application experiments. Solid and dashed curves are SRST and CDIT descriptions of the Ni (black) and Zn (blue) observed data, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

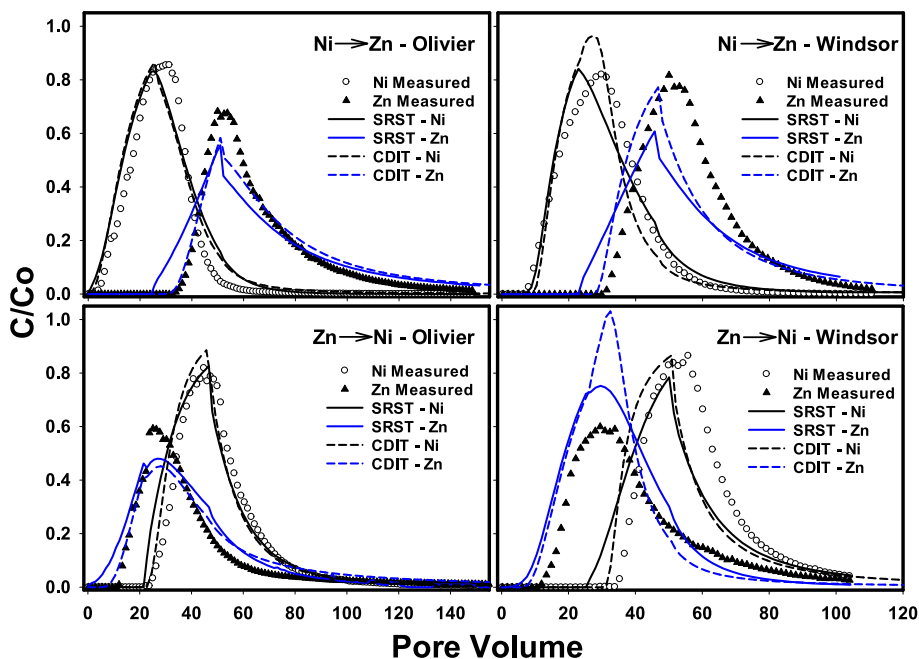


Fig. 5. Breakthrough curves of Ni (circles) and Zn (triangles) from Olivier and Windsor soils during consecutive pulse application experiments. Solid and dashed curves are SRST and CDIT descriptions of the Ni (black) and Zn (blue) observed data, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 3

SSE and r^2 for SRST and CDIT for each experiment, as well as the full data set (indicated by "Total").

Soil	Experiment	SRST		CDIT	
		SSE	r^2	SSE	r^2
Olivier	Ni Only	0.086	0.987	0.112	0.983
	Zn Only	0.033	0.987	0.036	0.986
	Ni + Zn	0.281	0.981	0.632	0.957
	Ni → Zn	1.432	0.889	0.983	0.924
	Zn → Ni	1.578	0.842	0.714	0.928
	Total	3.410	0.927	2.477	0.945
Windsor	Ni Only	0.278	0.942	0.312	0.934
	Zn Only	0.085	0.968	0.096	0.964
	Ni + Zn	0.462	0.964	0.932	0.932
	Ni → Zn	1.016	0.900	0.576	0.943
	Zn → Ni	2.256	0.735	3.060	0.641
	Total	4.098	0.895	4.976	0.875

0.05 level were conducted with results given in Supplemental Table S3. Values of K_{Ni} and K_{Zn} estimated by SRST were significantly different than those obtained from batch experiments, except for the Windsor K_{Ni} . Values of A_{Ni} and A_{Zn} estimated by the CDIT were significantly less than those obtained from batch experiments, except for the Olivier A_{Ni} . Discrepancies between model parameters obtained from batch and transport experiments are common within the literature and have been attributed to methodological differences (Zhang and Selim, 2007; Cai et al., 2015; Sun and Selim, 2017), namely, different solid:solution ratios, greater mixing in batch systems, and open vs closed systems. On the other hand, no significant differences between transport and batch values for B_{Ni} or B_{Zn} existed for any case, indicating good conformity between the two methods for capturing the effect of competition.

