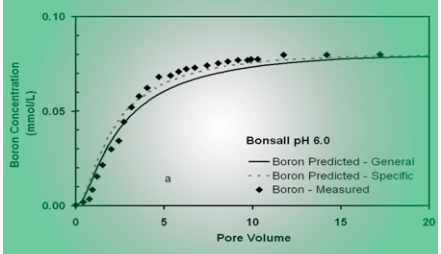
Special Section: Reactive Transport Modeling

D.L. Suarez
J.D. Wood
P.E. Taber, Jr.



Good prediction of B transport for three soils with applied water of pH 6 and 9 was obtained using the UNSATCHEM model with a B constant capacitance model subroutine and prediction of model constants for each soil based on available soil properties. We obtained good predictions without needing to characterize B adsorption properties for each soil.

U.S. Salinity Laboratory, USDA-ARS, 450 W Big Springs Rd., Riverside, CA. *Corresponding author (donald.suarez@ars.usda.gov).

Vadose Zone J.
doi:10.2136/vzj2011.0073
Received 27 June 2011.

Adsorption and Desorption of Boron in Column Studies as Related to pH: Results and Model Predictions

Reuse of agricultural drainage waters, treated municipal wastewaters, and brackish groundwaters is often impaired by elevated concentrations of B. Boron is an element with a narrow concentration range between deficiency and toxicity for plants. Knowledge of the B concentrations in soil solution and transport of B out of the root zone is essential for management of wastewaters. Prediction of B concentrations in the root zone requires consideration of soil adsorption and desorption of B, which are dependent on soil properties and solution composition, especially pH. We examine B transport in soil by first applying a 0.08-mmol L^{-1} B solution to three arid-land soils from southern California and subsequently leaching the soils with a low B solution. The experiment was conducted with irrigation water at pH 6.0 and 9.0. The data showed that transport was highly pH dependent. Results from the column experiments were generally well predicted using the UNSATCHEM transport model with the B subroutine that includes the constant capacitance model and prediction of the model constants for each soil based on the specific soil properties. Use of a single set of average constants for all soils in combination with a calculated surface area provided a less satisfactory fit to the experimental data, especially at elevated pH. These results indicate that B transport can be predicted without the need for time-consuming and soil-specific determinations of B adsorption characteristics if we utilize predictive relations to predict the CCM constants from individual soil properties.

Abbreviations: BTC, breakthrough curve; CCM, constant capacitance model; EGME, ethylene glycol monoethylether; PV, pore volumes.

Boron is an essential plant micronutrient, but there is a narrow range between deficiency and toxicity. Municipal wastewaters are often elevated in B, generally from the input of B-containing detergents. In addition, agricultural drainage waters, as well as many ground waters with elevated salinity, in the western United States and in other arid regions, often contain B concentrations at or above the levels that adversely impact crop yield (0.5–0.2 mmol L^{-1}, Grieve et al., 2012). Knowledge of B mobility is required for prediction of the impact of irrigation with high B wastewaters, recommendations regarding leaching for B management in soils, as well as reclamation of soils high in native B.

Boron adsorption and desorption are essential components to prediction of B transport. Water and solute transport models have utilized K_d coefficients representing the partition of a chemical between the solution and solid phase. This approach requires laboratory analysis but is relatively simple, hence its wide use. The approach has been criticized because K_d has been shown to depend on solution properties, including the concentration of the element to be modeled. Thus, rather than being a constant, K_d may vary orders of magnitude within a system.

Application of Langmuir and Freundlich isotherms are an improved approach over the use of K_d values in that these equations represent the adsorption affinity as a function of the concentration of the adsorbing ion (adsorption envelopes). These equations have been used by various researchers to model B adsorption on soils (Elrashidi and O'Connor, 1982), but they do not address the strong pH dependence of B adsorption and require detailed laboratory characterization of the adsorption behavior of each material. Mezuman and Keren (1981) measured B adsorption isotherms for various soils and several pH levels and developed an expression to represent pH dependence of B adsorption. Use of the model is experimentally demanding as it requires characterization of the adsorption envelope (isotherm) as well as information on the pH dependence (adsorption envelopes) for each

soil. The pH dependence of B adsorption (Mezuman and Keren, 1981; Goldberg and Glaubig, 1986) must be considered for prediction of B adsorption.

Alternatively, functional models can be used to predict B adsorption in soils. The constant capacitance model (CCM), originally developed by Schindler et al. (1976) and Stumm et al. (1980) and incorporated into the FITEQL 3.2 computer program (Herbelin and Westall, 1996) is a chemical model in that it defines surface complexes and considers chemical reactions and mass and charge balance (Sposito, 1983). The CCM has the advantage of having a chemical basis, thus providing the possibility of more robust application to varying soil conditions.

