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Surface Complexation Modeling

APPLICATION OF SURFACE COMPLEXATION MODELS TO ANION ADSORPTION BY NATURAL MATERIALS

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Abstract: Various chemical models of ion adsorption are presented and discussed. Chemical models, such as surface complexation models, provide a molecular description of anion adsorption reactions using an equilibrium approach. Two such models, the constant capacitance model and the triple layer model, are described in the present study. Characteristics common to all the surface complexation models are equilibrium constant expressions, mass and charge balances, and surface activity coefficient electrostatic potential terms. Methods for determining parameter values for surface site density, capacitances, and surface complexation constants also are discussed. Spectroscopic experimental methods of establishing ion adsorption mechanisms include vibrational spectroscopy, nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, X-ray absorption spectroscopy, and X-ray reflectivity. Experimental determinations of point of zero charge shifts and ionic strength dependence of adsorption results and molecular modeling calculations also can be used to deduce adsorption mechanisms. Applications of the surface complexation models to heterogeneous natural materials, such as soils, using the component additivity and the generalized composite approaches are described. Emphasis is on the generalized composite approach for predicting anion adsorption by soils. Continuing research is needed to develop consistent and realistic protocols for describing ion adsorption reactions on soil minerals and soils. The availability of standardized model parameter databases for use in chemical speciation–transport models is critical. *Environ Toxicol Chem* 2014;33:2172–2180. Published 2014 Wiley Periodicals Inc. on behalf of SETAC. This article is a US Government work and as such, is in the public domain in the United States.

Keywords: Constant capacitance model Triple-layer model Boron Molybdenum Soils

INTRODUCTION

The present study summarizes the keynote presentation that opened the special symposium entitled *Recent developments and surface complexation modeling: Trace element speciation and reactive transport modeling*, at the 2013 International Conference on the Biogeochemistry of Trace Elements in Athens, Georgia, USA, in June 2013. It introduces the use of surface complexation models to describe complex natural systems, with an emphasis on soils. In describing ion adsorption on heterogeneous natural materials, the challenge is twofold: 1) making the necessary approximations to describe heterogeneous systems, and 2) retaining as much fundamental chemical information as possible.

The present study addresses the application of 2 surface complexation models, the constant capacitance model and the triple-layer model, to describe anion adsorption on heterogeneous natural systems, specifically soils. It describes methods for obtaining values of the adjustable parameters: surface area, surface site density, capacitances, and surface complexation constants. Both microscopic spectroscopic and macroscopic experimental methods of establishing ion adsorption mechanisms are discussed. Applications of surface complexation models to natural systems focus on soils. Two case studies of the generalized composite approach are presented: 1) prediction of boron adsorption on a field scale, and 2) prediction of molybdenum adsorption by soils using both inner-sphere and outer-sphere mechanisms.

Adsorption is the accumulation of a chemical species at the interface between the solid phase and the liquid phase whereby a 2-dimensional surface structure is retained. Adsorption reactions play a critical role in controlling solution ion concentrations. Adsorbing surfaces such as oxide minerals, clay minerals, organic matter, and carbonates act as sources and sinks for adsorbing ions and therefore have the potential to attenuate ecotoxic ion concentrations in soil solutions, groundwaters, and water bodies. Detailed quantification of ion adsorption reactions is necessary to understand trace element fate and transport in soils and aquifers and their bioavailability to plants, animals, and humans.

Surface complexation models provide a molecular description of adsorption processes. Surface complexation models were originally developed to describe surface charging and ion adsorption at the oxide mineral–aqueous solution interface. Three such models are the constant capacitance model developed in the research groups of Schindler and Stumm in Switzerland [1,2], the triple-layer model developed in the research group of Leckie at Stanford University [3–5], and the charge distribution multisite complexation (CD-MUSIC) model developed at Wageningen University in the Netherlands [6,7]. These models use an equilibrium approach to define surface species, chemical reactions, mass balances, and charge balances and to calculate thermodynamic properties such as solid-phase activity coefficients and equilibrium constants mathematically. The major advancement of surface complexation models is consideration of charges on both the absorbing ion and the solid surface. All surface complexation models contain at least 1 electrostatic potential term to account for the effect of surface charge on surface complexation. These terms can be considered as solid-phase activity coefficients that correct for the charges on surface complexes.

These 3 surface complexation models have been applied to describe ion adsorption by soil surfaces. Adsorption reactions on soil minerals can attenuate elevated soil solution ion

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concentration. The dominant ion-adsorbing surfaces in soils are oxides, clay minerals, calcite, and organic matter. Modeling ion adsorption on heterogeneous natural materials such as soils involves 2 challenges: making the necessary approximations to describe heterogeneous systems and retaining as much fundamental chemical information as possible. Constant capacitance model applications to soil systems have been restricted to the adsorption of anions: phosphate [8], borate [9–16], selenite [17–20], arsenate [20–22], sulfate [23], and molybdate [24–27]. Triple-layer model applications to soils systems have been carried out for both cations (calcium and magnesium [28,29]) and anions (sulfate [28,30], chromate [31], molybdate [25,32], and selenite [33]). Applications of the CD-MUSIC model to soil systems have been carried out for the anions: phosphate, silicate, and arsenate [34,35]. To describe the adsorption of the cations: Cu, Cd, Zn, Ni, and Pb, a complex system of models has been used [36,37] including the CD-MUSIC model for crystalline iron hydroxides, the diffuse layer model [38] for amorphous iron hydroxides, the Donnan model [39] for clay, and the NICA-Donnan model [40] for soil organic matter. The present review treats the adsorption of the anions borate, molybdate, arsenate, and selenite by soil materials using both the constant capacitance model and the triple-layer model.

