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Predicting Boron Adsorption Isotherms by Midwestern Soils using the Constant Capacitance Model

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ABSTRACT

Prediction of B adsorption and transport has required detailed studies of B adsorption and subsequent determination of model parameters. In this study we tested a general regression model previously developed for predicting soil B surface complexation constants from easily measured soil chemical characteristics. The constant capacitance model, a chemical surface complexation model, was applied to B adsorption isotherms on 22 soils from the A and B horizons of 16 soil series from Oklahoma and Iowa. The measured chemical properties were surface area, organic C (OC) content, inorganic C (IOC) content, and Al oxide content. The prediction equations of Goldberg et al. (2000) were used to obtain constant capacitance model values for B surface complexation constants thereby providing a completely independent evaluation of the ability of the constant capacitance model to describe B adsorption. The model was well able to predict B adsorption isotherms on the majority of the soils. The regression model was used to obtain the parameters for the constant capacitance model. Then the constant capacitance model was used to predict the soil specific B adsorption. This is in contrast to regression models that fit adsorption of a series of soils. The distinction is that using the combined regression equations and the constant capacitance model only soil properties and not adsorption are needed to predict soil specific B adsorption data. The prediction equations developed from a set of soils primarily from California, were able to predict B adsorption on a set of soils from different parts of the country. This result suggests wide applicability of the model prediction equations developed previously, for describing B adsorption both as a function of solution B concentration and solution pH.

Boron is both an essential micronutrient element required for plant growth and a toxicant at elevated concentration. The range between B deficiency and toxicity is narrow, typically 0.028 to 0.093 mmol L^{-1} for sensitive crops and 0.37 to 1.39 mmol L^{-1} for tolerant crops (Keren and Bingham, 1985). Yield losses can occur both under conditions of B deficiency and B toxicity. In regions of plentiful rainfall, B deficiency occurs primarily on coarse-textured soils. Deficiency symptoms can also be triggered by liming of acid soils because of increased B adsorption at higher soil pH (Reisenauer et al., 1973). In arid regions, B toxicity occurs because of high levels of B in the soil solution and from additions of B via the irrigation water. Excessive soil solution B concentrations in saline soils are often caused by lack of drainage and are associated with elevated salinity.

The narrow range between deficiency and toxicity necessitates accurate quantification of soil solution B concentrations. Soil solution B concentrations are controlled by B adsorption–desorption reactions on soil minerals. Soil mineral and organic surfaces constitute the sinks that adsorb B and the sources that release B to soil solution for plant uptake. Because plants respond only to solution B concentrations (Keren et al., 1985), soil minerals can act to attenuate potentially phytotoxic soil solution B concentrations. Boron occurs as boric acid over most of the soil pH range. Boric acid acts as a Lewis acid by accepting a hydroxyl ion to form the tetrahedral borate anion, $pK_a = 9.2$.

Various modeling approaches have been used to describe B adsorption on soil materials. These include applications of chemical models called surface complexation models (Goldberg and Glaubig, 1986; Goldberg, 1999; Goldberg et al., 2000). The advantages of surface complexation models over empirical adsorption models, such as distribution coefficients, K_d, and adsorption isotherm equations, such as Langmuir and Freundlich approaches, are that they define specific surface species, chemical reactions, mass balances, and charge balances and they contain molecular features that can be given thermodynamic significance (Sposito, 1983). In a prior study (Goldberg et al., 2000), we developed a general regression model to obtain soil B surface complexation constants for use in the constant capacitance model to predict B adsorption. The constant capacitance model parameters are obtained from easily measured soil chemical properties: surface area, OC content, IOC content, and free Al oxide content. These are also soil properties that correlate with soil B adsorption capacity. The prediction equations were well able to predict B adsorption behavior on 15 additional soils primarily from California, providing a completely independent evaluation of the ability of the constant capacitance model to describe B adsorption. The objective of this approach is to avoid the necessity of performing time-consuming detailed adsorption studies for each specific soil. The B adsorption data used consisted of adsorption envelopes defined as: amount of B adsorbed as a function of solution pH per fixed total B concentration. The prediction equations have not yet been tested for their ability to predict B adsorption isotherms defined as: amount of B adsorbed as a function of equilibrium solution B concentration. In contrast to K_d, Langmuir, and Freundlich modeling, our constant capacitance model

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Abbreviations: AMSE, average mean squared error; EGME, ethylene glycol monoethyl ether; ICP, inductively coupled plasma; IOC, inorganic C; OC, organic C.