Goldberg and Glaubig (1986) utilized the CCM to characterize the adsorption behavior of B as a function of pH for a series of California soils. Other studies have characterized B adsorption on a variety of naturally occurring materials (Goldberg and Forster, 1991; Goldberg and Glaubig, 1985). These studies all provided a good fit of model predictions of pH-dependent adsorption, but use of the CCM is still limited due to the need for extensive laboratory characterization of the material.

Spectroscopic data indicate that the adsorbing B is a combination of trigonal and tetrahedrally coordinated species, depending on pH (Su and Suarez, 1995). The adsorption of a trigonal species at lower pH is consistent with the prevalence of trigonal boric acid (HBO_3) below pH 9.2 (pK_a of boric acid) and dominance of tetrahedral adsorbed B at higher pH, where tetrahedrally coordinated $H_2BO_4^-$ is the relevant solution species. However, the greater preference is for the tetrahedral species, and when fitting the CCM to experimental data, Goldberg et al. (2000) found no statistically significant improvement in the goodness of fit when the trigonal as well as tetrahedral species was utilized, when compared to fitting adsorption using the tetrahedral species alone. Selecting the surface species as $SH_3BO_4^-$, the surface reaction is written as:

$$SOH + H_3BO_3 \leftrightarrow SH_3BO_4^- + H^+ \quad [1]$$

The intrinsic equilibrium constants are given as (Goldberg et al., 2000)

$$K_+ = \frac{[SOH_2^+]}{[SOH][H^+]}\exp(F\psi/RT) \quad [2]$$

$$K_- = \frac{[SO^-][H^+]}{[SOH]}\exp(-F\psi/RT) \quad [3]$$

$$K_{B-} = \frac{[SH_3BO_4^-][H^+]}{[SOH][H_3BO_3]}\exp(-F\psi/RT) \quad [4]$$

where F is the Faraday constant (C $mol_c L^{-1}$), ψ is the surface potential (V), R is the molar gas constant, T is the absolute temperature (K), and brackets indicate concentrations (mol L^{-1}).

Application of the CCM or other chemical complexation models into transport models has been limited. Model applications have been hampered by the added modeling complexity and the need to have soil-specific characterization and model parameters. These characterizations require time-consuming laboratory studies determining both the adsorption envelopes (adsorption as a function of pH) and the adsorption isotherm (adsorption as related to change in concentration). Version 3.1 of the UNSATCHEM model (Suarez and Simunek, 1997) proposed the use of the CCM for B adsorption with a single set of average soil equilibrium constants and an estimate of the specific surface area of the soil based on clay content and mineralogy.

Goldberg et al. (2000) developed regression equations for the prediction of the three CCM surface complexation constants based on generally available soil properties. The following equations were based on batch equilibrium adsorption experiments conducted with 32 arid-land soils:

$$\log K_{B-} = -9.14 - 0.375\ln(SA) + 0.167\ln(OC) + 0.11\ln(IOC) + 0.466\ln(Al) \quad [5]$$

$$\log K_+ = 7.85 - 0.102\ln(OC) - 0.198\ln(IOC) - 0.622\ln(Al) \quad [6]$$

$$\log K_- = -11.97 + 0.302\ln(OC) + 0.0584\ln(IOC) + 0.302\ln(Al) \quad [7]$$

where SA is the surface area as measured by ethylene glycol monoethylether (EGME), OC is the organic carbon, IOC is the inorganic carbon, and Al is the extractable Al (absorbed, hydroxides and oxides). Using these relationships, Goldberg et al. (2000) satisfactorily predicted the adsorption envelopes (adsorption as a function of pH) for a series of arid-land soils. They concluded that the fits using the CCM with the constants determined from the above predictive equations were acceptable for use in modeling adsorption. Of these properties only the surface area term is not readily available with descriptions of soil properties. Surface area can be directly determined or estimated from the clay content and mineralogy of a soil.

Boron transport in soils has been examined by various researchers. Mahmood-Ul-Hassan et al. (2008) modeled B transport in two calcareous soils using B adsorption values obtained from Langmuir isotherms based on batch sorption studies of the soil. Corwin et al. (1999) simulated B transport in large column experiments, using a series of predictive models, including Freundlich, Langmuir, and pH-dependent adsorption isotherm equations. Communar and Keren (2006) predicted B transport at pH 7 and 9 for three soils

using the batch adsorption isotherms for the soils determined at the same pH values.

Keren and Communar (2009) reported on the enhanced mobility of B when irrigating with treated sewage effluent, attributed to complexation of B with dissolved organic carbon. They predicted B transport after characterizing the soil adsorption behavior in batch experiments at the same pH. A requirement in these approaches is that detailed experimental studies must be undertaken to characterize adsorption on the specific materials examined. Consideration of pH dependence requires experiments to determine adsorption isotherms in addition to other experiments to determine adsorption envelopes.