The constant capacitance model includes 4 assumptions [1,2]. First, all surface complexes are inner-sphere. Second, the constant ionic medium reference state determines the aqueous species activity and therefore no surface complexes are formed with the background electrolyte ions. Third, a single plane of charge represents the particle surface. Fourth, a linear relationship exists between the surface charge, σ_o, and the surface potential, ψ_o.

The triple-layer model includes 5 assumptions [3–5]. First, hydroxyl ions and protons form inner-sphere surface complexes, Second, other adsorbing ions form either inner-sphere or outer-sphere surface complexes. Third, background electrolyte ions form outer-sphere surface complexes. Fourth, the particle surface is represented by 3 planes of charge. Fifth, surface charges and surface potentials are related by 3 relationships: 1) a linear relationship between surface charge, σ_o, and surface potential, ψ_o; 2) a second linear relationship between surface charge, σ_β, and surface potential, ψ_β; and 3) the diffuse double-layer expression relating surface charge, σ_d, and surface potential, ψ_d.

OBTAINING VALUES OF ADJUSTABLE PARAMETERS

Surface complexation models contain a significant number of input parameters, including surface area, surface site density, capacitances, and surface complexation constants. To improve the chemical significance of surface complexation modeling, it is essential to determine as many of these model parameters experimentally as possible, thereby minimizing the number of adjustable parameters. Chemical significance suffers when input parameters whose values can be measured experimentally are instead optimized mathematically.

Surface area and surface site density

The surface site density, N_s (sites nm^{-2}), is related to the total number of reactive surface hydroxyl groups on oxide minerals and aluminol groups on clay mineral edges, SOH_T (mol L^{-1}), and the surface area, SA (m^2 g^{-1}), of the soil material:

$$N_s = SOH_T \frac{N_A}{SA10^{18}C_p} \tag{1}$$

where N_A is Avogadro's number and C_p is the particle concentration (g L^{-1}). Surface areas for soil samples are conventionally measured using ethylene glycol monoethyl ether adsorption [41]. This method measures both the edge and the interlayer surface area. A wide variety of methods exist for obtaining values of surface site density, including crystallographic calculation, tritium exchange, potentiometric titration, fluoride adsorption, and maximum adsorption [42]. For the iron oxide mineral goethite, there is an order of magnitude difference between the lowest surface site density value calculated using crystal dimensions and the highest value measured by tritium exchange [42]. Quality of fit to adsorption data and optimized values of surface complexation constants are highly sensitive to the choice of surface site density value [42]. To allow development of self-consistent databases, researchers should agree on a preferred methodology for determining surface site density. For purposes of standardizing surface complexation modeling, fixed site density values for all minerals have been recommended [43,44]. For the case studies in the present review, the surface site density was set equal to 2.31 sites nm^{-2} as recommended by Davis and Kent [43] for natural materials.

Capacitances

Although it has often been written that surface complexation model capacitances cannot be determined experimentally, and for this reason, their values must be chosen to optimize model fit, this is not strictly correct. Model capacitance values can be obtained from linear extrapolations of potentiometric or electrokinetic data. Capacitance values (C for the constant capacitance model and C_1 for the triple-layer model) can be attained graphically from slopes of plots of conditional protonation and dissociation constants versus surface charge [2,3]. Electrokinetic extrapolation is the only experimental method for determining both capacitance values C_1 and C_2 in the triple-layer model [45]. This method requires the somewhat tenuous assumption that the zeta potential is equal to the diffuse layer potential. Extrapolated values of capacitances obtained using data above the zero point of charge are not equal to those obtained using data below the zero point charge. Because of this variability, uncertainty in experimental capacitance values, and the requirement for a single value in computer models, capacitance values have almost universally been treated as adjustable parameters, with C_1 optimized to fit the experimental data and C_2 fixed at a value of 0.2 F m^{-2} [43].

Surface complexation constants

Values for the protonation and dissociation constants can be obtained from the same extrapolations used to obtain capacitance values. In the constant capacitance model, the protonation and dissociation constants are the intercepts obtained by extrapolations of titration curves to zero net surface charge. In the triple-layer model, the protonation and dissociation constants and the background electrolyte surface complexation constants are obtained from extrapolations to zero surface charge and zero and infinite electrolyte concentration. Values for the protonation and dissociation constants and the background electrolyte surface complexation constants also can be determined by computer optimization of potentiometric titration data.