Both models described the single cation experiments well ($r^2 > 0.96$) except for Ni transport in Windsor, although it was still reasonably well described ($r^2 > 0.93$). Simulated BTCs by both models were nearly identical in all cases. This was expected as the models are identical for the non-competitive case. Values of the competitive parameters (α_{Ni} and α_{Zn} for SRST, k_5 and k_6 for CDIT) were obtained by fitting both models to

the concurrent pulse experiments. Overall, both models described the observed data well with $r^2 \geq 0.93$ in all cases, although the SRST descriptions were slightly better as indicated by lower values of the SSE (Table 3). For Olivier, both models captured the timing and magnitude of peak concentrations well, while Zn retardation was underestimated and overestimated by the SRST and CDIT, respectively. For Windsor, the SRST correctly captured the timing and magnitude of the peak effluent concentrations whereas the CDIT overestimated peak concentrations for both Ni and Zn. However, while the SRST underestimated Ni and Zn retardation, the CDIT captured the retardation of both well.

Optimized parameters from single ion and concurrent pulse experiments were used to simulate consecutive pulse experiments (Fig. 5) (Zhang and Selim, 2007). The CDIT provided better descriptions of the consecutive pulse experiments except for the Windsor Zn → Ni experiment which both models described poorly. A consistent feature of the SRST simulations was an underestimation of the retardation of the second pulse, with simulated breakthrough occurring earlier than measured in all cases. The CDIT, however, captured such retardation to a much better extent in all cases. The overall shapes of the simulated BTCs were more consistent with those measured for Olivier, while Windsor BTCs were poorly approximated by both models. Specifically, the timing of maximum effluent concentrations of Zn were underestimated resulting in lower modeled than observed effluent concentrations during the falling limbs of the Zn BTCs. Both models overestimated peak Ni concentrations during Windsor Zn → Ni experiments, demonstrating that they overestimated the increase in Ni mobility in multicomponent systems for this scenario. For the entire data set (all five experiments for each soil), the CDIT was superior for Olivier while the SRST was superior for Windsor, indicating that the suitability of either approach was soil dependent. However, the overall r^2 values for Olivier and Windsor were >0.93 and 0.88 , respectively, indicating that either model provided a reasonable description of the total data set.

Others described competitive transport of metal cations using single component models (Tsang and Lo, 2006; Chotpantarat et al., 2012; Elbana et al., 2014). An obvious drawback to such approaches is that they require separate sets of parameters for single and multicomponent systems, greatly limiting their utility. Surface complexation models have

successfully been used to model competitive sorption and transport of metal cations in soils (Serrano et al., 2009, 2013), however, such models applied to soils have been argued as empirical, as the attribution of partitioning coefficients to specific adsorption mechanisms is questionable in heterogeneous media (Kretzschmar and Voegelin, 2001). As such, they provide no deeper insight into surface level mechanisms than the empirical SRST or CDIT but require more parameters. When using empirical approaches, Sposito (1989) argued that a model should be evaluated based on its ability to describe the observed data, and such models should contain as few parameters as possible to provide sufficient descriptions (Kretzschmar and Voegelin, 2001). Furthermore, surface complexation models assume chemical equilibrium, which may be inappropriate especially during flow conditions. To this effect, several authors demonstrated that the use of models that incorporate time-dependent reactions provide better descriptions than those that assume equilibrium (Selim et al., 1992; Tsang and Lo, 2006; Chotpanarat et al., 2012). Both the SRST and CDIT are nonequilibrium models, and since nonequilibrium was observed during transport experiments, were more appropriate for describing the current data. Overall, both transport models offer an advantage to single species kinetic models in that they require a single set of parameters to describe both single ion and multicomponent systems, and require fewer parameters than SCM based transport models.