Application of instantaneous equilibrium approaches to transport problems requires the assumption that adsorption and desorption are reversible processes, and that the rates of adsorption and desorption are sufficiently fast as to neglect consideration of kinetics. Communar and Keren (2006) determined that B transport in soil columns was affected by flow rates; B adsorption was initially slightly greater at flow rates of 0.19 cm h^{-1} as compared to rates at 2.9 cm h^{-1}, (later and steeper breakthrough curve [BTC]). The fit at higher flow rates was improved by addition of a rate-dependent B adsorption expression.

The UNSATCHEM model version 3.1 (Suarez and Simunek, 1997) previously utilized the CCM for B adsorption using average soil model parameters and input of only the specific surface area (EGME) of the soil to be modeled. In UNSATCHEM version 4.1, we have incorporated the predictive equations developed by Goldberg et al. (2000) and reported above (Eq. [5–7]) to calculate the model constants for each soil.

The UNSATCHEM model describes water and solute transport under variably saturated conditions. The model considers prediction of soil solution pH depending on solution alkalinity and CO_2. The CO_2 can be either specified or predicted from CO_2 production and transport routines in the model. The solution chemistry considers solution speciation (including B), cation exchange, precipitation and dissolution of carbonate phases, gypsum and Mg silicates, as well as a CCM submodule used for predicting B adsorption. While developed as a research model, a user friendly version (SWS) is available with default parameters and two sets of boundary conditions, free drainage and specified pressure head on the lower boundary, with specified flux on the upper boundary. This version also has the capability to model B adsorption. A complete description of the transport and chemical routines in UNSATCHEM is available (Suarez and Simunek, 1992) as is a detailed description of the CCM and parameters for B adsorption (Goldberg et al., 2000).

The objective of this study is to evaluate the ability of UNSATCHEM to predict the adsorption and desorption of B in column studies with three arid-land soils irrigated with waters of two different pH values representing the typical range in pH of irrigation waters. We evaluate the model using both average (or generalized) constants as well as the soil-specific constants predicted from the soil properties, as described in Goldberg et al. (2000).

Methods and Procedures

Three soils were selected for evaluation of the ability of the CCM to predict B adsorption and desorption in a flowing column experiment. We utilized surface (0–30 cm) samples of Pachappa (coarse-loamy, mixed, thermic mollic Haploxeralf), Fallbrook (fine-loamy, mixed typic Haploxeralf), and Bonsall (fine montmorillonitic, thermic natric Palexeralf). These are three noncalcareous arid-land soils from southern California with differing clay mineralogy. The Pachappa clay is primarily illite, the Bonsall clay primarily smectite, and the Fallbrook is a mixture of smectite and kaolinite.

The soils were air dried, screened to 5 mm, and packed into 5.3-cm-diameter polystyrene columns to a soil depth of 7.5 cm. The bulk densities expressed in Mg m^{-3} were 1.49 for Pachappa, 1.48 for Bonsall and 1.46 for Fallbrook. Solutions at pH 9.0 were prepared from deionized water with 2 $mmol_c$ L^{-1} of Na^+, HCO_3^-, Mg^{2+}, and Cl^-, and 0.082 mmol L^{-1} of B (as NaH_3BO_3). Solutions at pH 6.0 were prepared with 2 $mmol_c$ L^{-1} of Mg^{2+}, 2 $mmol_c$ L^{-1} of Na^+, 4 $mmol_c$ L^{-1} of Cl^-, and 0.082 mmol L^{-1} of B (as HBO_3). Minor pH adjustment was made with HCl. Hydraulic conductivity was not adversely impacted by these solution concentrations as the sodium adsorption ratio defined as $Na/[(Ca + Mg)/2]^{0.5}$ where concentrations are expressed in millimoles of charger per liter was 2.0 ($mmol_c^{0.5}$).

Soil columns were first saturated from the bottom by capillarity with solutions of Na^+, HCO_3^-, Mg^{2+}, and SO_4^{2-}, and free of Cl^-, B, and Br^-. After saturation the columns were run under saturated (ponded) conditions at flow rates of 0.125 to 0.21 cm h^{-1}. The flow rate was maintained by adjustment of the height of the end of the tube exiting the bottom of the column.

After the adsorption phase with addition of up to 3.1 L of water or almost 20 pore volumes (PV), the columns were stopped for up to 1 d, and the input solution was changed and leaching resumed. The columns were leached at the same pH and with similar solutions for the desorption phase, with the exception that they now contained only 0.008 mmol L^{-1} of B and had added Br^- as a tracer. Chloride was used as a tracer for the adsorption study, and Br^- was used as a tracer for the desorption phase of the experiment. All of the solution draining from the bottom of the columns was captured in a series of sample collection tubes. The solutions were analyzed for pH, electrical conductivity, Cl^- (by argentometric analyzer), Br^- by colorimetric analysis (Marti and Arozarena, 1981), and B by inductively coupled plasma optical emission spectroscopy.