Ion surface complexation constants in the constant capacitance model also can be evaluated graphically using the simplifying assumption that the surface potential (ψ) is 0. This assumption is not required when computer programs such as FITEQL [46] are used to optimize ion surface complexation constant values using adsorption isotherm (amount of ion adsorbed as a function of solution ion concentration) or adsorption edge (amount of ion adsorbed as a function of solution pH per fixed total ion concentration) experimental data. Computer optimizations have the advantage that they produce bias-free parameters, standard deviations, and quality-of-fit criteria [46].

Interdependence of model parameters and databases

Model parameter values such as surface site density, capacitances, and surface complexation constants are interdependent. Optimized values obtained for surface complexation constants are dependent on input parameter values chosen for surface site density and capacitances. Researchers must be aware of all input parameter values when extracting surface complexation values from the published literature.

The various surface complexation models contain different basic assumptions for the solid–solution interface. Because of this, surface chemical species that have been defined and surface complexation constants that have been obtained with 1 model must never be used in another surface complexation model. Each model requires its own separate parameter database. Extensive databases of ion adsorption constants are available for the diffuse layer model for amorphous iron oxide [38], goethite [47], and gibbsite [48]. The important advantage of these databases is that they are self-consistent: all ion surface complexation constants were optimized using the identical values of surface site density, protonation-dissociation constants, and aqueous thermodynamic data. Regrettably, no comparably extensive databases of surface complexation constants are available for the constant capacitance model or the triple-layer model.

ESTABLISHING ION ADSORPTION MECHANISMS

Surface complexation models specify adsorption mechanisms and define specific surface complexes for all adsorbing ions. Adsorption mechanisms can be either inner-sphere (forming surface complexes that contain no water between the adsorbing ion and the surface functional group) or outer-sphere (containing at least 1 water molecule between the adsorbing ion and the surface functional group). In the constant capacitance model, all adsorbing ions are considered to form inner-sphere surface complexes. Anion adsorption occurs via a ligand exchange mechanism. The triple-layer model allows the definition of either inner-sphere or outer-sphere surface complexes. Although triple-layer model applications have historically specified either an inner-sphere or an outer-sphere adsorption mechanism, the simultaneous consideration of both types of adsorption mechanisms is not precluded. Hydrogen bonding is not considered as an adsorption mechanism in surface complexation modeling. To maximize the chemical significance of the surface complexation model applications, ion adsorption mechanisms should be established from independent experiments.

Spectroscopic techniques

Spectroscopic techniques provide direct microscopic scale experimental evidence of ion adsorption mechanisms. Spectroscopic techniques can also elucidate denticity: the number of bonds the adsorbing ion forms with the mineral surface. The most common methods include vibrational spectroscopies, including Raman and Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, X-ray absorption spectroscopies including both X-ray absorption near edge structure, and extended X-ray absorption fine structure, X-ray reflectivity, and X-ray standing wave spectroscopy. A very extensive compilation of ion adsorption mechanisms obtained using these various spectroscopic techniques is provided in Table 1 of Goldberg et al. [49].

Examples in which spectroscopic results were used to define surface species in surface complexation models are the investigations of Villalobos and Leckie [50] and Dyer et al. [51]. Villalobos and Leckie [50] applied the triple-layer model to describe carbonate adsorption on goethite using monodentate inner-sphere surface complexes observed with attenuated total reflectance (ATR)-FTIR spectroscopy. Dyer et al. [51] used the X-ray absorption spectroscopic results of Trivedi et al. [52] to describe lead adsorption on ferrihydrite with the triple-layer model. The model application was successful using a combination of monodentate and bidentate inner-sphere Pb surface complexes consistent with spectroscopic observations.

Macroscopic measurements

Indirect macroscopic scale experimental measurements that can be used to deduce ion adsorption mechanisms include point of zero charge shifts, ionic strength dependence effects, and calorimetry. Molecular modeling such as quantum mechanics calculations and molecular simulations also can be used to provide mechanistic structural information, including ion solvation and the denticity of surface complexes [49].

Point of zero charge shifts

The point of zero charge is defined as the pH value at which the total charge of a mineral surface is equal to 0. The point of zero charge of a solid phase can be obtained directly from electrokinetic measurements and colloidal stability experiments. This parameter also can be measured indirectly using potentiometric titrations. Electrophoretic mobility measures movement of charged particles in an applied electric field, with electrophoretic mobility $= 0$ indicating zero total surface charge. Shifts in point of zero charge and reversals of electrophoretic mobility with increasing ion concentration can be considered indirect evidence of an inner-sphere adsorption mechanism [53]. Such is the case for arsenate adsorption on amorphous iron oxide, which exhibits point of zero charge shifts and electrophoretic mobility reversals upon adsorption of increasing amounts of arsenate ion (Figure 1A). Adsorption of arsenite on amorphous aluminum oxide produces only a very small shift in the point of zero charge (Figure 2A). Although lack of shift in the point of zero charge has often been considered indicative of an outer-sphere adsorption mechanism, it also can result from the formation of inner-sphere surface complexes that do not produce a change in net surface charge.