5. Conclusion

Reduced sorption of Ni and Zn by Olivier and Windsor soils in multicomponent batch experiments confirmed that both metal cations compete for sorption sites. Based on relative reductions in sorbed concentrations, Zn sorption was dominant in Olivier while Ni was dominant in Windsor. A novel multicomponent isotherm (CDI) was presented and compared to the SRS isotherm for describing competitive sorption of Ni and Zn by both soils. The SRS isotherm provided reasonable descriptions of Olivier batch data for the highest input concentrations, however, sorption was generally underestimated for the lower input concentrations. On the other hand, the CDI provided good descriptions of sorbed concentrations across the entire range of solution concentrations. SRS descriptions of the multicomponent Windsor data were poor for both Ni and Zn. CDI descriptions of the Windsor Ni data were also generally poor, however, Zn sorption data was described well. For both soils, the CDI was superior to the SRS isotherm while requiring the same number of adjustable parameters. During transport studies, the mobility of Ni and Zn increased in both soils during concurrent pulse experiments. In consecutive pulse experiments, the cation applied first was generally unaffected whereas the mobility of the cation applied second increased. A novel multicomponent kinetic transport model, the CDIT, was developed and compared to an SRS-based kinetic transport model (SRST) for describing competitive transport of Ni and Zn in both soils. Both the SRST and CDIT models gave good descriptions of the transport of Ni and Zn during single cation as well as concurrent application experiments, indicating that both are appropriate for describing competitive transport. Consecutive pulse experiments were generally better described by CDIT except for the Windsor Zn → Ni experiment, which both models described poorly. All five experiments were best described by the CDIT for Olivier while the SRST better described the Windsor transport data. Overall, the better description of batch data by the CDI coupled with comparable descriptions of transport data by both models suggest the CDI/CDIT approach for describing competitive sorption and transport of Ni and Zn is preferable to previous empirical multicomponent approaches.

CRedit authorship contribution statement

Joshua T. Padilla: Conceptualization, Data curation, Formal analysis, Software, Writing – original draft. **H. Magdi Selim:** Conceptualization, Methodology, Resources, Supervision. **Lewis A. Gaston:** Formal

analysis, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jconhyd.2022.104108>.