The effluent concentration data are reported in PV corresponding to the midpoint between the starting and final cumulative volume for each sample. The data were converted to PV based on the calculated volumetric porosity. Porosity was calculated from soil mass and soil volume when packed, assuming a soil mineral density of 2.65 Mg m^{-3}.

The soil properties listed in Table 1 were the only data utilized for prediction of the constants in the CCM. The three constants (K_+, K_-, and K_b) were either the generalized or mean values from the soils evaluated by Goldberg et al. (2000) or those calculated based on the specific soil parameters given in Table 1 using the regression equations developed by Goldberg et al. (2000). The earlier UNSATCHEM version 3.1 (Suarez and Simunek, 1997) utilized the trigonal boric acids species rather than the tetrahedral $B(OH)_4$ species now utilized as the adsorbing species; thus, the generalized CCM constants were recalculated.

The water flow characteristics for each soil were based on the descriptions of soil texture. The water flow parameters used in the predictions were initially set as 5 cm for the dispersivity in water and 0.5 cm^2 d^{-1} for the diffusion coefficient. The transport model assumes an instantaneous B equilibrium between the solution and solid phase. The pH of the system was modeled by generation of CO_2 gradients in the column in combination with the input alkalinity. The fits utilize the applied water pH (6.0 and 9.0) at the top boundary and the average pH measured as column effluent. The columns were run in duplicate and the results reported are the average values for all parameters. The PV data were corrected for the volume of water in the exit tube (lack of correction would result in an offset of the breakthrough curves).

Results and Discussion

The Cl^- breakthrough curve is considered to represent water flow because Cl^- adsorption is not significant at these pH values (6–9). We adjusted the model parameters for dispersivity to best match the Cl^- breakthrough. The diffusion coefficient value of 0.5 cm^2 d^{-1} was unchanged, but the dispersivity terms fit to optimize the model predictions for Cl^- and Br^- were 4.0, 2.5 and 0.75 cm for Bonsall, Fallbrook, and Pachappa, respectively. There was no need to alter the dispersivity value for different columns of the same soil. Thus, predictions at different pH and adsorption and desorption were all run with the same water flow parameters.

As seen in Fig. 1a the Cl^- breakthrough curve (BTC) for the Bonsall soil at pH 6.0 (experimental data) was very well matched by the model predicted BTC, as was the Fallbrook Cl^- data for pH 6 columns (Fig. 1b) and the Pachappa Cl^- data (not shown). Also shown in Fig. 1c and 1d, respectively, are the matches for observed and predicted Br^- BTC for Bonsall soil (pH 6) and Br^- for the Pachappa soil, pH 9 (desorption experiment). The data indicated that it required 2.0 PV for the Cl^- concentration to reach 90% of the input value for the Bonsall soil. The sharpness of the predicted front is comparable to the experimental data; thus, the dispersion term and assumption of homogenous media seem reasonable (eliminating the need to consider multiple flow domains). Similar results were observed for the other columns (data not shown).

Omission of the fitting of dispersivity values and dead space at the bottom of the column resulted in poorer fits, but these would still be adequate for field-scale recommendations or predictions (data not shown). After adjustment of the dispersivity term to fit the Cl^- data, flow is sufficiently close to allow for evaluation of the subsequent B transport predictions in terms of chemical rather than physical processes.

The model predictions of B adsorption and transport require information about the pH of the system. Under saturated conditions and flow rates of 0.1 to 0.2 cm h^{-1} the CO_2 concentration in the columns reflects both input CO_2 concentrations and production in the column. As mentioned in the methods section, the model inputs were the irrigation water composition and pH at the upper boundary. The lower boundary pH was taken as the mean effluent pH of the columns. The upper and lower boundary pH was reproduced by use of alkalinity values and adjustment of the CO_2 concentration. The pH within the columns was calculated from the input alkalinity and CO_2, with CO_2 linearly interpolated within the column. As expected the pH 6.0 input solutions increased in pH as they passed through the columns, and the solutions initially at pH 9.0 decreased as they passed through the columns. The mean pH of the effluent solutions for Fallbrook, Bonsall, and Pachappa were 7.9, 7.63, and 7.42, respectively, for the initial pH 6.0 solutions. This increase in pH or lack of equilibrium in the column is attributed to several factors, including a decrease in CO_2 and thus rise in pH related to a slight dissolution of calcite in a closed system (Suarez and Frenkel, 1981), and to buffering of the soil pH by variable charge material, especially organic matter. For the initial pH

Table 1. Chemical properties of soils and calculated constant capacitance model constants.