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approach can predict differences in B adsorption based on changes in soil chemical properties.

The objectives of the present study are: (i) to apply the constant capacitance model to describe B adsorption isotherms on a set of soils not originating from California; (ii) to test the ability of the previously developed regression model equations of Goldberg et al. (2000) to predict constant capacitance model parameters and subsequently B adsorption isotherms on these new soils.

MATERIALS AND METHODS

Boron adsorption was determined on 22 soil samples from the A and B horizons of 13 soil series from Oklahoma and three soil series from Iowa belonging to three different soil orders: 5 alfisols, 14 mollisols, and 3 vertisols. Soil classifications and physical and chemical characteristics are provided in Table 1. Cation exchange capacities were determined with the method described by Rhoades (1982). Surface areas were measured using ethylene glycol monoethyl ether (EGME) adsorption as described by Cihacek and Bremner (1979). Free Fe and Al oxides were extracted using the method of Coffin (1963). In this method the soil samples were reacted in a water bath at 50°C with a 0.15 *M* sodium citrate/0.05 *M* citric acid buffer and 0.5 g of sodium hydrosulphite for 30 min. Aluminum and Fe concentrations in the extracts were determined by inductively coupled plasma (ICP) emission spectrometry. Organic C and IOC contents were determined using a UIC Full Carbon System 150 with a C coulometer (UIC, Inc., Joliet, IL). Organic C was determined directly by furnace combustion at 375°C; IOC was determined using an acidification module and heating. The soil samples represented a broad range of characteristics: clay, 3.8 to 58.8%; pH, 4.1 to 8.4; cation exchange capacity, 3.7 to 384 mmol kg^{-1}; surface area, 12.3 to 240 m^2 g^{-1}; IOC, 0.0007 to 63 g kg^{-1}; OC, 2.1 to 34 g kg^{-1}; free Fe oxide, 0.9 to 30 g kg^{-1}; free Al oxide, 0.13 to 4.1 g kg^{-1}.

Boron adsorption experiments were performed in batch systems to determine adsorption isotherms (amount of B adsorbed as a function of equilibrium solution B concentration). Five-gram samples of soil were mixed with 25 mL of equilibrating solutions for 20 h on a reciprocating shaker (160 strokes per min). Reaction temperature was 24.4 ± 0.1°C. The equilibrating solutions contained 0, 0.0925, 0.185, 0.463, 0.925, 1.39, 2.31, 4.63, 9.25, 13.9, 18.5, and 23.1 mmol B L^{-1} from H_3BO_3 and a background electrolyte of 0.1 *M* NaCl. After completion of the mixing time, the samples were centrifuged for 20 min at a relative centrifugal force of 7800 × *g* at 25°C. The liquid decanted was analyzed for pH, filtered through 0.45-μm membrane filters, and analyzed for B concentration using ICP emission spectrometry.

A detailed discussion of the theory and assumptions of the constant capacitance model can be found in Goldberg (1992). The present application of the model to B adsorption uses the same surface complexation reactions and equilibrium constant expressions as in the study of Goldberg et al. (2000). The protonation–dissociation and B surface complexation reactions are:

$$SOH_{(S)} + H^+_{(aq)} \rightleftharpoons SOH^+_{2(s)} \quad [1]$$

$$SOH_{(s)} \rightleftharpoons SO^-_{(s)} + H^+_{(aq)} \quad [2]$$

$$SOH_{(s)} + H_3BO_{3(aq)} \rightleftharpoons SH_3BO^-_{4(s)} + H^+_{(aq)} \quad [3]$$

and the equilibrium constant expressions are:

$$K_+(\text{int}) = \frac{[SOH^+_2]}{[SOH][H^+]} \exp(F\psi/RT) \quad [4]$$

$$K_-(\text{int}) = \frac{[SO^-][H^+]}{[SOH]} \exp(-F\psi/RT) \quad [5]$$

$$K_{B-}(\text{int}) = \frac{[SH_3BO^-_4][H^+]}{[SOH][H_3BO_3]} \exp(-F\psi/RT) \quad [6]$$

where SOH represents reactive surface hydroxyl groups on oxides and clay minerals in soils, *F* is the Faraday constant (C mol_c^{-1}), ψ is the surface potential (V), *R* is the molar gas constant (J mol^{-1} K^{-1}), *T* is the absolute temperature (K), and square brackets indicate concentrations (mol L^{-1}). The exponential term can be considered as a solid phase activity coefficient correcting for the charge on the B surface complex. Mass balance for the reactive surface functional group is defined as:

Table 1. Classifications and chemical characteristics of soils.†

Soil series	Soil horizon	pH	Clay	CEC	S	IOC	OC	Fe	Al
			g kg^{-1}	$mmol_c$ kg^{-1}	m^2 g^{-1}	g kg^{-1}			
Bernow (fine-loamy, siliceous, thermic Glossic Paleudalf)	B	5.6	238	77.6	46.4	0.0028	3.8	8.1	1.1
Canisteo (fine-loamy, mixed, superactive, calcareous, mesic Typic Endoaquoll)	A	7.8	175	195	152	14.8	34.3	1.7	0.44
Dennis (fine, mixed, thermic Aquic Argiudoll)	A	6.2	225	85.5	40.3	0.0014	18.6	12.9	1.7
	B	6.5	381	63.1	72.4	0.0010	5.2	30.0	4.1
Dougherty (loamy, mixed, active, thermic Arenic Haplustalf)	A	5.7	38	3.67	241	0.0010	7.0	1.7	0.28
Hanlon (coarse-loamy, mixed, superactive, mesic Cumulic Hapludoll)	A	7.7	125	142	58.7	2.6	15.1	3.7	0.45
Kirkland (fine, mixed, superactive, thermic Udertic Paleustoll)	A	5.5	300	154	42.1	0.014	12.3	5.6	0.80
Luton (fine, smectitic, mesic Typic Endoaquert)	A	7.4	588	317	169	0.099	21.1	9.1	0.99
Mansic (fine-loamy, mixed, superactive, thermic Aridic Calciustoll)	A	8.0	225	142	42.2	16.7	10.1	2.7	0.40
	B	8.4	275	88.1	35.5	63.4	9.0	1.1	0.23
Norge (fine-silty, mixed, active, thermic Udic Paleustoll)	A	4.1	175	62.1	21.9	0.0010	11.6	6.1	0.75
Osage (fine, smectitic, thermic Typic Epiaquert)	A	7.2	325	377	134	0.59	29.2	15.9	1.4
	B	6.6	413	384	143	0.0100	18.9	16.5	1.3
Pond Creek (fine-silty, mixed, superactive, thermic Pachic Argiustoll)	A	5.2	213	141	35.4	0.0023	16.6	5.2	0.70
	B	6.0	325	106	59.6	0.016	5.0	5.1	0.81
Pratt (sandy, mixed, mesic Lamellic Haplustalf)	A	6.7	63	23.9	12.3	0.0026	4.2	1.2	0.18
	B	6.1	63	23.3	117	0.0007	2.1	0.92	0.13
Richfield (fine, smectitic, mesic Aridic Argiustoll)	B	7.2	375	275	82.0	0.040	8.0	5.4	0.76
Summit (fine, smectitic, thermic Oxyaquic Vertic Argiudoll)	A	7.6	288	374	218	0.25	26.7	16.2	2.3
	B	7.0	413	384	169	0.0079	10.3	17.8	2.5
Taloka (fine, mixed, thermic Mollic Albaqualf)	A	4.9	113	47.4	87.0	0.0021	9.3	3.6	0.62
Teller (fine-loamy, mixed, active, thermic Udic Argiustoll)	A	4.4	94	43.1	227	0.0008	6.8	3.2	0.53

† CEC, cation-exchange capacity; IOC, inorganic C; OC, organic C.