Ionic strength effects

Ionic strength dependence of adsorption has been used to indirectly distinguish between inner- and outer-sphere adsorption mechanisms for both cations [54] and anions [55]. Ions showing little ionic strength dependence of adsorption were considered to form strong inner-sphere surface complexes; ions showing marked ionic strength dependence were considered to be weakly adsorbed as outer-sphere surface complexes. McBride [56] refined the interpretation of ionic strength–dependent adsorption. Ions that form weak outer-sphere surface complexes must show decreasing adsorption with increasing ionic strength because of competition from the background electrolyte. Ions forming strong inner-sphere surface complexes show either little ionic strength dependence or increasing adsorption with increasing ionic strength. Increased ion adsorption with increasing ionic strength can be explained as the mass action effect whereby the higher activity of background

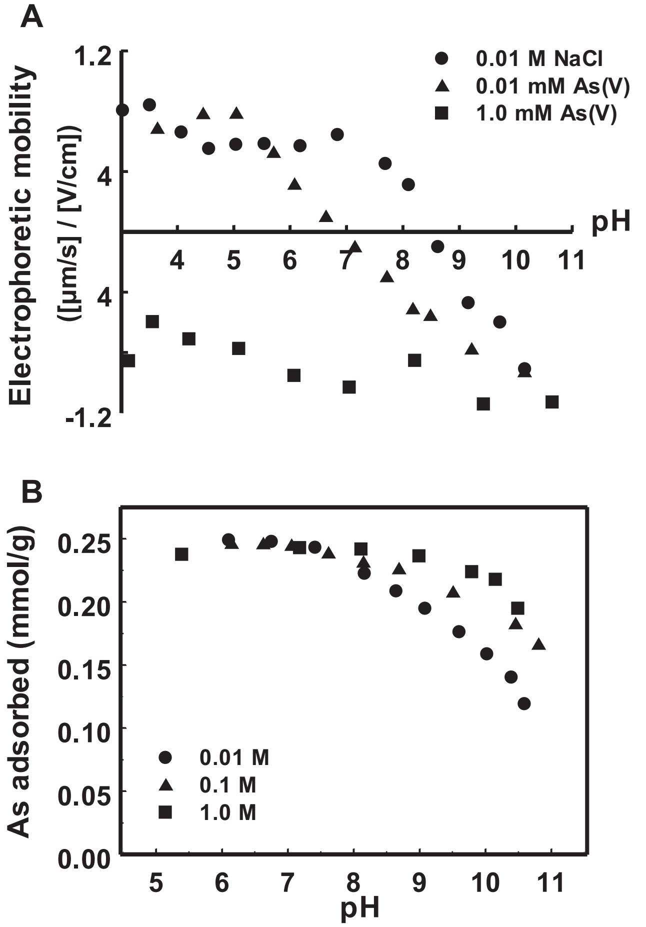

Figure 1. Electrophoretic mobility and As(V) adsorption on amorphous iron oxide as a function of solution pH and ionic strength: (**A**) electrophoretic mobility in 0.01 M NaCl. Circles represent the zero As(V) treatment. Data from Suarez et al. [73]. (**B**) As(V) adsorption in NaCl background electrolyte. Data from Goldberg and Johnston [57].

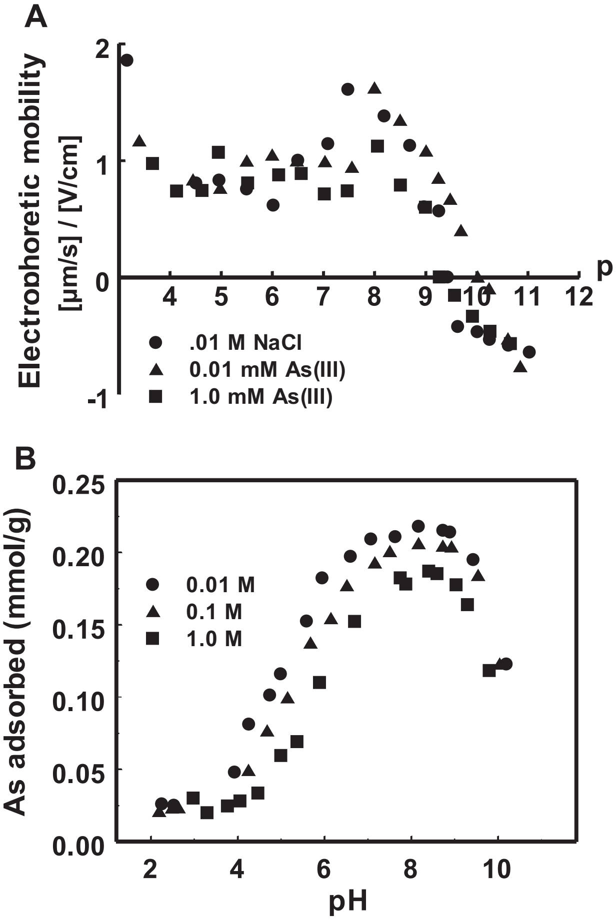

Figure 2. Electrophoretic mobility and As(III) adsorption on amorphous aluminum oxide as a function of solution pH and ionic strength: (**A**) electrophoretic mobility in 0.01 M NaCl. Circles represent the zero As(III) treatment. (**B**) As(III) adsorption in NaCl background electrolyte. Data from Goldberg and Johnston [57].

electrolyte ions available in solution compensates for the surface charge generated by specific ion adsorption [56].