Soil	Surface area	Organic C	Inorganic C	Al	Clay mineralogy	Log K_B	Log K_+	Log K_-
	m^2 g^{-1}	g kg^{-1}						
Bonsall	32.9	4.7	0.13	0.45	smectite	−8.19	−11.85	8.59
Fallbrok	68.3	3.5	0.0023	0.36	smectite and kaolinite	−8.82	−12.12	9.11
Pachappa	36.3	3.8	0.026	0.67	illite	−8.26	−11.90	8.69
General model	100					−7.97	−11.4	7.62

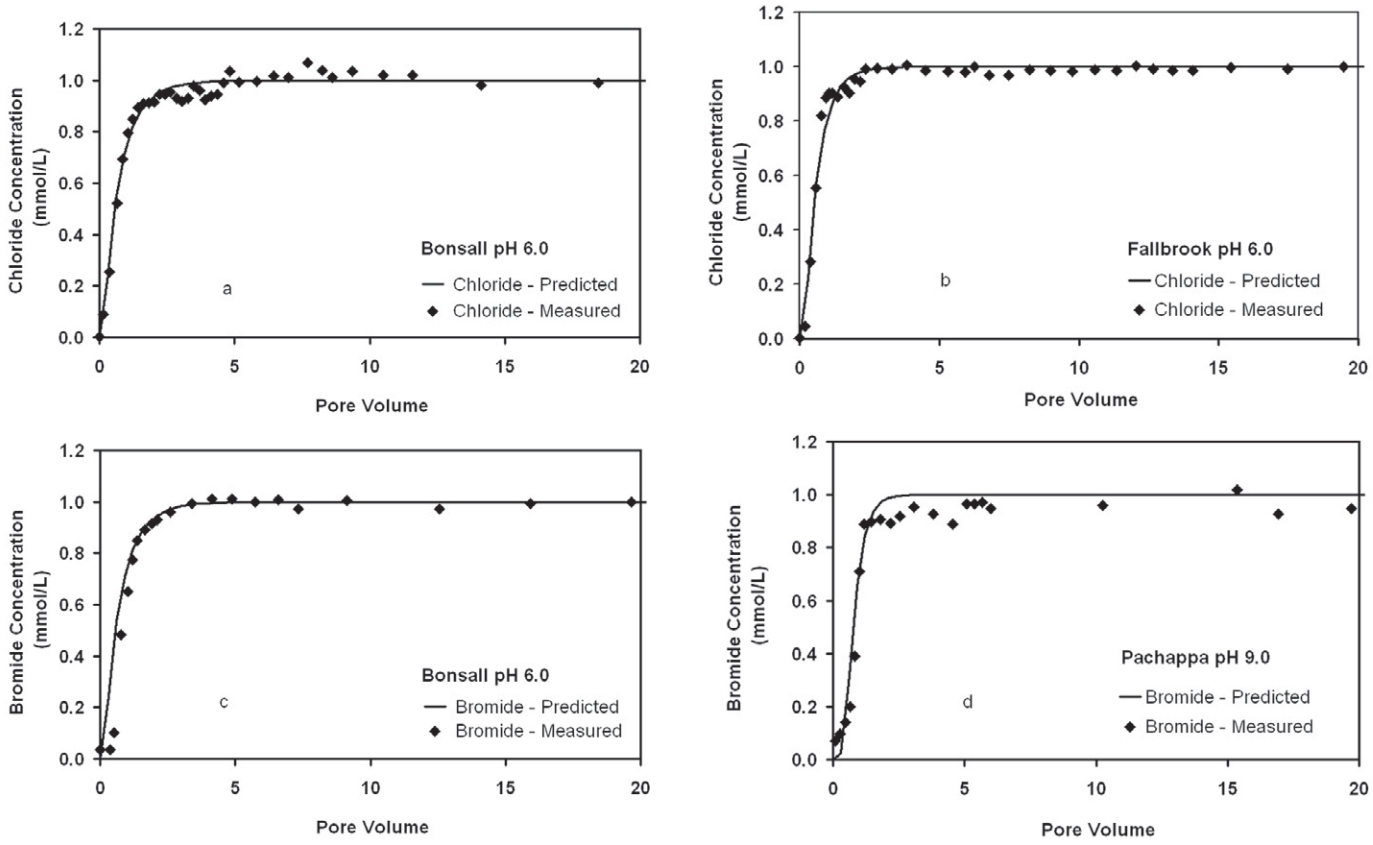


Fig. 1. Comparison of predicted versus observed (a) Cl^- in Bonsall soil at pH 6.0, (b) Cl^- in Fallbrook soil at pH 6.0, (c) Br^- in Bonsall soil at pH 6.0, and (d) Br^- in Pachappa soil at pH 9.0, all as a function of pore volumes of applied water.

9.0 solutions the mean effluent pH values for Fallbrook, Bonsall, and Pachappa were, 8.58, 8.58, and 8.72, respectively, demonstrating a slight increase in CO_2 concentration.