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$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + [SOH_3BO_4^-] \quad [7]$$

The charge balance expression is:

$$\sigma = [SOH_2^+] - [SO^-] - [SH_3BO_4^-] \quad [8]$$

The computer code FITEQL 3.2 (Herbelin and Westall, 1996) was used as a chemical speciation program to evaluate predictions of B adsorption behavior using the regression model of Goldberg et al. (2000) to predict values of the surface complexation constants from soil chemical properties. As in the prior study, fixed input parameter values were capacitance: $C = 1.06$ F m^{-2}, and surface site density: $N_s = 2.31$ sites nm^{-2} (recommended for natural materials by Davis and Kent, 1990). Constant values of these parameters are necessary to allow application of the predictive equations to new soils. The total number of reactive surface functional groups for constant surface site density is obtained from the expression:

$$[SOH]_T = \frac{2.31 \times 10^{18} Sa}{N_A} \quad [9]$$

where S is the surface area, a is the suspension density of solid, and N_A is Avogadro's number. The prediction equations for the surface complexation constants previously developed for soils primarily from California are (see Table 4 of Goldberg et al., 2000):

$$\log K_{B-} = -9.14 - 0.375\ln(S) + 0.167\ln(OC) + 0.111\ln(IOC) + 0.466\ln(Al) \quad [10]$$

$$\text{Log } K_+ = 7.85 - 0.102\ln(OC) - 0.198\ln(IOC) - 0.622\ln(Al) \quad [11]$$

$$\text{Log } K_- = -11.97 + 0.302\ln(OC) + 0.0584\ln(IOC) + 0.302\ln(Al) \quad [12]$$

where the units of OC, IOC, and Al are (g kg^{-1}). Surface complexation constant values, $\log K_{B-}$, $\log K_+$, and $\log K_-$, were calculated for each of the new soils from the chemical properties: surface area, OC, IOC, and Al oxide content (Al) and these equations. Using these predicted surface complexation constants, B adsorption isotherms were in turn predicted for each soil and compared with experimentally determined adsorption values.

An analysis of the experimentally derived versus model predicted B data was performed to assess both the relative precision and absolute accuracy of the modeling results. The difference between the experimentally determined equilibrium solution B and CC model predicted equilibrium solution B (as calculated using the regression model prediction coefficients) is defined as:

$$\text{Error_Eq} = \text{Eq}_m - \text{Eq}_e \quad [13]$$

where the m and e subscripts stand for model and experimental, respectively. Likewise, the difference between the experimentally determined adsorbed B and constant capacitance model predicted adsorbed B (again calculated from the constant capacitance model using regression model prediction coefficients) is defined as:

$$\text{Error_Ad} = \text{Ad}_m - \text{Ad}_e \quad [14]$$

Using these definitions, the total mean squared error (TMSE) is defined as the corresponding uncorrected sum of squares error estimates:

$$\text{USS(Eq)} = \sum_{i=1}^{N} (\text{Error_Eq})^2 \quad [15]$$

$$\text{USS(Ad)} = \sum_{i=1}^{N} (\text{Error_Ad})^2 \quad [16]$$

and the corresponding average mean squared errors (AMSE) to be the USS(Eq) and USS(Ad) estimates divided by the sample size, N. These AMSE estimates were used to quantify both the average prediction variance and the average squared bias (Myers and Montgomery, 2002), where the variance and bias reflect the relative precision and absolute accuracy between the experimental and predicted B data sets.

In addition to calculating the AMSE estimates, a coefficient-of-variation type statistic was also calculated. Specifically, the coefficient-of-imprecision, CIp, was defined to be

$$\text{CIp} = \frac{\sqrt{\text{USS(Error)/N}}}{(\overline{Y}_e + \overline{Y}_m)/2} \quad [17]$$

where the numerator represents the appropriate AMSE estimate and the denominator represents the average of experimental, Y_e, and modeled, Y_m, the two corresponding mean equilibrium solution B or adsorbed B levels, respectively. This latter statistic was used to quantify the relative variation in the equilibrium solution B and adsorbed B error distributions.

Note that the constant capacitance model was not actually fit to any of the experimental B data in this study. Rather, constant capacitance model predictions were instead generated using the regression model prediction coefficients. Given this fact, it is reasonable to expect that for any specific soil there may be some consistent amount of prediction bias (i.e., a consistent shift in location between the experimentally determined versus constant capacitance model predicted B levels). To test for such effects, we fit a one-way analysis of variance, ANOVA model to each error distribution, defined as:

$$\text{Error_Eq}_{ij} \text{ or Error_Ad}_{ij} = \mu + \alpha_i + \varepsilon_{ij} \quad [18]$$

where $i = 1$ to 22 represents the 22 specific soils analyzed in this study, and $j = 1$ to n_i represents the individual observations collected for each soil at the various equilibrium solution levels (Montgomery, 1997). In this model, the F-test on the soil type effects (α) corresponds to a test for detectable within-soil prediction bias. In addition to the standard (parametric) ANOVA analysis, Eq. [18] was also analyzed using a non-parametric Kruskal–Wallis test (Hollander and Wolfe, 1999) to facilitate a more robust assessment of this within-soil bias effect.

