

Prediction of Boron Adsorption by Field Samples of Diverse Textures

Sabine Goldberg,* D. L. Corwin, P. J. Shouse, and D. L. Suarez

ABSTRACT

Soil texture often varies dramatically in both vertical and horizontal directions in field situations and affects the amount of B adsorbed and B movement. This study was conducted to evaluate the effect of clay content on B adsorption and to test the predictive ability of the constant capacitance model to describe B adsorption as related to changes in clay content. Boron adsorption on 15 soil samples constituting five depths of each of three sites in the western San Joaquin Valley of California was investigated. Boron adsorption increased with increasing pH, reached an adsorption maximum around pH 9, and decreased with further increases in pH. The model was able to describe B adsorption on the soils by simultaneously optimizing three surface complexation constants. The model was able to predict B adsorption by using surface complexation constants calculated from easily measured chemical parameters. The model was also able to predict B adsorption at all of the depths using the surface complexation constants predicted with the chemical properties of one of the surface depths and a surface area value calculated from clay content. These results are very encouraging, suggesting that for a particular soil series, B adsorption for various sites and depths in a field can be predicted using only clay content and the chemical information from a different site in the same field. Incorporation of the prediction equations into chemical speciation-transport models will allow simulation of soil solution B concentrations in horizontal and vertical space under diverse environmental and agricultural conditions.

BORON IS A trace element essential for the growth of higher plants, but the plant sufficiency range is narrow (Reisenauer et al., 1973). In areas of plentiful rainfall, plant deficiency symptoms are often observed because of small soil solution B concentrations and large amounts of B leaching (Keren and Bingham, 1985). In arid areas, B toxicity symptoms are primarily the result of large soil solution B concentrations and application of large amounts of B in irrigation waters (Nable et al., 1997). Both B deficiency and toxicity conditions inhibit plant growth leading to marked yield reductions of crop plants and economic losses to growers.

Soil solution B concentrations equilibrate with B adsorbed onto various organic and mineral surfaces (Goldberg, 1993). Adsorption sites on organic matter, oxide minerals, clay minerals, and carbonates act as sources and sinks for B. Adsorbed B is neither directly available nor toxic to plants (Keren et al., 1985). Thus, the adsorption complex plays a critical role in controlling soil solution B concentrations. Boron deficiency often occurs on sandy soils because of their small B adsorption capacity (Goldberg, 1993). Soils with large amounts of clay con-

tent, on the other hand, have the potential to attenuate phytotoxic B concentrations (Goldberg, 1993). Detailed quantification of B adsorption reactions is necessary to understand the fate and transport of B in soils. This knowledge is essential for determining appropriate applications of B fertilizer, management of irrigation waters containing large amounts of B, and reclamation of soils containing large amounts of B.

Boron adsorption on soil constituents has been described by various empirical and chemical modeling approaches. The parameters obtained with empirical models such as the distribution coefficient, K_d , and Langmuir and Freundlich adsorption isotherm equations are only valid for the particular conditions of the measurement (Goldberg, 1993). Chemical models, such as surface complexation models, account for molecular features and define specific surface species, chemical reactions, mass balances, and charge balances thermodynamically (Sposito, 1983). These characteristics allow chemical models to have more general predictive capability. This has been demonstrated in prior studies for B adsorption using the constant capacitance model, a surface complexation model (Goldberg et al., 2000, 2004).

A general regression model was developed to predict B adsorption on soils by calculating surface complexation constants for the constant capacitance model from prediction equations (Goldberg et al., 2000). These prediction equations relate the three surface complexation constants: the B adsorption constant, K_{B-} , the protonation constant, K_+ , and the dissociation constant, K_- , to the easily measured soil chemical parameters: surface area, organic carbon (OC) content, inorganic carbon (IOC) content, and free aluminum oxide content. The equations reliably predicted B adsorption envelopes (amount of B adsorbed as a function of solution pH at a fixed total B concentration) with reasonable accuracy on 15 soils primarily from California (Goldberg et al., 2000) and B adsorption isotherms (amount of B adsorbed as a function of equilibrium solution B concentration) on 22 Midwestern soils (Goldberg et al., 2004). These applications demonstrated a completely independent evaluation of the predictive capability of the constant capacitance model to describe B adsorption by soils.

The amount of B adsorbed on soil constituents has been correlated with soil clay content (Elrashidi and O'Connor, 1982). Previous research showed that the regression model and prediction equations of Goldberg et al. (2000) were able to satisfactorily describe B adsorption on soils of diverse textures in a field situation

Contribution from USDA-ARS, George E. Brown Jr., Salinity Lab., 450 W. Big Springs Road, Riverside, CA 92507. Received 9 Nov. 2004. *Corresponding author (sgoldberg@ussl.ars.usda.gov).

Published in Soil Sci. Soc. Am. J. 69:1379–1388 (2005).

Soil Chemistry

doi:10.2136/sssaj2004.0354

© Soil Science Society of America

677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: CRM, coefficient of residual mass; IOC, inorganic carbon; M, mean difference; OC, organic carbon; OF, optimized fit; PE, depth-specific prediction; PEs9, prediction with parameters for Site 9 0- to 30-cm depth; PEs33, prediction with parameters for Site 33 0- to 30-cm depth; PEs49, prediction with parameters for Site 49 0- to 30-cm depth; RMSE, root mean square error; SA, surface area.

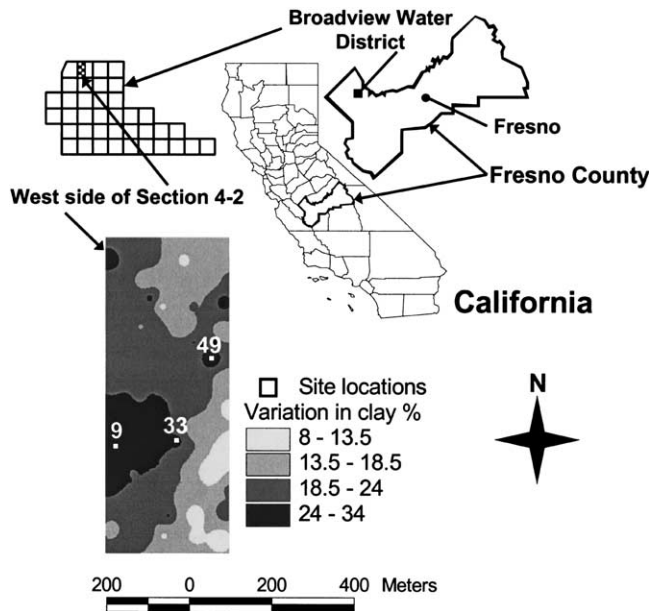


Fig. 1. Map showing Section 4-2 of the Broadview Water District in the San Joaquin Valley of California. Variations in clay content with depth from 0 to 150 cm are shown. Locations of Sites 9, 33, and 49 are also indicated.

(Vaughan et al., 2004) but only after laboratory characterization of B adsorption behavior and chemical properties. Texture often varies dramatically in field situations both in the vertical and horizontal directions. It would facilitate descriptions of B movement at the field scale to be able to use the parameters of the surface horizon to describe B adsorption in the entire soil profile or on other sites in the same field. This would simplify the description of soil solution B concentration with chemical speciation-transport models.

The objectives of the present study were: (i) to determine B adsorption envelopes on three soil profiles having large variations in clay content with depth; (ii) to test the ability of the constant capacitance model to fit B adsorption behavior as a function of solution pH; (iii) to evaluate the ability of the general regression model and prediction equations of Goldberg et al. (2000) to predict B adsorption behavior as a function of solution pH; and (iv) to test whether the model could accurately

describe B adsorption behavior of all horizons using the surface complexation constant values predicted for one of the surface horizons.