The B concentration in the Bonsall soil column effluent as a function of applied water, expressed in PV, is shown in Fig. 2a for the pH 6 irrigation water. Based on a comparison of Fig. 2a with Fig. 1a, we conclude that it required about 7.2 PV, or 3.6 times as many PV, to achieve 90% of the input concentration for B as it did for Cl^-. This value is slightly above the generally utilized approximation that it takes three times as much water to leach B as compared to salinity.

The model predictions based on parameters calculated by Eq. [5–7] from soil properties (Table 1) were slightly better than the predictions using the general parameters. In both instances they slightly overpredicted the B in the initial portions of the BTC and later slightly underpredicted the B concentration. Both predictions are likely adequate for modeling and management purposes, especially when we consider that no adsorption data were determined or fit for this soil and no calibration or fit was made to match the B data and model predictions.

The B concentration in the Fallbrook soil column effluent as a function of applied water at pH 6.0 is shown in Fig. 2b. It took approximately 6 PV of water to reach 90% of the input B concentration. As shown in Fig. 2b, for Fallbrook soil at pH 6.0, the predictions of B transport using the CCM with soil-specific parameters based on Eq. [5–7] and soil properties in Table 1 were not better than those using the generalized CCM parameters. The soil-specific prediction overestimated the B concentration in the early parts of the BTC and slightly underestimated B in the latter parts. The generalized parameters overestimated B concentrations in the first 2.5 PV.

As shown in Fig. 2c the transport of B in Pachappa soil at pH 6 was somewhat different than for the other two soils, showing a sharper front and less adsorption. The B breakthrough occurred earlier, at 3 PV, only 1.5 times more than water than for Cl^-. The soil-specific parameter model underpredicted adsorption in the region of 0 to 2.5 PV. The experimental BTC was steeper and occurred later than predicted by the soil-specific model, suggesting that either the soil B adsorption capacity (calculated by the model from input site surface density) was underpredicted, or the B affinity slightly underpredicted. In this instance the model predictions were marginally acceptable. The generalized parameter predictions

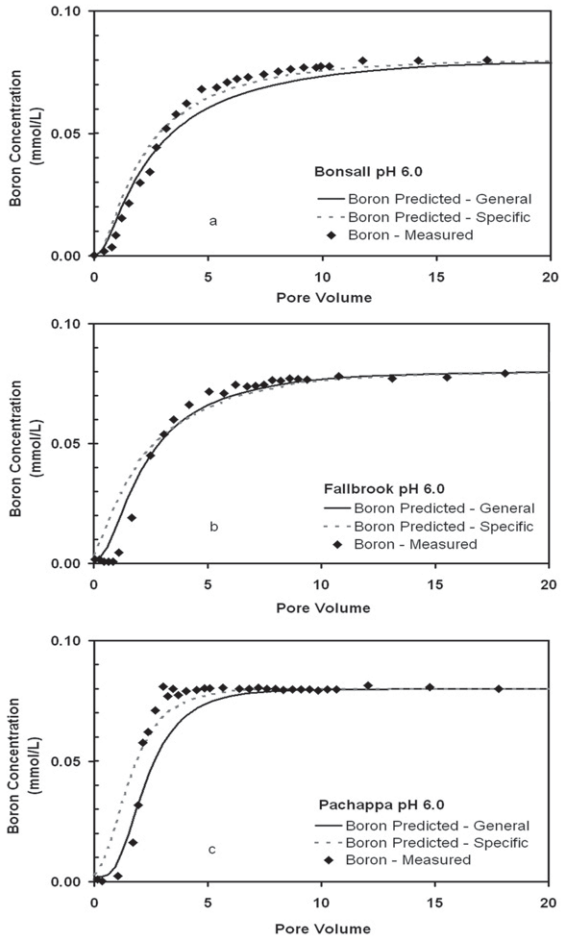


Fig. 2. Comparison of predicted versus observed B movement through (a) Bonsall, (b) Fallbrook, and (c) Pachappa soil as a function of pore volumes of applied water (adsorption) at pH 6.0. The general prediction is based on the average soil constants, while the specific predictions are based on the constant capacitance model constants derived from soil properties in Table 1 and Eq. [5–7].