The ANOVA model defined in Eq. [18] was used to test for within-soil prediction bias. To test for between-soil prediction bias, we calculated the mean equilibrium and adsorption errors (for each soil) and then analyzed the overall average values of these errors using both t tests and nonparametric sign-rank tests.

RESULTS AND DISCUSSION

The B adsorption affinity of the Midwestern soils was greater than that of the California soils at equal amounts of B addition. This observation is in agreement with a higher range in the properties of the Midwestern soils that are correlated with B adsorption capacity: OC and IOC contents and Al and Fe oxide contents. The Midwestern soils exhibit a lower range in pH value consistent with the higher rainfall experienced in this part of the country over California. The set of Midwestern soils consists mainly of mollisols with some alfisols and vertisols. In contrast the set of California soils consists mainly of alfisols and entisols with some vertisols, mollisols, an inceptisol, and an aridisol. Mollisols would be expected

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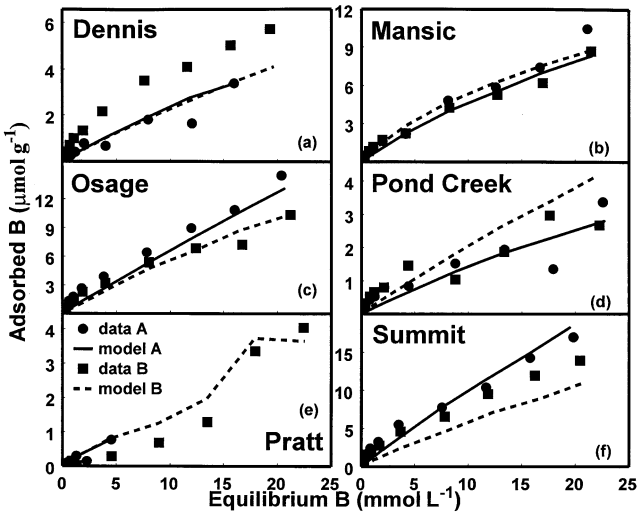

Fig. 1. Prediction of B adsorption with the constant capacitance model: (a) Dennis soil; (b) Mansic soil; (c) Osage soil; (d) Pond Creek soil; (e) Pratt soil; (f) Summit soil. Experimental data are represented by circles (A horizon) and squares (B horizon). Model predictions are represented by solid lines (A horizon) and dashed lines (B horizon).

to show greater B adsorption capacity than alfisols, entisols, and aridisols because of their higher organic matter content.

Figure 1 presents a comparison of the experimental results and the constant capacitance model predictions of B adsorption on a subset of Midwestern soils. The predictions result from using the previously developed regression relations to obtain the constants (Eq. [10]–[12]). The subset of soils chosen for presentation in this figure was the soils for which we were able to determine B adsorption isotherms on both A and B horizons. The range in quality of the model predictions is well representative of the entire set of soils studied. For each soil, the model prediction is comparable in quality for both horizons. The ability of the model to describe the data is very encouraging, especially since the prediction equations were determined on a set of soils primarily from California developed under different pedological conditions. It is also very encouraging that a regression model developed to describe B adsorption envelopes was able to adequately predict B adsorption isotherms. Boron adsorption envelopes were determined at a fixed concentration of total B and variable solution pH, while B adsorption isotherms were determined at fixed pH and variable total B concentration.

The regression model was used to obtain the parameters for the constant capacitance model. Then the constant capacitance model was used to predict the soil specific B adsorption. This is in contrast to regression models that fit adsorption of a series of soils. The distinction is that using the combined regression equations and the constant capacitance model only soil properties and not adsorption are needed to predict soil specific B adsorption data. Model predictions for those soils that are not pictured are comparable in quality to those shown in Fig. 1 with the exception of Bernow, Hanlon, Norge, and Teller soils which showed the greatest deviations. Table 2 provides surface complexation constants predicted by the regression model for all soils studied.