References

- Antoniadis, V., Tsadilas, C.D., 2007. Sorption of cadmium, nickel, and zinc in mono- and multivalent systems. *Appl. Geochem.* 22 (11), 2375–2380.
- Barrow, N.J., Cartes, P., Mora, M.L., 2005. Modifications to the Freundlich equation to describe anion sorption over a large range and to describe competition between pairs of ions. *Eur. J. Soil Sci.* 56, 601–606.
- Bradl, H.G., 2004. Adsorption of heavy metal ions on soils and soils constituents. *J. Colloid Interface Sci.* 277, 1–18.
- Brusseau, M.L., Rao, P.S.C., Jessup, R.E., Davidson, J.M., 1989. Flow interruption: a method for investigating sorption nonequilibrium. *J. Contam. Hydrol.* 4 (3), 223–240.
- Cai, Y., Li, L., Zhang, H., 2015. Kinetic modeling of pH-dependent antimony (V) sorption and transport in iron oxide-coated sand. *Chemosphere* 138, 758–764.
- Chao, T.T., Zhou, L., 1983. Extraction technique for selective dissolution of amorphous iron oxides from soils and sediments. *Soil Sci. Soc. Am. J.* 47, 225–232.
- Choi, J., Septian, A., Shin, W.S., 2020. The influence of salinity on the removal of Ni and Zn by sorption onto iron oxide- and manganese oxide-coated sand. *Sustainability* 12, 5815.
- Chotpanarat, S., Ong, S.K., Sutthirat, C., Osathaphan, K., 2011. Competitive sorption and transport of Pb^{2+} , Ni^{2+} , Mn^{2+} , and Zn^{2+} in lateritic soil columns. *J. Hazard. Mater.* 190, 391–396.
- Chotpanarat, S., Ong, S.K., Sutthirat, C., Osathaphan, K., 2012. Competitive modeling of sorption and transport of Pb^{2+} , Ni^{2+} , Mn^{2+} , and Zn^{2+} under binary and multi-metal systems in lateritic soil columns. *Geoderma* 189–190, 278–287.
- Covelo, E.F., Vega, F.A., Andrade, M.L., 2007a. Competitive sorption and desorption of heavy metals by individual soil components. *J. Hazard. Mater.* 140, 308–315.
- Covelo, E.F., Vega, F.A., Andrade, M.L., 2007b. Simultaneous sorption and desorption of Cd, Cr, Cu, Ni, Pb, and Zn in acid soils I. Selectivity sequences. *J. Hazard. Mater.* 147, 852–861.
- Dermont, G., Bergeron, M., Richer-Lafleche, M., Mercier, G., 2010. Remediation of metal-contaminated urban soil using flotation technique. *Sci. Total Environ.* 408 (5), 1199–1211.
- Du, A.J., Sun, D.D., Leckie, J.O., 2011. Selective sorption of divalent cations using a high capacity sorbent. *J. Hazard. Mater.* 187, 96–100.
- Elbana, T.A., Selim, H.M., 2010. Cadmium transport in alkaline and acidic soils: miscible displacement experiments. *Soil Sci. Soc. Am. J.* 74, 1956–1966.
- Elbana, T.A., Sparks, D.L., Selim, H.M., 2014. Transport of tin and lead in soils: miscible displacement experiments and second-order modeling. *Soil Sci. Soc. Am. J.* 78 (3), 701–712.
- Elbana, T.A., Selim, H.M., Akrami, N., Newman, A., Shaheen, S.M., Rinklebe, J., 2018. Freundlich sorption parameters for cadmium, copper, nickel, lead, and zinc for different soils: influence of kinetics. *Geoderma* 324, 80–88.
- Ferreira, C.M., Pinto, I.S., Soares, E.V., Soares, H.M., 2015. (Un) suitability of the use of pH buffers in biological, biochemical and environmental studies and their interaction with metal ions—a review. *RSC Adv.* 5 (39), 30989–31003.
- Flogeac, K., Guillon, E., Aplincourt, M., 2007. Competitive sorption of metal ions onto a North-Eastern France soil. Isotherms and XAFS studies. *Geoderma* 139 (1–2), 180–189.
- Fonseca, B., Figueiredo, H., Rodrigues, J., Queiroz, A., Tavares, T., 2011. Mobility of Cr, Pb, Cu, and Zn in a loamy sand soil: a comparative study. *Geoderma* 164, 232–237.
- Guo, W., Siebecker, M.G., Wang, Z., Li, W., 2018. Competitive sorption of Ni and Zn at the aluminum oxide/water interface: an XAFS study. *Geochem. Trans.* 19, 1–12. <https://doi.org/10.1186/s12932-018-0054-7>.
- Hinz, C., Selim, H.M., 1994. Transport of Zn and cadmium in soils: experimental evidence and modeling approaches. *Soil Sci. Soc. Am. J.* 58, 1316–1327.
- Jardine, P.M., O'Brien, R., Wilson, G.V., Gwo, J.P., 1998. Experimental techniques for confirming and quantifying physical nonequilibrium processes in soils. In: *Physical Nonequilibrium in Soils Modeling and Application*. Ann Arbor Press, Chelsea, MI.
- Kretzschmar, R., Voegelin, A., 2001. Modeling competitive sorption and release of heavy metals in soils. In: *Heavy Metals Release in Soils*. CRC Press, Boca Raton, FL, USA.