MATERIALS AND METHODS

Boron adsorption was investigated using soil samples obtained from three sites in Section 4-2 of the Broadview Water District in the San Joaquin Valley of California (see Fig. 1). These samples had been collected for the study of Corwin et al. (2003). Soil samples were taken in 30-cm increments to a depth of 150 cm. The soils belong to the Lillis soil series classified as very-fine, smectitic, thermic Halic Haploxererts. The three sites were chosen from the 60 sites studied by Corwin et al. (2003) because they exhibited large textural changes with changes in depth from 0 to 150 cm (see Fig. 1). Soil physical and chemical characteristics are provided in Table 1. Detailed descriptions of experimental methods for soil analysis were provided in Goldberg et al. (2000). Briefly, surface area was measured according to the method of Cihacek and Bremner (1979), free aluminum and iron oxides were analyzed by the Coffin (1963) method, and OC and IOC were determined by carbon coulometry using a UIC Full Carbon System 150¹ (UIC, Inc., Joliet, IL).

Boron adsorption envelopes for the soils were determined as described in the study of Goldberg and Glaubig (1986a) using a total B addition of 5 g m⁻³. The complete experimental adsorption procedure was provided in this reference. Boron adsorption envelopes were determined in batch systems. Five grams of air-dried soil were added to 50-mL polypropylene centrifuge tubes and equilibrated with 25 mL of a 0.1 M NaCl background electrolyte solution on a reciprocating shaker for 20 h. The reaction temperature was 25.0 ± 0.07°C. After reaction, the samples were centrifuged and the decantates analyzed for pH, filtered and analyzed for B concentration using inductively coupled plasma emission (ICP) spectrometry. Boron release from the soils into 0.1 M NaCl electrolyte solution was studied under identical experimental conditions as for the B adsorption study. Boron adsorption values were corrected for B release at each solution pH (Goldberg and Glaubig, 1986b). To obtain accurate definition of the shape of the B adsorption envelope, we chose to evaluate a large number of solution pH values rather than analyzing replicate samples.

A detailed explanation of the theory and assumptions of

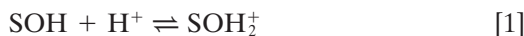
¹ Trade names and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment of the product listed by the USDA.

Table 1. Characteristics of the soils.†

| Soil | Depth cm | pH 0.1 M NaCl | Clay g kg ⁻¹ | SA km ² kg ⁻¹ | g kg ⁻¹ | | | Fe | Al |
|---------|-------------|------------------|----------------------------|--|--------------------|------|------|------|----|
| | | | | | IOC | OC | | | |
| Site 9 | 0-30 | 6.58 | 493 | 0.177 | 1.5 | 10.1 | 12.7 | 0.92 | |
| | 30-60 | 6.73 | 514 | 0.180 | 1.7 | 8.4 | 13.1 | 0.96 | |
| | 60-90 | 6.72 | 461 | 0.127 | 1.4 | 4.1 | 11.1 | 0.74 | |
| | 90-120 | 6.66 | 323 | 0.104 | 4.0 | 2.7 | 9.5 | 0.54 | |
| | 120-150 | 6.55 | 271 | 0.0762 | 3.4 | 3.2 | 9.3 | 0.48 | |
| Site 33 | 0-30 | 5.66 | 414 | 0.174 | 0.29 | 9.2 | 11.3 | 0.85 | |
| | 30-60 | 6.15 | 432 | 0.171 | 0.54 | 7.3 | 11.3 | 0.84 | |
| | 60-90 | 6.60 | 325 | 0.142 | 1.2 | 3.8 | 10.4 | 0.70 | |
| | 90-120 | 6.71 | 216 | 0.0813 | 5.3 | 1.7 | 8.6 | 0.41 | |
| | 120-150 | 6.79 | 183 | 0.0600 | 4.7 | 1.0 | 7.9 | 0.36 | |
| Site 49 | 0-30 | 6.41 | 389 | 0.164 | 0.59 | 9.3 | 11.5 | 0.91 | |
| | 30-60 | 6.72 | 439 | 0.145 | 1.1 | 8.0 | 11.7 | 0.91 | |
| | 60-90 | 6.60 | 458 | 0.174 | 2.3 | 5.7 | 12.4 | 0.91 | |
| | 90-120 | 6.71 | 235 | 0.107 | 9.4 | 2.9 | 10.1 | 0.64 | |
| | 120-150 | 7.08 | 177 | 0.0621 | 3.0 | 1.5 | 9.5 | 0.47 | |

† SA = surface area, IOC = inorganic carbon, OC = organic carbon.

surface complexation modeling of adsorption was provided by Goldberg (1992). In the present application of the constant capacitance model to B adsorption, three surface complexation reactions were considered:



where SOH, the surface functional group, represents both reactive surface hydroxyl groups on oxides and aluminol groups on clay minerals in soils. Equilibrium constants for the surface complexation reactions were:

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

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

$$K_{\text{B-}}(\text{int}) = \frac{[\text{SH}_3\text{BO}_4^-][\text{H}^+]}{[\text{SOH}][\text{H}_3\text{BO}_3]} \exp(-F\psi/RT) \quad [6]$$

where square brackets indicate concentrations (mol L^{-1}), F is the Faraday constant (C mol^{-1}), ψ is the surface potential (V), R is the molar gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K), and the exponential terms represent solid

phase activity coefficients that correct for the charges on the surface complexes. These reactions and equilibrium constants were previously considered in modeling and prediction of soil B adsorption envelopes (Goldberg et al., 2000) and isotherms (Goldberg et al., 2004).

The computer program FITEQL 3.2 (Herbelin and Westall, 1996) uses a nonlinear least squares optimization routine to fit equilibrium constants to experimental data and contains the constant capacitance model of adsorption. As in a prior study (Goldberg et al., 2000), the FITEQL program was used to fit surface complexation constants, optimized fit (OF), to the experimental B adsorption envelope data and to test the ability of the surface complexation constants calculated with the general regression model to predict B adsorption. As before, initial input parameter values were capacitance: $C = 1.06 \text{ F m}^{-2}$ and surface site density: $N_s = 2.31 \text{ sites nm}^{-2}$. The general regression model prediction equations for the surface complexation constants were (Goldberg et al., 2000):

$$\text{Log}K_{\text{B-}} = -9.14 - 0.375\ln(\text{SA}) + 0.167\ln(\text{OC}) + 0.111\ln(\text{IOC}) + 0.466\ln(\text{Al}) \quad [7]$$

$$\text{Log}K_{+} = 7.85 - 0.102\ln(\text{OC}) - 0.198\ln(\text{IOC}) - 0.622\ln(\text{Al}) \quad [8]$$

$$\text{Log}K_{-} = -11.97 + 0.302\ln(\text{OC}) + 0.0584\ln(\text{IOC}) + 0.302\ln(\text{Al}) \quad [9]$$