Adsorption of arsenite on amorphous aluminum oxide exhibits decreasing adsorption with increasing solution ionic strength (Figure 2B). This is indirect evidence for outer-sphere surface complex formation and is consistent with the lack of shift in the point of zero charge observed in the electrophoretic mobility data (Figure 2A). Arsenate adsorption on amorphous iron oxide, conversely, shows no ionic strength dependence at pH values less than 7 and pronounced increasing adsorption with increasing solution ionic strength at pH values greater than 7 (Figure 1B). Both of these characteristics are indirect evidence for inner-sphere surface complex formation and are consistent with the pronounced shifts in the point of zero charge and dramatic charge reversals observed in the electrophoretic mobility data (Figure 1A). Arsenic surface complexes defined in the constant capacitance and triple-layer model applications to these adsorption data were constrained to be in agreement with these macroscopic experimental results [57].

APPLICATION OF SURFACE COMPLEXATION MODELS TO NATURAL MATERIALS

In the application of surface complexation models, the assumption is made that adsorption takes place on 1, 2, or at most 3 sets of homogeneous, variably charged, reactive surface functional groups. This assumption has been used in model application to oxides, clay minerals, and soils. However, experimental evidence indicates that even mineral surfaces, such as iron oxides, contain 3 to 5 types of reactive surface functional groups [58–60]. Because soils are complex multisite mixtures of multisite minerals, this assumption is clearly a gross simplification. In the application of surface complexation models to clay minerals and soils, the assumption is usually made that adsorbing ions interact with hydroxyl groups on oxide minerals and aluminol groups at the edges of clay particles. Most often, the effect of permanent negative charges located on the basal planes of clay minerals is ignored. This simplification may be especially inappropriate for anions whose extent of adsorption on clay edge sites may be affected by the permanent negative charges on the basal planes [61]. Adsorption of metal ions on the clay mineral kaolinite has been modeled using both permanent and variably charged sites [62,63].

Two surface complexation modeling approaches have been used to describe ion adsorption on heterogeneous natural materials, including soils: the component additivity approach [64] and the generalized composite approach. The component additivity approach attempts to predict adsorption on a complex natural material by treating it as an assemblage of minerals. The component additivity surface complexation model application consists of using an assemblage of surface complexation models parameterized for individual pure reference minerals combined with estimates of the reactive surface area of each mineral in the soil material. Therefore, in the component additivity approach, surface complexation models are not fit to the adsorption data of the natural material but used in a predictive mode. The Surface Chemistry Assemblage Model for Particles approach includes surface complexation modeling with 3 sets of sites, a coulombic fitting parameter, and an adjustable parameter to describe heterogeneity [65]. A required assumption for the component additivity approach is that the constituent minerals in the assemblage are uncoated and do not interact with each other. This assumption is almost always violated in soils because of the presence of oxide and organic matter coatings. A component additivity approach was able to describe arsenate adsorption in a spodosol containing allophane and ferrihydrite by using surface complexation constants from gibbsite to represent allophane [66].

The generalized composite approach assumes that the adsorption behavior of a natural material can be described using surface complexation reactions written for generic surface functional groups that represent average properties of the mineral assemblage as a whole rather than specific mineral phases. This means that surface complexation constants resulting from generalized composite modeling are conditional constants that are valid only for the range of chemical conditions considered in the experiment. Therefore, generalized composite predictions are valid only for interpolation within the ranges of experimental chemical conditions and not for extrapolation outside these ranges [67].

GENERALIZED COMPOSITE APPROACH: CASE STUDIES

All applications of the constant capacitance model to describe ion adsorption on soil materials (references listed in the *Introduction*) have used the generalized composite approach. With the exception of the work of Zachara et al. [31], who used the component additivity approach to describe chromate adsorption, applications of the triple-layer model to describe ion adsorption by soils have used the generalized composite approach.