- Liao, X., Li, Y., Yan, X., 2016. Removal of heavy metals and arsenic from a co-contaminated soil by sieving combined with washing process. *J. Environ. Sci.* 41, 202–210.
- Liao, L., Selim, H.M., 2010. Transport of nickel in different soils: column experiments and kinetic modeling. *Soil Sci. Soc. Am. J.* 74, 1946–1955.
- Liu, Z., Xu, Z., Xu, L., Buyong, F., Chay, T.C., Li, Z., Cai, Y., Hu, B., Zhu, Y., Wang, X., 2022. Modified biochar: synthesis and mechanism for removal of environmental heavy metals. *Carbon Res.* 1, 8.
- Lu, Y., Cai, Y., Zhang, S., Zhuang, L., Hu, B., Wang, S., Chen, J., Wang, X., 2022. Application of biochar-based photocatalysts for adsorption-(photo)degradation/reduction of environmental contaminants: mechanism, challenges and perspective. *Biochar* 4, 45.
- Mehra, Q.P., Jackson, M.L., 1960. Iron oxide removal from soils and clays by a dithionite-citrate system with sodium bicarbonate buffer. *Clay Clay Miner.* 7, 317–327.
- Misono, M., Ochiai, E., Saito, Y., Yoneda, Y., 1967. A new dual parameter scale for the strength of Lewis acids and bases with the evaluation of their softness. *J. Inorg. Nucl. Chem.* 29 (11), 2685–2691.
- Nelson, D.W., Sommers, L.E., 1982. Total carbon, organic carbon and organic matter. In: *Methods of Soil Analysis Part 2 – Chemical and Microbiological Properties*, pp. 539–579.
- Padilla, J.T., Selim, H.M., 2021. Modeling the kinetics of competitive sorption and desorption of Zn(II), Ni(II), and Pb(II) in an acidic soil: stirred-flow experiments. *Soil Sci. Soc. Am. J.* 85, 560–573.
- Padilla, J.T., Selim, H.M., Gaston, L.A., 2022. Modeling the sorption of Ni(II) and Zn(II) by Mn oxide-coated sand: equilibrium and kinetic approaches. *J. Environ. Qual.* <https://doi.org/10.1002/jeq2.20404> (accepted) In press.
- Peng, L., Shi, Z., Wang, P., Li, W., Lin, Z., Dang, Z., Sparks, D.L., 2018. A novel multi-reaction model for kinetics of Zn release from soils: roles of soil binding sites. *J. Colloid Interface Sci.* 514, 146–155.
- Qin, F., Wen, B., Shan, Z., Xie, Y., Liu, T., Zhang, S., Khan, S.U., 2006. Mechanisms of competitive adsorption of Pb, Cu, and Cd on peat. *Environ. Pollut.* 144, 669–680.
- Reedy, O.C., Jardine, P.M., Wilson, G.V., Selim, H.M., 1996. Quantifying the diffusive mass transfer of nonreactive solutes in columns of fractured Saprolite using flow interruption. *Soil Sci. Soc. Am. J.* 60 (5), 1376–1384.
- Roy, W.R., Hassett, J.J., Griffin, R.A., 1986. Competitive coefficients for the adsorption of arsenate, molybdate, and phosphate mixtures by soils. *Soil Sci. Soc. Am. J.* 50, 1176–1182.
- Selim, H.M., 2013a. Competitive sorption of heavy metals in soils: experimental evidence. In: *Competitive Sorption and Transport of Heavy Metals in Soils and Geological Media*. CRC Press, Boca Raton, FL, USA.
- Selim, H.M., 2013b. Transport and retention of heavy metal in soils: competitive sorption. In: *Advances in Agronomy*, 119. Academic Press, pp. 275–308.
- Selim, H.M., 2014. *Transport and Fate of Chemicals in Soils: Principles and Applications*. CRC Press, Boca Raton, FL.
- Selim, H.M., Buchter, B., Hinz, Y., Ma, L., 1992. Modeling the transport and retention of cadmium in soils: multireaction and multicomponent approaches. *Soil Sci. Soc. Am. J.* 56, 1004–1015.
- Selim, H.M., Elbana, T.A., Zhao, K., Xu, J., Fergusson, E.L., 2013. Miscible displacement of zinc in soil columns: linear and nonlinear modeling. *Soil Sci. Soc. Am. J.* 77, 391–402.
- Serrano, S., Garrido, F., Campbell, C.G., García-González, M.T., 2005. Competitive sorption of cadmium and lead in acid soils of Central Spain. *Geoderma* 124, 91–104.
- Serrano, S., O'Day, P.A., Vlassopoulos, D., García-González, M.T., Garrido, F., 2009. A surface complexation and ion exchange model of Pb and Cd competitive sorption on natural soils. *Geochim. Cosmochim. Acta* 73, 543–558.