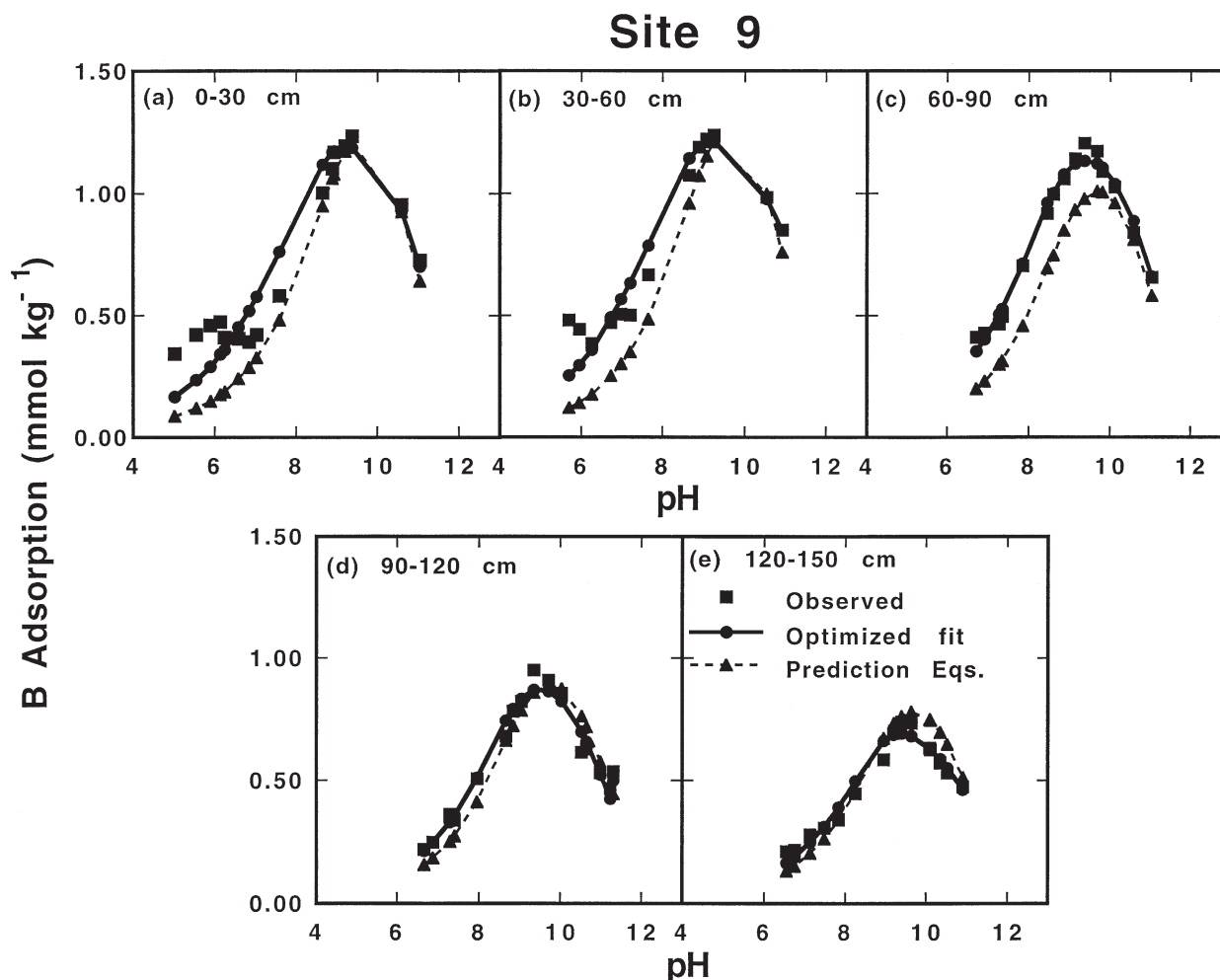


Fig. 2. Constant capacitance modeling of B adsorption on Site 9 of the Lillis soil: a) 0- to 30-cm depth; b) 30- to 60-cm depth; c) 60- to 90-cm depth; d) 90- to 120-cm depth; e) 120- to 150-cm depth. Squares represent experimental data. Model fits are represented by solid lines. Depth-specific model predictions are represented by dashed lines.

where the units of surface area are ($\text{km}^2 \text{kg}^{-1}$) and units of OC, IOC, and Al are (g kg^{-1}). Surface complexation constants $\log K_{B-}$, $\log K_{+}$, and $\log K_{-}$ were calculated for each soil sample depth from the chemical properties: SA, surface area, OC, organic carbon, IOC, inorganic carbon, and Al, aluminum and these equations. Using these predicted constants, B adsorption envelopes were predicted for each soil sample, PE, and compared with the experimentally determined adsorption values. For each depth, the depth-specific prediction was also compared with that obtained using the predicted surface complexation constant values for each of the surface horizons, PEs9, for Site 9, PEs33, for Site 33, and PEs49, for Site 49. For this approach, surface area for each depth was calculated from depth-specific clay content using the linear regression equation obtained for the 15 soil samples:

$$SA = 5.654 + 348.9(\text{clay mass fraction}) \quad [10]$$

where $R^2 = 0.906^{**}$. Other than clay content, no depth-specific measurement was used to predict the B adsorption.

Statistical criteria and graphical displays were used to evaluate the model simulations. The statistical criteria were the model evaluation parameters: root mean square error (RMSE), mean difference (M), and coefficient of residual mass, (CRM). The RMSE parameter is the sum of the squared differences between the observed and predicted data normalized to the number of observations:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (P_i - O_i)^2} \quad [11]$$

where n is the sample size, P_i are the model predicted data, and O_i are the observed data. The M parameter is the mean difference between measurements and model simulations (Whitmore, 1991):

$$M = \frac{1}{n} \sum_{i=1}^n (O_i - P_i) \quad [12]$$

The CRM parameter is (Loague and Green, 1991):

$$CRM = \frac{\left(\sum_{i=1}^n O_i - \sum_{i=1}^n P_i \right)}{\sum_{i=1}^n O_i} \quad [13]$$

The RMSE and M parameters are both indicators of error and provide insight into quality of fit, whereas the CRM parameter indicates whether the predicted values over- or underestimate the observed values and the extent of that over- or underestimation. When $RMSE = 0$, the predicted values match the observed values, whereas when $RMSE > 0$, the predictions deviate from the observed values. A positive value of CRM indicates that the prediction underestimates the observed