The predictive capability to describe ion adsorption by soils has been tested for the constant capacitance model [13–15,19,22,26] and the triple-layer model [32,33]. In this predictive approach, a general regression model was developed to predict surface complexation constant values for individual soils from their measured chemical properties: cation exchange capacity (CEC), SA, organic carbon content (OC), inorganic carbon content (IOC), aluminum oxide content (Al), and iron oxide content (Fe). The initial regression model was defined as

$$\begin{aligned}\log K_j^i(\text{int}) &= \beta_0 + \beta_1(\ln CEC_i) + \beta_2(\ln SA_i) + \beta_3(\ln OC_i) \\ &\quad + \beta_4(\ln IOC_i) + \beta_5(\ln Al_i) + \beta_6(\ln Fe_i) + \varepsilon_i\end{aligned} \tag{2}$$

where log K^{i}_{j}(int) represents the *i*th surface complexation constant of the *j*th adsorbing element, β_i represents the empirically derived regression coefficients, and ε_i represents the residual error component. Normal errors are assumed in the regression modeling. The optimization criterion used was that the final selected prediction equations should exhibit the smallest possible jack-knifed prediction errors [68]. For details on the development of the regression model equations, see, for example, Goldberg et al. [32]. This generalized composite approach provides a completely independent model evaluation and is well able to predict boron [13–15], molybdenum [26,32], arsenate [22], and selenite [19] adsorption by numerous soils of diverse soil orders having a wide range of chemical characteristics. Because the approach is predictive, it contains zero adjustable parameters.

Prediction of boron adsorption on a field scale

In field situations, soil texture often varies dramatically in both the vertical and the horizontal direction. Nevertheless, researchers often use chemical and physical characterizations for only 1 location to represent an entire field when conducting chemical speciation-transport modeling studies. The constant capacitance model was fit to B adsorption as a function of solution pH by 5 depths of 3 sites in a quarter section of the Broadview Water District in the San Joaquin Valley of California, USA [15]. The constant capacitance model fit provided a quantitative description of the B adsorption data at all 3 sites (see Figures 2–4 of Goldberg et al. [15]). The surface complexation equilibria considered in this application are

$$SOH + H^+ \leftrightarrow SOH_2^+ \tag{3}$$

$$SOH \leftrightarrow SO^- + H^+ \tag{4}$$

$$SOH + H_3BO_3 \leftrightarrow SH_3BO_4^- + H^+ \tag{5}$$

The generalized composite regression model was evaluated for its ability to predict B adsorption for each individual soil depth by using surface complexation constants calculated from easily measured chemical parameters and the prediction equations of Goldberg et al. [13]

$$\begin{aligned}\log K_+ = 7.85 - 0.102\ln(OC) - 0.198\ln(IOC) \\ - 0.622\ln(Al)\end{aligned} \tag{6}$$

$$\begin{aligned}\log K_- = -11.97 + 0.302\ln(OC) + 0.0584\ln(IOC) \\ + 0.302\ln(Al)\end{aligned} \tag{7}$$

$$\begin{aligned}\log K_{B-} = -9.14 - 0.375\ln(SA) + 0.167\ln(OC) \\ + 0.111\ln(IOC) + 0.466\ln(Al)\end{aligned} \tag{8}$$

Units are m^2 kg^{-1} for SA and g kg^{-1} for OC, IOC, and Al.

The generalized composite model was also evaluated for its ability to predict adsorption at all 5 depths of all 3 sites using surface complexation constants predicted for 1 of the surface depths. In this evaluation, the only depth-specific model parameter was surface area, which was calculated from depth-specific clay content using the linear regression equation

$$SA = 5.65 + 349(clay\,mass\,fraction) \quad R^2 = 0.91^{**} \tag{9}$$

Generalized composite model predictions for 1 of the sites are presented in Figure 3. Model predictions for each individual soil depth (represented by solid lines) closely tracked the experimental adsorption data (represented by circles) except at low pH values, where there was greater uncertainty in the amounts of adsorbed B. The best model predictions occurred at the lower soil depths, where the clay content was least. Model predictions for B adsorption by all of the subsurface depths predicted using the surface complexation constants calculated from the chemical properties, and surface area estimates (Equations 6–9) for any of the surface depths were also of high quality (Figure 3B). Therefore, the results suggest that for a particular soil series, B adsorption for various locations and depths in a field can be