Results pertaining to the specific statistical analyses results are discussed and presented in Appendix 1 and Tables A1 and A2. Overall, the observed errors in the constant capacitance model predicted versus experimentally determined equilibrium solution B levels were quite small, and the relative precision between these two data sets was extremely high. The observed errors in the predicted versus experimentally determined adsorbed B levels were somewhat larger, with the calculated AMSE (on an equivalent mmol L^{-1} basis) being about 4.6 times greater than the corresponding equilibrium solution estimate (see Table A1). Four of the 22 soils clearly show large within-soil bias effects with respect to the adsorbed B errors, but across all 22 soils this within-soil bias accounts for just slightly more than one-third of the total observed variability in the study.

Table 2. Constant capacitance model surface complexation constants.

Soil series	State	Soil horizon		From prediction equations		
			$\log K_{B-}$†	$\mathrm{Log}K_{B-}$	$\mathrm{Log}K_{+}$	$\mathrm{Log}K_{-}$
Bernow	Oklahoma	B	−6.52	−8.35	8.79	−11.87
Canisteo	Iowa	A	−7.75	−7.92	7.47	−10.99
Dennis	Oklahoma	A	−7.15	−7.93	8.53	−11.31
		B	−7.05	−7.98	8.17	−11.44
Dougherty	Oklahoma	A	−8.06	−9.64	9.82	−12.17
Hanlon	Iowa	A	−7.67	−7.89	7.88	−11.33
Kirkland	Oklahoma	A	−7.01	−8.11	8.58	−11.53
Luton	Iowa	A	−7.71	−8.22	8.01	−11.19
Mansic	Oklahoma	A	−7.12	−7.68	7.63	−11.38
		B	−7.25	−7.74	7.73	−11.51
Norge	Oklahoma	A	−6.54	−8.20	9.15	−11.72
Osage	Oklahoma	A	−7.36	−7.70	7.38	−10.87
		B	−7.45	−8.29	8.28	−11.26
Pond Creek	Oklahoma	A	−7.10	−8.26	8.99	−11.58
		B	−7.49	−8.36	8.63	−11.79
Pratt	Oklahoma	A	−7.05	−8.72	9.96	−12.41
		B	−8.07	−9.97	10.49	−12.79
Richfield	Oklahoma	B	−7.30	−8.33	8.44	−11.61
Summit	Oklahoma	A	−7.52	−7.78	7.27	−10.80
		B	−7.38	−8.20	8.01	−11.27
Taloka	Oklahoma	A	−7.76	−8.75	9.14	−11.80
Teller	Oklahoma	A	−7.73	−9.35	9.46	−12.00

† Optimized with protonation-dissociation constants fixed at $\log K_{+} = 7.35$, $\log K_{-} = -8.95$.

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Finally, both parametric and nonparametric statistical tests confirm the presence of detectable within-soil bias in the equilibrium solution and adsorption error distributions, but fail to detect any between-soil bias effects in the mean error distributions. Hence, the constant capacitance model predictions appeared to remain globally unbiased (across different soils) when the regression model prediction coefficients were used in place of optimized (fitted) coefficients.

For the sake of completeness, Table 2 indicates optimized values of the B surface complexation constant, $\log K_{B-}$, obtained by fitting the constant capacitance model to the B adsorption isotherm data. In this case values of the protonation–dissociation constants were held constant at $\log K_{+} = 7.35$ and $\log K_{-} = -8.95$ (averages of a literature compilation for crystalline and amorphous Al and Fe oxides from Goldberg and Sposito, 1984) and only the B surface complexation constant was optimized. The fits are universally good, optimizing only one adjustable parameter. Average values of the B surface complexation constants and protonation constants obtained from the prediction equations and those obtained by optimization were not statistically significantly different at the 95% level of confidence. The average value of the dissociation constant obtained with the prediction equations for soils was statistically significantly different from the average value obtained for Al and Fe oxides. This result is not surprising given the effect of permanent negative charge in soils. Constant capacitance model fits using one adjustable parameter are of comparable quality to those obtained with Langmuir and Freundlich isotherms containing two empirical adjustable parameters (see Fig. 2). This result again highlights the advantages of surface complexation models over empirical approaches.

The constant capacitance model contains the assumption that ion adsorption takes place on one set of reactive surface sites. This is clearly a simplification since soils are complex mixtures having a variety of reactive surface functional groups. Our model predictions often show a greater underprediction of B adsorption at the lowest equilibrium B concentrations (see Fig. 1). This observation would indicate that the soils contain sets of B reactive sites of differing affinity. The model assumption of one set of sites leads to underprediction of B adsorption on the highest affinity sites, which are filled initially at the lowest solution B concentration.