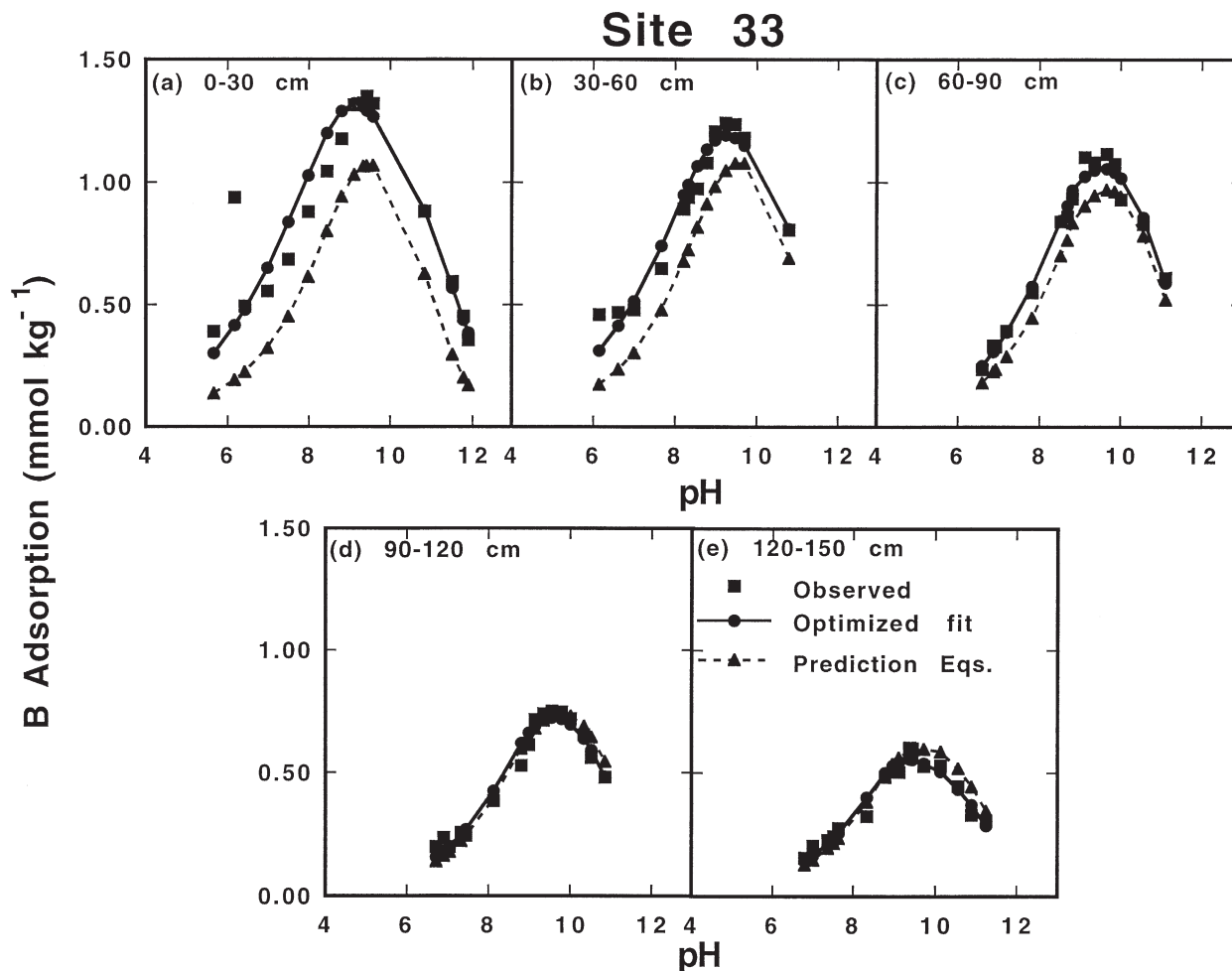


Fig. 3. Constant capacitance modeling of B adsorption on Site 33 of the Lillis soil: a) 0- to 30-cm depth; b) 30- to 60-cm depth; c) 60- to 90-cm depth; d) 90- to 120-cm depth; e) 120- to 150-cm depth. Squares represent experimental data. Model fits are represented by solid lines. Depth-specific model predictions are represented by dashed lines.

value, whereas a negative CRM value indicates that the prediction overestimates the observed value. In other words, CRM does not give an indication of the closeness of individual predicted to observed values but rather the overall tendency of the model to over- or underestimate.

Graphical displays used in this study include B adsorption versus pH and model predicted versus observed B adsorption. Predicted versus observed relationships are informative in establishing the quality of fit of the model because a linear regression and coefficient of determination, R^2 , can be calculated showing the closeness to 1:1 correspondence between experimentally observed and model predicted data.

RESULTS AND DISCUSSION

Boron adsorption as a function of solution pH was determined for 15 arid zone soil samples and is presented for Site 9 in Fig. 2, Site 33 in Fig. 3, and Site 49 in Fig. 4. Boron adsorption envelopes on all samples increased with increasing solution pH, reached an adsorption maximum near pH 9, and decreased with further increases in solution pH. This type of parabolic adsorption envelope is characteristic of B adsorption behavior on soils (Goldberg and Glaubig, 1986a; Goldberg, 1999; Goldberg et al., 2000). Boron adsorption behavior at all three sites was similar. The amount of B adsorption decreased with increasing soil depth as

soil texture became coarser. This trend was probably the result of the decrease in B adsorption sites occurring with decreasing clay content. The apparent increase in B adsorption at low solution pH was likely caused by some uncertainty in the large B-release corrections needed at these pH values. A single outlier apparent in Fig. 3a, indicated a quality control error in the experimental procedure.

The constant capacitance model was fit to the B adsorption envelopes of all soil samples optimizing three surface complexation constants: $\log K_{B-}(\text{int})$ for B adsorption, $\log K_{+}(\text{int})$ for protonation, and $\log K_{-}(\text{int})$ for dissociation. These three constants had been simultaneously optimized previously to describe B adsorption envelopes on soils (Goldberg et al., 2000). Optimized values of the surface complexation constants are provided in Table 2. Figures 2 to 4 indicate the ability of the constant capacitance model to describe B adsorption envelopes on all soil samples by optimizing $\log K_{B-}(\text{int})$, $\log K_{+}(\text{int})$, and $\log K_{-}(\text{int})$ simultaneously. The model provided a quantitative description of the B adsorption envelopes, with a few exceptions, especially at low pH values where there was greater uncertainty in the amount of adsorbed B.

Average values and standard deviations of the three

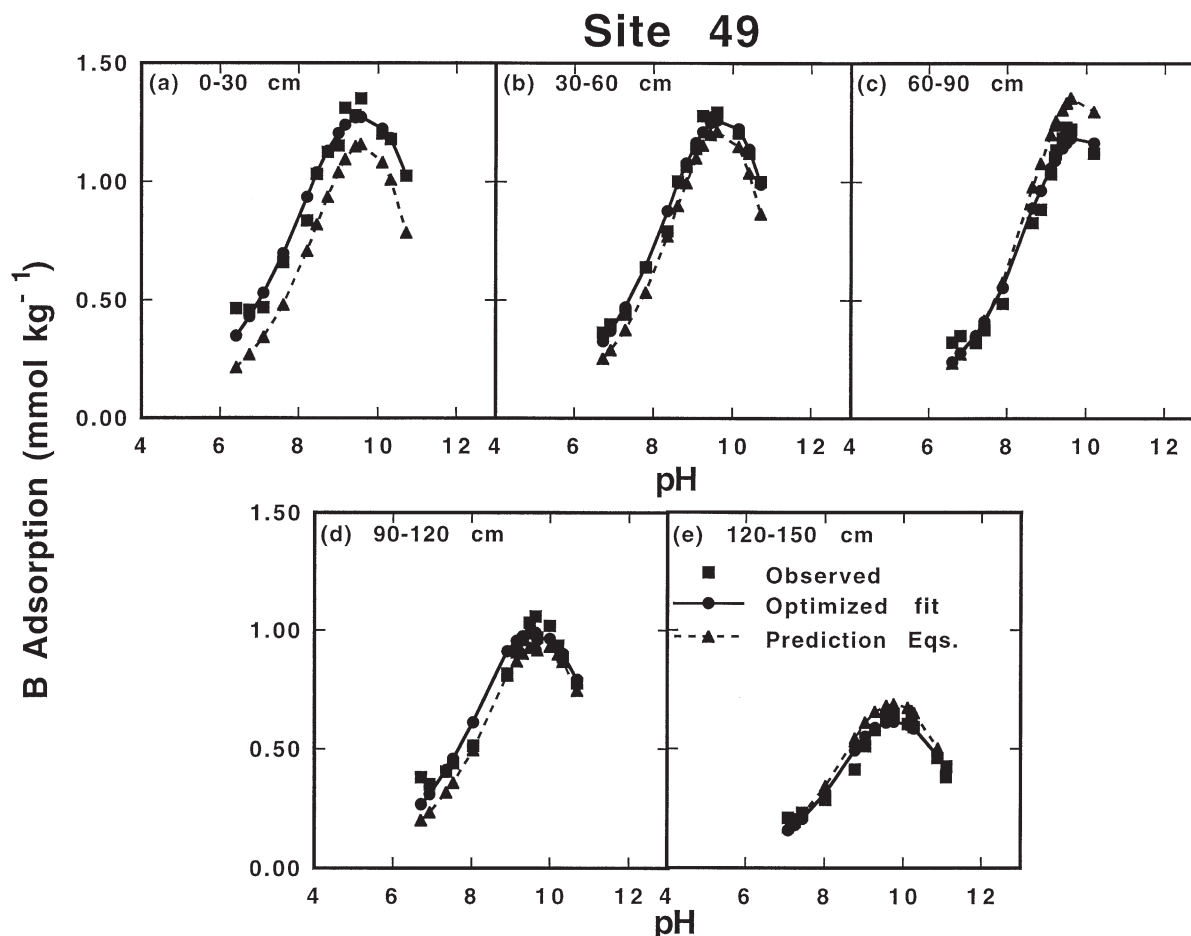


Fig. 4. Constant capacitance modeling of B adsorption on Site 49 of the Lillis soil: a) 0- to 30-cm depth; b) 30- to 60-cm depth; c) 60- to 90-cm depth; d) 90- to 120-cm depth; e) 120- to 150-cm depth. Squares represent experimental data. Model fits are represented by solid lines. Depth-specific model predictions are represented by dashed lines.