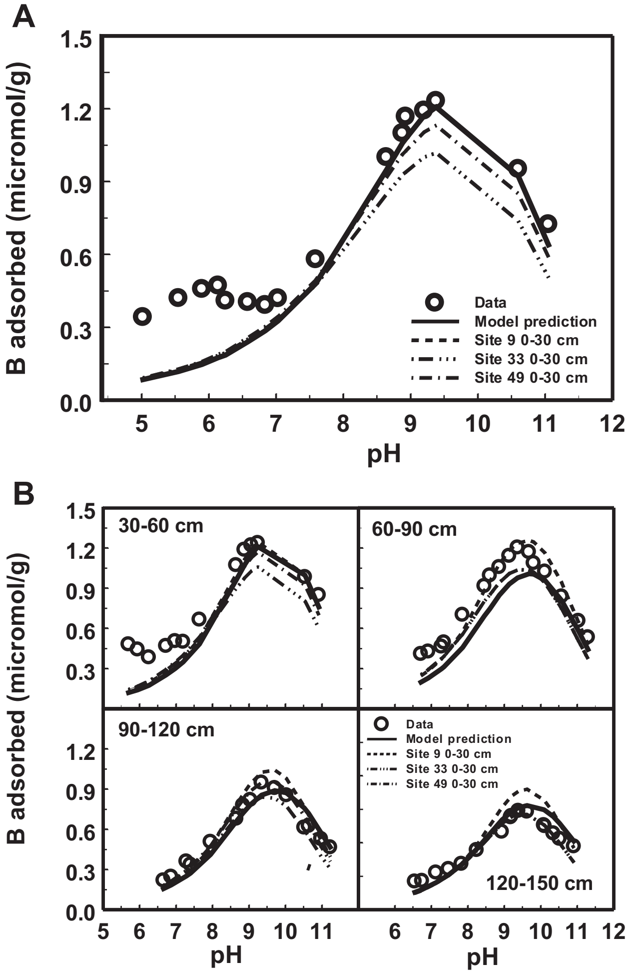

Figure 3. Constant capacitance modeling predictions of B adsorption on site 9 of the Lillis soil series, San Joaquin Valley, California, USA, at various depths: (**A**) surface depth, 0–30 cm; and (**B**) lower depths. Circles represent the experimental data. Solid lines represent model prediction for the specific site and depth. Dashed lines represent model predictions using various surface depths and sites. Data from Goldberg et al. [15].

predicted using only measurements of clay content, SA, OC, IOC, and Al from a single different surface site within the field. This leads to a significant reduction in the requirement for tedious, costly, and time-consuming B adsorption experiments. The generalized composite prediction model can be incorporated into chemical speciation-transport models, allowing simulation of soil solution B concentrations on a vertical and horizontal scale to address a variety of agricultural and environmental problems.

Prediction of molybdenum adsorption using both inner-sphere and outer-sphere mechanisms

The constant capacitance model was fit to Mo adsorption data as a function of solution pH on 36 soil samples primarily from California, USA [26]. A single monodentate inner-sphere surface Mo complexation constant was optimized as defined by the surface complexation reaction,

$$SOH_{(s)} + H_2MoO_{4(aq)} \leftrightarrow SHMoO_{4(s)} + H_2O \qquad (10)$$

The ability of the model to describe the experimental data was good, although underprediction was observed above pH 6 (see Figure 4A for a representative soil). The constant capacitance model was able to describe the pH-dependent experimental adsorption data optimizing just 1 adjustable parameter. Although surface site density and capacitance also can be adjusted, they were fixed at a constant value during the optimization. The single adjustable parameter compares very favorably with the Langmuir and Freundlich adsorption isotherm equations, which contain 1 additional adjustable parameter and yet cannot define specific surface species or consider changes in solution pH.

A generalized composite constant capacitance regression model was developed to predict the Mo surface complexation constant from the experimentally measured chemical properties: cation exchange capacity, OC, IOC, and Fe for the 36 soil samples [26]. The prediction equation for the single inner-sphere surface complexation constant is

$$\log K^1_{Mo} = 7.81 - 0.363 \ln(CEC) + 0.219 \ln(OC) + 0.385 \ln(IOC) + 0.716 \ln(Fe) \qquad (11)$$

This approach provided good prediction of Mo adsorption independent of any experimental measurement of Mo adsorption on soils (Figure 4C).

Vibrational spectroscopic observations of both ATR-FTIR and Raman spectroscopies had provided evidence for predominately inner-sphere Mo surface complex formation on amorphous Al oxide at low pH and predominantly outer-sphere surface complexation at high pH [32]. Simultaneous formation of both inner- and outer-sphere surface complexes on oxide minerals has previously been observed for other anion species, both weakly held selenate [69] and arsenite [70] as well as very strongly sorbing selenite [71] and arsenate [72]. The triple-layer model was fit to the Mo adsorption data on the 36 soil samples by simultaneously optimizing 1 inner-sphere and 1 outer-sphere Mo surface complex. In addition to the inner-sphere surface complex previously defined in Equation (10), an outer-sphere complex was considered as defined by the surface complexation reaction

$$SOH_{(s)} + H_2MoO_{4(aq)} \leftrightarrow SOH_2^+ - MoO^{2-}_{4(s)} + H^+_{(aq)} \qquad (12)$$

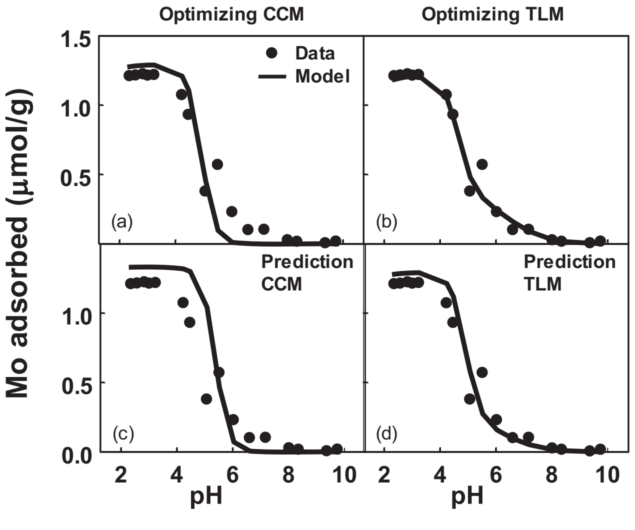

Figure 4. Surface complexation modeling of Mo adsorption on Fallbrook subsoil, California, USA: (**A**) constant capacitance model fit; (**B**) triple-layer model inner-sphere and outer-sphere fit; (**C**) constant capacitance model prediction; and (**D**) triple-layer model inner-sphere and outer-sphere prediction. Circles represent experimental data. Model results are represented by lines. Experimental data from Goldberg et al. [26].