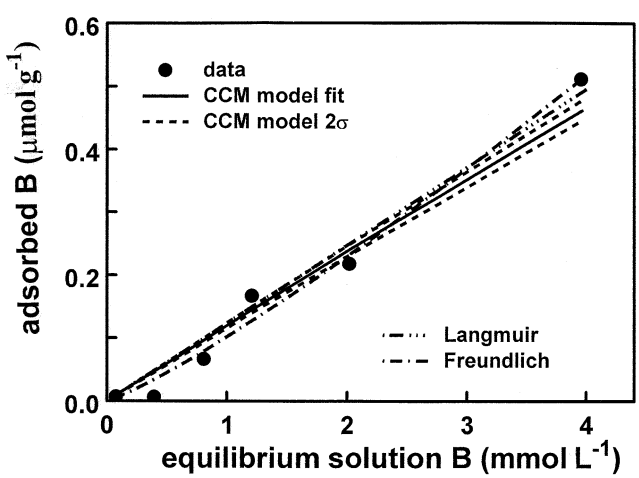

Fig. 2. Comparison of the chemical constant capacitance model fit with one adjustable parameter ($\log K_{B-} = -8.061$, $\sigma = 0.0077$) to empirical Langmuir ($R^2 = 0.975$) and Freundlich ($R^2 = 0.985$**) fits with two adjustable parameters.**

Although predictions of B adsorption on some soils were not good, for the majority of soils the predictions were able to accurately describe B adsorption. The model predictions were obtained independent of any experimental measurement of B adsorption on these soils using values of easily measured soil chemical parameters. Since our model results are predictions, our approach, of course, uses zero adjustable parameters. That the prediction equations, developed from describing B adsorption envelopes on a set of soils primarily from California, were able to predict B adsorption isotherms on a set of soils from Oklahoma and Iowa is all the more encouraging. This result suggests wide applicability of the regression model prediction equations for describing B adsorption both as a function of solution B concentration and solution pH. Our prediction equations have been incorporated into the UNSATCHEM chemical speciation-transport model (Suarez and Simunek, 1997) allowing us to simulate B concentrations in soil solution under diverse environmental and agricultural conditions. Studies are underway in our laboratory to describe B movement in soil lysimeters and in field situations.

APPENDIX 1

Both relative precision and absolute accuracy statistics are shown in Table A1 for each soil analyzed in this study. These statistics include the Pearson correlation coefficients (which measure the relative precision after adjusting out any bias), and the AMSE and CIp estimates (which quantify both relative precision and absolute accuracy). Statistics pertaining to both the equilibrium solution and adsorbed B data are given separately in Table A1.

The equilibrium solution correlation coefficients all exceeded 0.9998, confirming a high degree of relative precision between the constant capacitance model predicted and experimentally determined equilibrium B levels for each soil. The AMSE estimate calculated from the pooled equilibrium solution errors was 0.062 mmol L^{-1}, implying that this error distribution exhibited a (uncorrected) standard deviation of 0.249 mmol L^{-1}. The corresponding pooled CIp estimate was <5%, and the largest individual soil CIp estimate was only 10%.

The adsorption correlation coefficients suggest that somewhat less relative precision was obtained between the constant capacitance model predicted and experimentally determined adsorbed B levels for each soil. These calculated correlation levels ranged from 0.8877 (Taloka A soil) to 0.9968 (Osage A and Summit B soils). The AMSE estimate calculated from the pooled adsorption errors was 1.419 μmol g^{-1}, implying that this error distribution exhibited an (uncorrected) standard deviation of 1.191 μmol g^{-1}. The corresponding mmol L^{-1}

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Table A1. Relative precision and absolute accuracy statistics for experimentally derived versus constant capacitance model predicted B levels (for both equilibrium solution and adsorbed B data).