Table 2. Surface complexation constants for the constant capacitance model.

| Soil | Depth cm | Optimized | | | From prediction equations | | |
|----------------|---------------------|--------------------|----------------------|---------------------|---------------------------|----------------------|-------------------|
| | | LogK _{B-} | LogK ₊ | LogK ₋ | LogK _{B-} | LogK ₊ | LogK ₋ |
| Site 9 | 0–30 | -8.42 | 8.56 | -12.01 | -8.09 | 7.59 | -11.27 |
| | 30–60 | -8.47 | 8.62 | -12.22 | -8.10 | 7.55 | -11.31 |
| | 60–90 | -8.25 | 8.28 | -11.76 | -8.23 | 7.83 | -11.61 |
| | 90–120 | -8.33 | 8.20 | -11.92 | -8.25 | 7.86 | -11.77 |
| | 120–150 | -8.40 | 8.44 | -12.16 | -8.18 | 7.95 | -11.77 |
| Site 33 | 0–30 | -8.48 | 8.76 | -12.23 | -8.32 | 7.97 | -11.42 |
| | 30–60 | -8.42 | 8.49 | -11.92 | -8.29 | 7.88 | -11.46 |
| | 60–90 | -8.31 | 8.10 | -11.75 | -8.33 | 7.90 | -11.66 |
| | 90–120 | -8.36 | 8.14 | -11.88 | -8.33 | 8.02 | -11.98 |
| | 120–150 | -8.50 | 8.44 | -12.24 | -8.38 | 8.18 | -12.18 |
| Site 49 | 0–30 | -8.26 | 8.24 | -11.86 | -8.19 | 7.79 | -11.35 |
| | 30–60 | -8.12 | 7.92 | -11.60 | -8.09 | 7.67 | -11.36 |
| | 60–90 | -8.32 | 7.87 | -11.72 | -8.14 | 7.57 | -11.42 |
| | 90–120 | -8.37 | 8.29 | -11.98 | -8.33 | 8.03 | -11.79 |
| | 120–150 | -8.35 | 8.16 | -12.17 | -8.26 | 8.07 | -12.01 |
| Average | -8.36 ± 0.10 | 8.30 ± 0.24 | -11.96 ± 0.20 | -8.23 ± 0.09 | 7.86 ± 0.19 | -11.62 ± 0.28 | |

K_{B-} = B surface complexation constant, K₊ = protonation constant, K₋ = dissociation constant.

surface complexation constants are listed in Table 2. The average values of the surface complexation constants optimized in this study were not statistically significantly different at the 95% level of confidence from the average values of these constants determined by Goldberg et al. (2000) for soils: logK_{B-}(int) = -8.23 ± 0.39, logK₊(int) = 8.18 ± 0.65, logK₋(int) = -11.61 ± 0.56.

The standard deviations for the average surface complexation constants in the present study were smaller than those obtained in the previous investigation. This was likely due to the fact that all 15 soil samples were from the same soil series.

The ability of the constant capacitance model to predict B adsorption as a function of solution pH is also

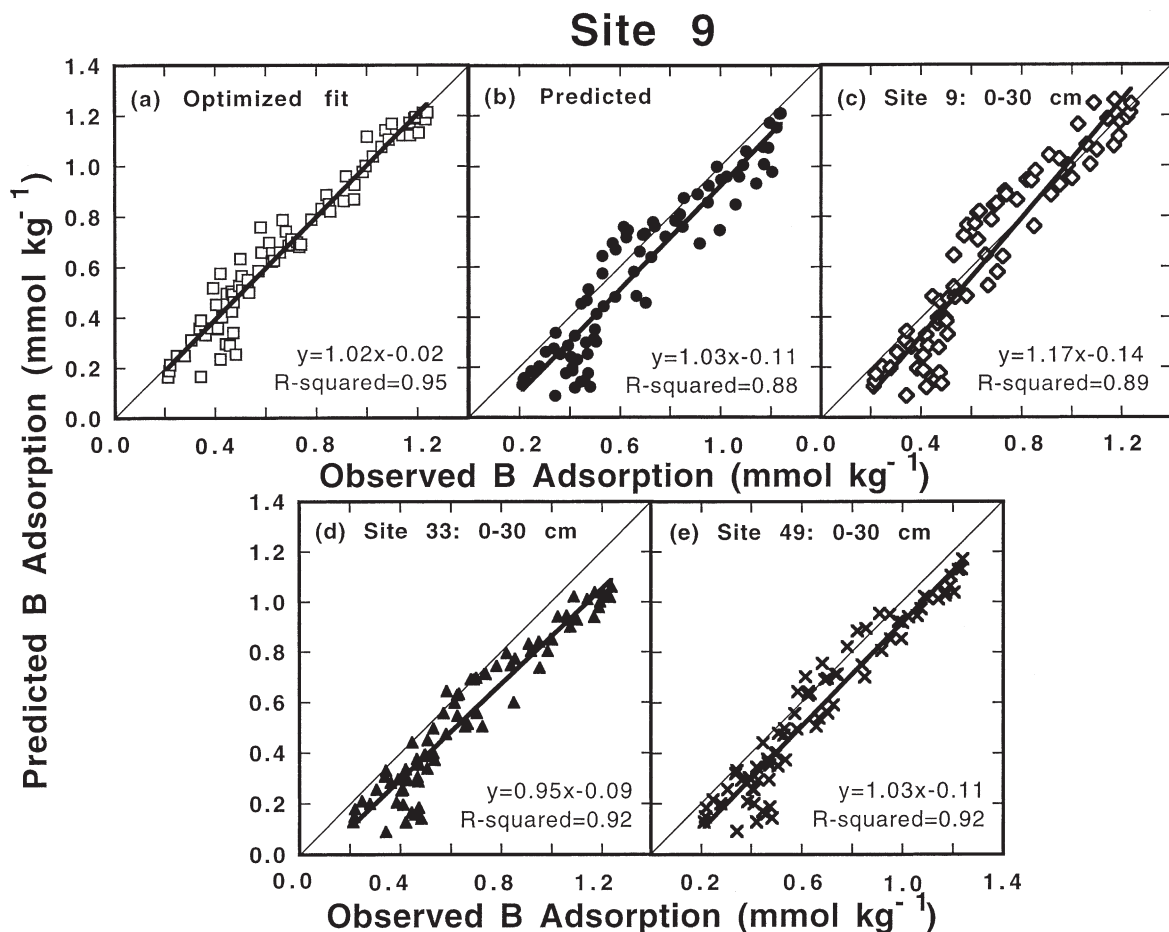


Fig. 5. Model predicted versus experimentally observed B adsorption for Site 9: a) optimized fit, OF; b) predicted from prediction equations for that specific depth, PE; c) predicted using parameters for Site 9 0- to 30-cm depth, PEs9; d) predicted using parameters for Site 33 0- to 30-cm depth, PEs33; e) predicted using parameters for Site 49 0- to 30-cm depth, PEs49.

indicated in Fig. 2 to 4. To obtain the model results, surface complexation constants were calculated after entering the soil chemical properties: SA, OC, IOC, and AI into the prediction Eq. [7] to [9]. These surface complexation constants were subsequently used in the FITEQL program to speciate the chemical system and to predict B adsorption. The dashed lines represent the prediction of B adsorption behavior for each soil depth from its chemical properties (Goldberg et al., 2000). The model predictions (represented by dashed lines and triangles) were very close to the experimental data (represented by squares) considering they were obtained without consideration of any soil specific B adsorption data. The model predictions described the experimental data best at the lower soil depths where clay content, OC content, and Fe content are least. The predictions should be suitable for transport modeling applications. Because the model results were predictions, no model parameters were adjusted or optimized. The surface complexation constants obtained using this prediction approach are listed in Table 2. They are not statistically significantly different from the optimized surface complexation constants or the average surface complexation constants determined by Goldberg et al. (2000) at the 95% level of confidence.