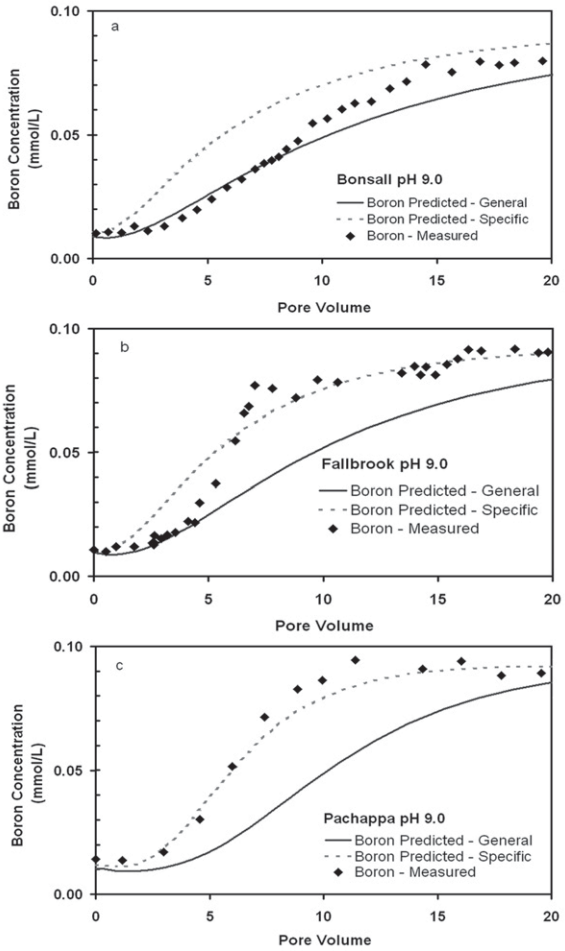


Fig. 3. The predicted pH dependence on B transport in (a) Bonsall, (b) Fallbrook, and (c) Pachappa soil as a function of pore volumes of applied water at pH 9.0. The general prediction is based on average soil constants, while the specific predictions are based on the constant capacitance model constants derived from soil properties in Table 1 and Eq. [5–7].

were satisfactory for the initial 2.5 PV and then underpredicted B concentrations for the remainder of the BTC. The modeling results also predicted the order of B retention by the soils: Pachappa > Fallbrook > Bonsall.

It can be seen that B transport is extremely dependent on pH by comparing the results when applying pH 6.0 water (Fig. 2) and pH 9.0 water (Fig. 3). At pH 9.0 there is greater adsorption than at pH 6.0; thus, all the BTCs occur considerably later. Boron transport in Bonsall soil at pH 9.0 was not well predicted using the soil-specific parameters (Fig. 3a), but satisfactory using the generalized parameters. Fallbrook B transport was satisfactorily predicted using the soil-specific parameters (Fig. 3b), while the generalized model highly underpredicted B transport. In contrast to pH 6, there were large differences in the predictions using the generalized parameters versus the soil-specific parameters. The predictions using the specific soil constants fit the Pachappa, pH 9.0 data very well, while the generalized model predictions were not satisfactory (Fig. 3c).

The desorption of B from the soil columns at pH 6 is shown in Fig. 4 for all three soils. The model predictions for Bonsall were very good for both modeling approaches, but slightly better for the predictions using the soil-specific parameters (Fig. 4a). The Fallbrook predictions for the pH 6 solutions were also very good, with essentially identical predictions for both modeling approaches (Fig. 4b). The Pachappa predictions were very good for the generalized parameters and less accurate but still satisfactory for the soil-specific parameter predictions (Fig. 4c). The faster initial B release may be related to pH fluctuations (decrease in pH) as the flow was suspended and different solutions applied. It appears that model predictions for adsorption and desorption are sufficiently similar so that hysteresis in the adsorption–desorption process does not have to be considered for recently adsorbed B and with moderate flow rates (0.1–0.2 cm h^{-1}). As with the adsorption curves, the order of B retention was: Pachappa > Fallbrook > Bonsall.