- Serrano, S., Vlassopoulos, D., Garrido, F., O'Day, P.A., 2013. A combined site-specific metals sorption and transport model for intact soil columns. *Vadose Zone J.* 12 (4) <https://doi.org/10.2136/vzj2012.0152>.
- Shaheen, S.M., Derbalag, A.S., Moghanm, F.S., 2012. Removal of heavy metals from aqueous solution by zeolite in competitive sorption system. *Int. J. Environ. Sci. Dev.* 3 (4), 362–367.
- Shaheen, S.M., Tsadilas, C.D., Rinklebe, J., 2013. A review of the distribution coefficients of trace elements in soils: influence of sorption system, element characteristics, and soil colloidal properties. *Adv. Colloid Interf. Sci.* 201, 43–56.
- Sheindorf, C., Rebhun, M., Sheintuch, M., 1981. A Freundlich-type multicomponent isotherm. *J. Colloid Interface Sci.* 79, 136–142.
- Shi, Z., Di Toro, D.M., Allen, H.E., Sparks, D.L., 2013. A general model for kinetics of heavy metal adsorption and desorption on soils. *Environ. Sci. Technol.* 47 (8), 3761–3767.
- Simunek, J., Van Genuchten, M.T., Sejna, M., Toride, N., Leij, F.J., 1999. The STANMOD Computer Software for Evaluating Solute Transport in Porous Media using Analytical Solutions of the Convection-Dispersion Equation; Versions 1.0 and 2.0; IGWMC-TPS-71. International Ground Water Modeling Center, Colorado School of Mines, Golden, CO, USA.
- Sips, R., 1948. On the structure of a catalyst surface. *J. Chem. Phys.* 16 (5), 490–495.
- Soil Survey Laboratory Methods Manual, 1996. *Soil Survey Investigations Report No. 42*. Version 3.0. USDA-NRCS-NSSC.
- Sposito, G., 1989. *The Chemistry of Soils*. Oxford University Press, New York, NY.
- Sun, W., Selim, H.M., 2017. Molybdenum-phosphate retention and transport in soils. *Geoderma* 308, 60–68.
- Tinnacher, R.M., Nico, P.S., Davis, J.A., Honeyman, B., 2013. Effects of fulvic acid on uranium(VI) sorption kinetics. *Environ. Sci. Technol.* 47, 6214–6222.
- Trivedi, P., Axe, L., Dyer, J., 2001. Adsorption of metal ions onto goethite: single-adsorbate and competitive systems. *Colloids Surf. A: Physicochem. Eng. Asp.* 191 (1–2), 107–121.
- Tsang, D.C.W., Lo, I.M.C., 2006. Competitive Cu and Cd sorption and transport in soils: a combined batch kinetics, column, and sequential extraction study. *Environ. Sci. Technol.* 40, 6655–6661.
- Usman, A.R.A., 2008. The relative adsorption selectivities of Pb, Cu, Zn, Cd, and Ni by soils developed on shale in New Valley, Egypt. *Geoderma* 144 (1–2), 334–343.
- van Genuchten, M.Th., Simunek, J., Leij, F.J., Toride, N., Sejna, M., 2012. STANMOD: model use, calibration, and validation. *Trans. Am. Soc. Agric. Biol. Eng.* 55 (4), 1353–1366.
- Vidal, M., Santos, M.J., Abrão, T., Rodríguez, J., Rigol, A., 2009. Modeling competitive metal sorption in a mineral soil. *Geoderma* 149, 189–198.
- Violante, A., 2013. Elucidating mechanisms of competitive sorption at the mineral/water interface. In: *Advances in Agronomy*, 118. Academic Press, pp. 111–176.
- Voegelin, A., Vulava, V.M., Kretzschmar, R., 2001. Reaction-based model describing competitive sorption and transport of Cd, Zn, and Ni in an acidic soil. *Environ. Sci. Technol.* 35, 1651–1657.
- Zhang, H., 2007. Evaluating Physical and Chemical Non-Equilibrium during Arsenic(III) Transport in Soils. ASA-CSSA-SSSA Annual Meeting, New Orleans, LA, USA.
- Zhang, H., Selim, H.M., 2007. Modeling competitive arsenate-phosphate retention and transport in soils: a multi-component multi-reaction approach. *Soil Sci. Soc. Am. J.* 71 (4), 1267–1277.
- Zhao, K., Selim, H.M., 2010. Adsorption-desorption kinetics of Zn in soils: influence of phosphate. *Soil Sci.* 175 (4), 145–153.
- Zhao, D., Pignatello, J.J., White, J.C., Braid, W., 2001. Dual-mode modeling of polycyclic aromatic hydrocarbons in soils. *Water Resour. Res.* 37, 2205–2212.