Figures 5 to 7 depict the quality of the fits of the model

B adsorption data versus the experimentally observed B adsorption data. The OFs are shown in Fig. 5a, 6a, and 7a for comparison with the B adsorption data obtained with the prediction equation approaches. Figures 5b, 6b, and 7b represent the quality of the prediction of B adsorption behavior for each individual soil depth from its chemical properties, PE. Figures 5c to 5e, 6c to 6e, and 7b to 7e depict the quality of the model predictions of B adsorption obtained from the FITEQL speciation program using the surface complexation constants predicted from the chemical properties for a particular surface depth and the surface area estimates from clay content using Eq. [10]. For each site, results predicted using the parameters for the surface depths from Site 9, Site 33, or Site 49 are represented by the abbreviations, PEs9 (Fig. 5c, 6c, and 7c), PEs33 (Fig. 5d, 6d, and 7d), and PEs49 (Fig. 5e, 6e, and 7e), respectively.

Of all the approaches, the OF model B adsorption values most closely fit the observed B adsorption data. This result is also indicated in Table 3 where the RMSE and M values for the OF approach were the lowest for each site. Furthermore, for each site, the CRM values for OF modeling were the closest to 0 indicating that the overall underestimation was least for this approach.

All prediction equation approaches, PE, PEs9, PEs33, and PEs49, were able to predict B adsorption based

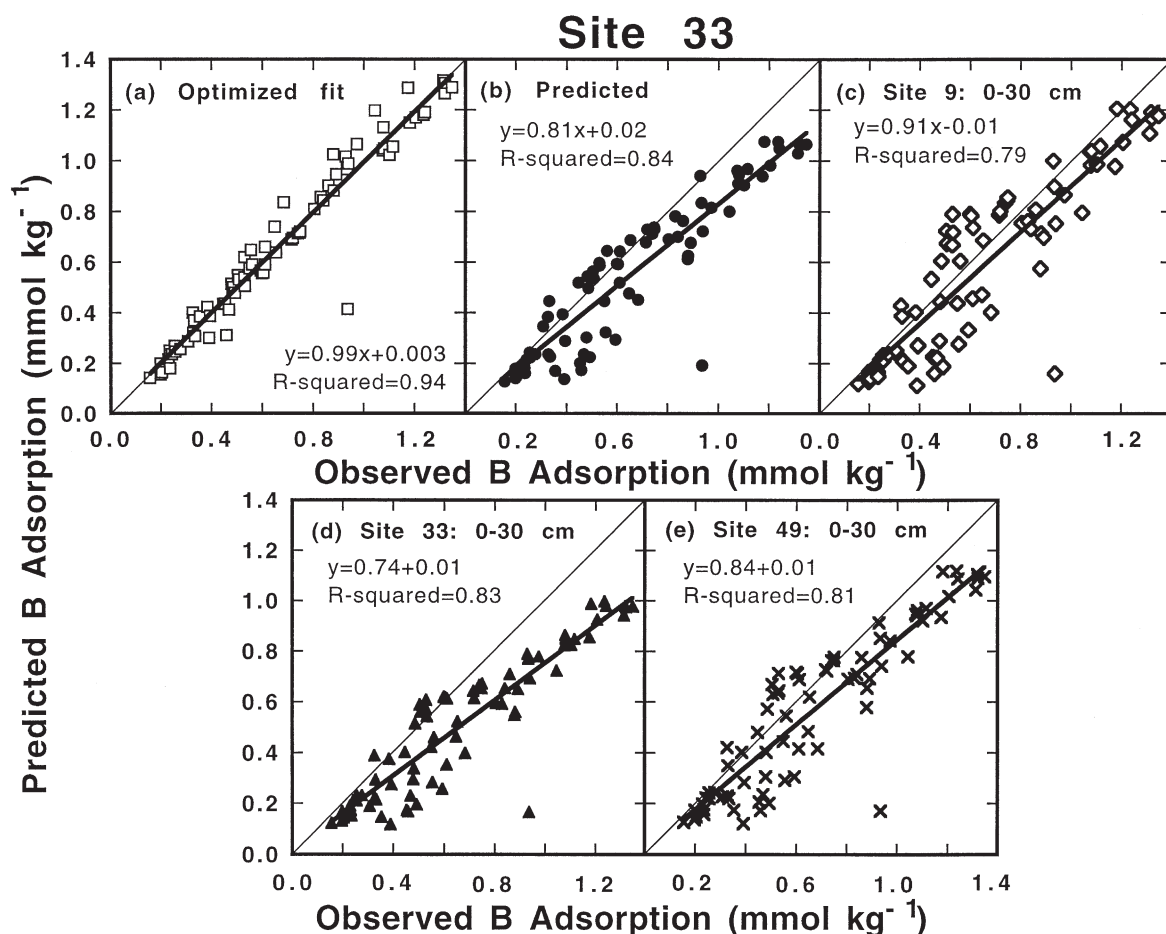


Fig. 6. Model predicted versus experimentally observed B adsorption for Site 33: a) optimized fit, OF; b) predicted from prediction equations for that specific depth, PE; c) predicted using parameters for Site 9 0- to 30-cm depth, PEs9; d) predicted using parameters for Site 33 0- to 30-cm depth, PEs33; e) predicted using parameters for Site 49 0- to 30-cm depth, PEs49.