The triple-layer model fit (Figure 4B) was much improved over the constant capacitance model fit (Figure 4A), especially at solution pH values greater than 6. Some of the improvement in fit must be attributed to the fact that 2 parameters were optimized, rather than 1. This chemical surface complexation model representation of the soil–solution interface is in agreement with vibrational spectroscopic observations on amorphous Al oxide.

A generalized composite triple-layer regression model was developed to predict the inner-sphere and outer-sphere Mo surface complexation constants from the experimentally measured chemical soil properties [32]. The prediction equations are

$$\log K_{Mo}^{1is} = 4.72 + 0.183\ln(OC) + 0.318\ln(Fe) \qquad (13)$$

$$\log K_{Mo}^{2os} = 1.67 + 0.412\ln(CEC) + 0.131\ln(OC) + 178\ln(Fe) \qquad (14)$$

This approach provided excellent prediction of experimental Mo adsorption independent of any experimental measurement on soil (Figure 4D). The vast improvement in the triple-layer model prediction at pH values greater than 7 (Figure 4D) over the constant capacitance model prediction (Figure 4C) is especially important for describing Mo adsorption behavior in arid-zone soils where Mo can accumulate in forage plant tissues to levels detrimental to the health of grazing ruminant animals. The predicted Mo soil surface speciation is presented in Figure 5. The inner-sphere surface complex predominates up to a pH value of 5.5 and the outer-sphere surface complex predominates at high pH values. This predicted speciation is consistent with vibrational spectroscopic results for Mo adsorption on amorphous Al oxide [32], as well as adsorption of other anion species on oxides: selenate [69], arsenite [70], selenite [71], and arsenate [72].

SUMMARY AND FUTURE RESEARCH NEEDS

The constant capacitance model and the triple-layer model are 2 surface complexation models that provide a molecular description of the solid–solution interface by defining specific surface complexes and using an equilibrium approach and have been used to describe ion adsorption by soil materials. Model parameter values for surface site density, capacitances, and surface complexation constants can be obtained experimentally or optimized to fit data. Ion adsorption mechanisms can be established directly, using various spectroscopic experimental methods. Point of zero charge shifts and ionic strength dependence experiments can provide indirect macroscopic information on ion adsorption mechanisms. Molecular modeling simulations and quantum mechanics calculations also can provide mechanistic structural information. Surface complexation modeling of heterogeneous natural systems such as soils has primarily used the generalized composite, rather than the component additivity approach. Two case studies using the generalized composite approach were presented: B adsorption on a field scale was predicted using the constant capacitance model and soil chemical properties and clay content of any surface depth, and prediction of Mo adsorption as a function of solution pH on a large set of soils was successful using both inner-sphere and outer-sphere surface complexes in the triple-layer model.

Future research needs in surface complexation modeling include compilation of additional extensive databases of surface complexation constants for natural materials, especially amorphous Al oxide, clay minerals, and soils; development of generalized composite prediction models for all important constituent ions in soil systems; evaluation and inclusion of competitive ion effects on adsorption processes; and consideration of soil organic matter both as an adsorbate on soil mineral surfaces and as an adsorbent of dissolved ions from soil solution. Subsequently, the chemical and physical information obtained from these research fronts will need to be incorporated into chemical-speciation transport models to allow predictions of ion movement in natural systems, including agricultural fields, drainage basins, watersheds, and groundwaters.

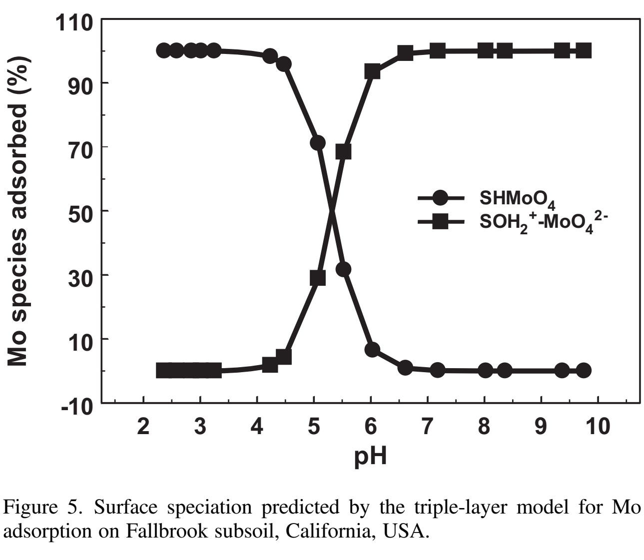

Figure 5. Surface speciation predicted by the triple-layer model for Mo adsorption on Fallbrook subsoil, California, USA.

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