Soil	Equilibrium solution B			Adsorbed B		
	Corr (Eq)	AMSE (Eq)	CIp (Eq)	Corr (Ad)	AMSE (Eq)	CIp (Ad)
		mmol L^{-1}			μmol g^{-1}	
Bernow	0.9998	0.079	9.45	0.9765	0.402	187.82
Canisteo	>0.9999	0.531	10.00	0.9894	2.657	70.16
Dennis A	0.9999	0.082	1.84	0.9530	0.379	38.61
Dennis B	>0.9999	0.222	3.89	0.9904	1.072	61.30
Dougherty	>0.9999	0.006	0.43	0.9920	0.031	18.92
Hanlon	>0.9999	0.556	9.84	0.9754	2.367	109.48
Kirkland	>0.9999	0.104	1.76	0.9630	0.526	52.68
Luton	0.9999	0.456	8.42	0.9884	2.085	61.68
Mansic A	0.9999	0.142	2.31	0.9926	0.743	25.12
Mansic B	0.9999	0.109	1.77	0.9915	0.553	18.65
Norge	>0.9999	0.161	2.70	0.9586	0.815	169.14
Osage A	0.9999	0.157	2.66	0.9968	0.880	20.53
Osage B	0.9999	0.128	2.11	0.9873	0.686	20.17
Pond Creek A	>0.9999	0.070	1.07	0.9241	0.394	41.62
Pond Creek B	>0.9999	0.122	1.89	0.9491	0.616	50.61
Pratt A	0.9999	0.025	1.59	0.9159	0.116	42.62
Pratt B	>0.9999	0.063	0.99	0.9748	0.359	35.82
Richfield	0.9999	0.128	2.12	0.9918	0.705	19.34
Summit A	0.9999	0.191	3.69	0.9950	0.863	16.62
Summit B	0.9999	0.334	5.62	0.9968	1.730	41.27
Taloka A	0.9999	0.143	2.11	0.8877	0.706	64.89
Teller A	0.9999	0.303	4.55	0.9412	1.517	231.43
Average	0.9994	0.062	4.47	0.9355	1.419	53.53

AMSE and standard deviation for the adsorption errors is 0.284 mmol L^{-1} and 0.533 mmol L^{-1}, respectively. Thus, the calculated AMSE of the adsorption errors appears to be about 4.6 times as large (as the equilibrium solution errors). The corresponding pooled CIp estimate was about 54%, but four soils produced CIp estimates in excess of 100% (Bernow, Hanlon, Norge, and Teller). The predictions for these latter soils appear to exhibit significant within-soil bias effects.

The formal test results for within-soil bias effects are given in the upper portion of Table A2. The ANOVA models for both the equilibrium solution and adsorbed B errors explain about one-third of the total error variation, and the F scores pertaining to the within-soil effects are clearly significant ($F = 5.17$ and 5.34, $p < 0.0001$ for both models). The nonparametric Kruskal–Wallis chi-square tests confirm these parametric results ($\chi^2 = 103.7$ and 104.6, $p < 0.0001$ for both models). As expected, there is detectable bias in both the equilibrium solution and adsorbed B errors for specific soils. This within-soil bias has been introduced into the constant capacitance model predictions specifically because regression model prediction coefficients have been used in place of optimized coefficients.

Table A2. Parametric and non-parametric tests for prediction bias in experimentally derived versus constant capacitance model predicted B levels (for both equilibrium solution and adsorbed B data).

		Equilibrium solution B	Adsorbed B
	Individual experimental versus model predictions		
	N	226	226
	USS/*N*	0.0619	1.4186
ANOVA	MSE	0.0446	1.0071
	R-square	0.3472	0.3545
	F-score	5.17	5.34
	ndf, ddf	21 204	21 204
	Prob > *F*	<0.0001	<0.0001
Kruskal–Wallis	Chi-square	103.7	104.6
	df	21	21
	Prob > Chi	<0.0001	<0.0001
	Average error analysis (averaged across soil types)		
	N	22	22
	mean	0.0113	−0.0976
	std. dev.	0.1451	0.7007
	t-score	0.365	−0.654
	Prob > |t|	0.719	0.521
Signed rank	sr-score	27.5	−32.5
	Prob ≥ |sr|	0.384	0.302

The formal test results for between-soil bias effects are shown in the lower portion of Table A2. The t test and signed rank test results are clearly nonsignificant for both the average equilibrium solution and adsorbed B errors. These results suggest that there is no global bias present in the average constant capacitance model prediction errors across the 22 specific soils analyzed in this study. In other words, the use of regression model prediction coefficients (in the constant capacitance model) does not appear to cause any detectable between-soil bias effects.

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