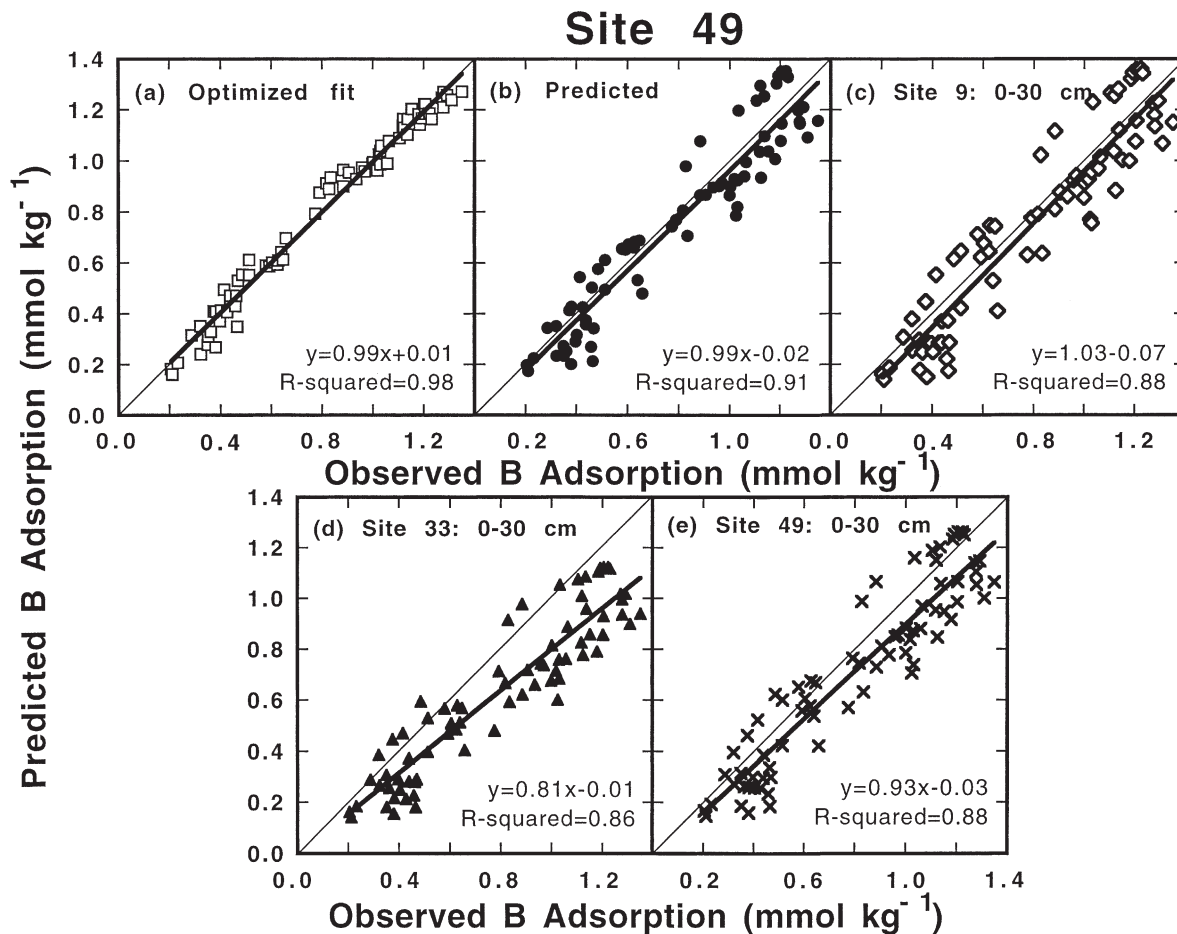


Fig. 7. Model predicted versus experimentally observed B adsorption for Site 49: a) optimized fit, OF; b) predicted from prediction equations for that specific depth, PE; c) predicted using parameters for Site 9 0- to 30-cm depth, PEs9; d) predicted using parameters for Site 33 0- to 30-cm depth, PEs33; e) predicted using parameters for Site 49 0- to 30-cm depth, PEs49.

strictly on soil properties that are considerably easier to measure than conducting adsorption experiments. There was no significant difference in the quality of the fit for the different PE type data sets (Fig. 5b to 5f, 6b to 6f, and 7b to 7f). It is especially encouraging that the

quality of the predictions for PEs9, PEs33, and PEs49 was similar to the soil depth-specific PE result indicating that all soil depths could be represented using the parameters for the surface depth of any of the sites. Comparison of the various PE approaches and their associated RMSE and M values indicated that PEs9 performed the best (see Table 3).

Table 4 provides a more detailed look at the quality of fit of the predicted and observed data based on model performance evaluation parameters for each soil depth increment: 0 to 30, 30 to 60, 60 to 90, 90 to 120, and 120 to 150 cm. Even though there was a slight improvement in the prediction of B adsorption with increased depth, as evidenced by decreasing values of RMSE, this trend was not overwhelming. The most significant fact conveyed by Table 4 is the reasonably good correspondence of predicted and observed B adsorption regardless of depth.

The constant capacitance model was able to describe B adsorption on 15 soil samples from three sites as a function of solution B by optimizing three surface complexation constants, OF. The model was able to predict B adsorption, PE, using surface complexation constants calculated from easily measured chemical parameters using the regression prediction equations pre-

Table 3. Overall statistical criteria for B adsorption data.

| Criterion [†] | Model [‡] | Site 9 | Site 33 | Site 49 |
|------------------------|--------------------|--------|---------|---------|
| RMSE | OF | 0.072 | 0.081 | 0.047 |
| RMSE | PE | 0.145 | 0.172 | 0.116 |
| RMSE | PEs9 | 0.134 | 0.173 | 0.138 |
| RMSE | PEs33 | 0.148 | 0.213 | 0.208 |
| RMSE | PEs49 | 0.126 | 0.176 | 0.152 |
| CRM | OF | 0.005 | 0.003 | 0.002 |
| CRM | PE | 0.130 | 0.160 | 0.042 |
| CRM | PEs9 | 0.045 | 0.102 | 0.057 |
| CRM | PEs33 | 0.179 | 0.239 | 0.204 |
| CRM | PEs49 | 0.133 | 0.151 | 0.112 |
| M | OF | 0.003 | 0.002 | 0.002 |
| M | PE | 0.088 | 0.107 | 0.034 |
| M | PEs9 | 0.031 | 0.068 | 0.045 |
| M | PEs33 | 0.121 | 0.160 | 0.162 |
| M | PEs49 | 0.090 | 0.101 | 0.089 |

[†] RMSE = root mean square error; CRM = coefficient of residual mass; M = mean difference.

[‡] OF = optimized fit; PE = depth-specific prediction; PEs9 = prediction with parameters for Site 9 0- to 30-cm depth; PEs33 = prediction with parameters for Site 33 0- to 30-cm depth; PEs49 = prediction with parameters for Site 49 0- to 30-cm depth.

Table 4. Statistical criteria for B adsorption data by depth.

| | | OF | PE | PEs9 | PEs33 | PEs49 |
|----------------|------|--------|--------|--------|-------|--------|
| Site 9 | | | | | | |
| 0-30 | RMSE | 0.115 | 0.172 | 0.171 | 0.210 | 0.174 |
| | CRM | 0.011 | 0.195 | 0.193 | 0.283 | 0.219 |
| | M | 0.008 | 0.137 | 0.136 | 0.199 | 0.154 |
| 30-60 | RMSE | 0.095 | 0.186 | 0.166 | 0.208 | 0.168 |
| | CRM | 0.004 | 0.203 | 0.169 | 0.260 | 0.195 |
| | M | 0.003 | 0.156 | 0.130 | 0.200 | 0.150 |
| 60-90 | RMSE | 0.036 | 0.183 | 0.100 | 0.125 | 0.125 |
| | CRM | -0.000 | 0.201 | 0.010 | 0.145 | 0.144 |
| | M | -0.000 | 0.169 | 0.009 | 0.122 | 0.121 |
| 90-120 | RMSE | 0.041 | 0.074 | 0.088 | 0.085 | 0.067 |
| | CRM | 0.007 | 0.043 | -0.054 | 0.118 | 0.015 |
| | M | 0.006 | 0.026 | -0.032 | 0.070 | 0.009 |
| 120-150 | RMSE | 0.036 | 0.074 | 0.127 | 0.051 | 0.051 |
| | CRM | 0.003 | -0.058 | -0.145 | 0.056 | 0.056 |
| | M | 0.002 | -0.030 | -0.073 | 0.028 | 0.028 |
| Site 33 | | | | | | |
| 0-30 | RMSE | 0.154 | 0.309 | 0.297 | 0.360 | 0.313 |
| | CRM | 0.007 | 0.330 | 0.302 | 0.396 | 0.333 |
| | M | 0.006 | 0.283 | 0.259 | 0.340 | 0.286 |
| 30-60 | RMSE | 0.068 | 0.191 | 0.161 | 0.232 | 0.175 |
| | CRM | -0.001 | 0.208 | 0.152 | 0.257 | 0.186 |
| | M | -0.001 | 0.185 | 0.136 | 0.229 | 0.166 |
| 60-90 | RMSE | 0.041 | 0.111 | 0.093 | 0.191 | 0.121 |
| | CRM | 0.002 | 0.135 | 0.101 | 0.240 | 0.151 |
| | M | 0.002 | 0.101 | 0.076 | 0.179 | 0.113 |
| 90-120 | RMSE | 0.037 | 0.044 | 0.078 | 0.079 | 0.049 |
| | CRM | 0.004 | -0.002 | -0.065 | 0.126 | 0.006 |
| | M | 0.002 | -0.001 | -0.033 | 0.063 | 0.003 |
| 120-150 | RMSE | 0.033 | 0.052 | 0.136 | 0.054 | 0.095 |
| | CRM | 0.005 | -0.050 | -0.209 | 0.008 | -0.127 |
| | M | 0.002 | -0.019 | -0.082 | 0.003 | -0.050 |
| Site 49 | | | | | | |
| 0-30 | RMSE | 0.056 | 0.181 | 0.218 | 0.330 | 0.255 |
| | CRM | 0.001 | 0.182 | 0.220 | 0.333 | 0.259 |
| | M | 0.001 | 0.176 | 0.212 | 0.322 | 0.251 |
| 30-60 | RMSE | 0.036 | 0.090 | 0.084 | 0.213 | 0.127 |
| | CRM | 0.001 | 0.090 | 0.082 | 0.211 | 0.127 |
| | M | 0.001 | 0.084 | 0.076 | 0.195 | 0.118 |
| 60-90 | RMSE | 0.051 | 0.126 | 0.142 | 0.078 | 0.091 |
| | CRM | 0.004 | -0.111 | -0.135 | 0.021 | -0.077 |
| | M | 0.003 | -0.097 | -0.118 | 0.018 | -0.068 |
| 90-120 | RMSE | 0.056 | 0.084 | 0.115 | 0.229 | 0.152 |
| | CRM | 0.002 | 0.092 | 0.129 | 0.290 | 0.192 |
| | M | 0.001 | 0.070 | 0.098 | 0.221 | 0.146 |
| 120-150 | RMSE | 0.033 | 0.060 | 0.094 | 0.107 | 0.081 |
| | CRM | 0.004 | -0.094 | -0.038 | 0.168 | 0.042 |
| | M | 0.002 | -0.043 | -0.017 | 0.076 | 0.019 |

RMSE = root mean square error; CRM = coefficient of residual mass; M = mean difference; OF = optimized fit, PE = depth-specific prediction; PEs9 = prediction with parameters for Site 9 0- to 30-cm depth; PEs33 = prediction with parameters for Site 33 0- to 30-cm depth, PEs49 = prediction with parameters for Site 49 0- to 30-cm depth.

viously developed (Goldberg et al., 2000). The model was able to predict B adsorption at each soil depth of each site using the surface complexation constants predicted with the chemical properties for any of the surface depths and the surface area estimates from depth specific clay content, PEs9, PEs33, and PEs49.

Although additional corroborative work is needed at other field sites, this study indicates that the prediction equations of Goldberg et al. (2000), Eq. [7] to [9], for surface complexation model constants to describe B adsorption can be generalized for an entire field. The implication is that knowledge of the physicochemical properties of SA, OC, IOC, and AI will be sufficient to estimate surface complexation constants for a field or basin scale. Results indicate that the measured soil properties used to predict surface complexation constants

for B adsorption from Eq. [7] to [9] can be obtained from various locations throughout the field without significantly altering the quality of B adsorption predictions. This indicates that within a given field reasonable estimates of surface complexation constants can be obtained from the measurement of SA, OC, IOC, and AI regardless of depth or position within the field. The impact of this finding is a significant reduction in the need for tedious, costly, time-consuming B adsorption experiments. Our predictions should be suitable for transport modeling applications. Our results will facilitate and simplify the description of B movement on a field scale using chemical speciation-transport models such as UNSATCHEM (Suarez and Simunek, 1997). Simulations and predictions of B concentrations in soil solution of environmental and agricultural interest include irrigation with waters containing large amounts of B and reclamation of soils containing large amounts of B.

ACKNOWLEDGMENTS

Gratitude is expressed to Ms. J. Fargelund, Mr. H.S. Forster, and Mr. J. Jobes for technical assistance.

REFERENCES

- Cihacek, L.J., and J.M. Bremner. 1979. A simplified ethylene glycol monoethyl ether procedure for assessing soil surface area. *Soil Sci. Soc. Am. J.* 43:821-822.
- Coffin, D.E. 1963. A method for the determination of free iron oxide in soils and clays. *Can. J. Soil Sci.* 43:7-17.
- Corwin, D.L., S.M. Lesch, P.J. Shouse, R. Soppe, and J.E. Ayars. 2003. Identifying soil properties that influence cotton yield using soil sampling directed by apparent soil electrical conductivity. *Agron. J.* 95:352-364.
- Elrashidi, M.A., and G.A. O'Connor. 1982. Boron sorption and desorption in soils. *Soil Sci. Soc. Am. J.* 46:27-31.
- Goldberg, S. 1993. Chemistry and mineralogy of boron in soils. p. 3-44. *In* Boron and its role in crop production. U.C. Gupta (ed.) CRC Press, Boca Raton, FL.
- Goldberg, S. 1992. Use of surface complexation models in soil chemical systems. *Adv. Agron.* 47:233-329.
- Goldberg, S. 1999. Reanalysis of boron adsorption on soils and soil minerals using the constant capacitance model. *Soil Sci. Soc. Am. J.* 63:823-829.
- Goldberg, S., and R.A. Glaubig. 1986a. Boron adsorption on California soils. *Soil Sci. Soc. Am. J.* 50:1173-1176.
- Goldberg, S., and R.A. Glaubig. 1986b. Boron adsorption and silicon release by the clay minerals kaolinite, montmorillonite, and illite. *Soil Sci. Soc. Am. J.* 50:1442-1448.
- Goldberg, S., S.M. Lesch, and D.L. Suarez. 2000. Predicting boron adsorption by soils using soil chemical parameters in the constant capacitance model. *Soil Sci. Soc. Am. J.* 64:1356-1363.
- Goldberg, S., D.L. Suarez, N.T. Basta, and S.M. Lesch. 2004. Predicting boron adsorption by Midwestern soils using the constant capacitance model. *Soil Sci. Soc. Am. J.* 68:795-801.
- Herbelin, A.L., and J.C. Westall. 1996. FITEQL: A computer program for determination of chemical equilibrium constants from experimental data. Rep. 96-01. Ver. 3.2, Dep. of Chemistry, Oregon State Univ., Corvallis, OR.
- Keren, R., and F.T. Bingham. 1985. Boron in water, soils, and plants. *Adv. Soil Sci.* 1:229-276.
- Keren, R., F.T. Bingham, and J.D. Rhoades. 1985. Plant uptake of boron as affected by boron distribution between liquid and solid phases in soil. *Soil Sci. Soc. Am. J.* 49:297-302.
- Loague, K., and R.E. Green. 1991. Statistical and graphical methods for evaluating solute transport models: Overview and application. *J. Contam. Hydrol.* 7:51-73.
- Nable, R.O., G.S. Banuelos, and J.G. Paull. 1997. Boron toxicity. p.

- 181–198. *In* B. Dell et al. (ed.) *Boron in soils and plants: Reviews*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Reisenauer, H.M., L.M. Walsh, and R.G. Hoelt. 1973. Testing soils for sulphur, boron, molybdenum, and chlorine. p. 173–200. *In* L.M. Walsh and J.D. Beaton (ed.) *Soil testing and plant analysis*. SSSA, Madison, WI.
- Sposito, G. 1983. Foundations of surface complexation models of the oxide-aqueous solution interface. *J. Colloid Interface Sci.* 91:329–340.
- Suarez, D.L., and J. Simunek. 1997. UNSATCHEM: Unsaturated water and solute transport model with equilibrium and kinetic chemistry. *Soil Sci. Soc. Am. J.* 61:1633–1646.
- Vaughan, P.J., P.J. Shouse, S. Goldberg, D.L. Suarez, and J.E. Ayars. 2004. Boron transport within an agricultural field: Uniform flow versus mobile-immobile water model simulations. *Soil Sci.* 169:401–412.
- Whitmore, A.P. 1991. A method for assessing the goodness of computer simulation of soil processes. *J. Soil Sci.* 42:289–299.