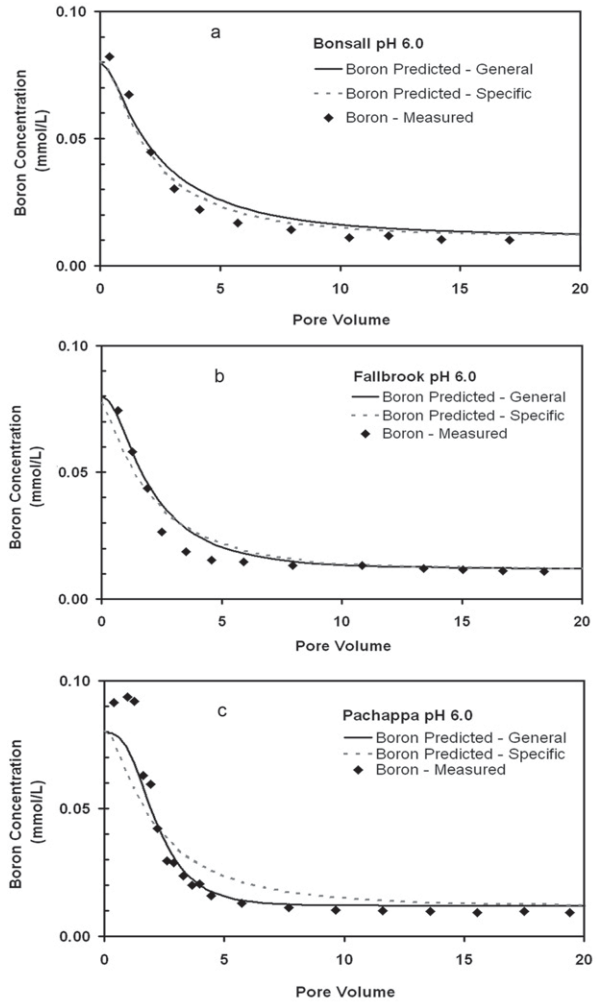


Fig. 4. Comparison of predicted versus observed B movement through (a) Bonsall, (b) Fallbrook, and (c) Pachappa soil as a function of pore volumes of applied leaching water (desorption) at pH 6.0. The general prediction is based on the average soil constants, while the specific predictions are based on the constant capacitance model constants derived from soil properties in Table 1 and Eq. [5–7].

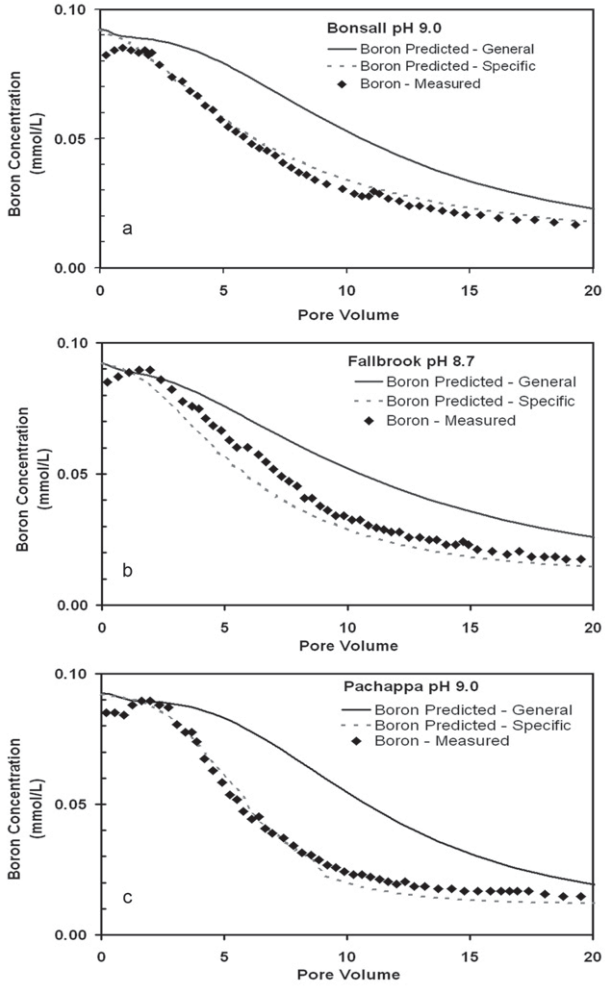


Fig. 5. Comparison of predicted versus observed B movement through (a) Bonsall, (b) Fallbrook, and (c) Pachappa soil as a function of PV of applied leaching water (desorption) at pH 9.0. The general prediction is based on the average soil parameters, while the specific predictions are based on the constant capacitance model constants derived from soil properties in Table 1 and Eq. [5–7].

As shown in Fig. 5, B leaching and transport were much slower at pH 9.0 than at pH 6.0 (compare Fig. 5 to Fig. 4). These results are consistent with the known increased B adsorption at higher pH. As with adsorption, there was a large difference between the generalized and soil-specific model predictions at pH 9.0 as compared to pH 6.0. The generalized model unsatisfactorily overpredicted the B release during desorption (Fig. 5a), while the soil-specific parameters provided an excellent prediction of the data. Similarly, for Fallbrook soil the generalized parameter predictions were not satisfactory, while the soil-specific parameters provided a very good fit to the data (Fig. 5b). For Fallbrook soil at pH 9.0 again the generalized parameter predictions were very unsatisfactory, while the soil-specific parameter predictions were excellent (Fig. 5c).

A major part of the discrepancy between data and model predictions using the soil-specific parameters is likely related to pH variations. The pH inside the soil column was not determined; thus, while the predicted pH based on the linear interpolation of CO_2 may be reasonable, other assumptions could have been made. The predicted pH for the Bonsall soil column leached with pH 6 water is shown in Fig. 6a. Since the water was relatively unbuffered (no added alkalinity) dissolution of trace amounts of calcite in the soil result in a sharp increase in pH. In contrast the more buffered pH 9.0 solutions were predicted to have a smaller change in pH (Fig. 6b).

Model simulations of B transport for Bonsall soil as related to solution pH are presented in Fig. 7a for adsorption and Fig. 7b for desorption. The B transport is very dependent on solution pH as evidenced by the BTC. It required 3 PV to reach 90% of the input B concentration at pH 6 and more than 30 PV at pH 9. These model predictions differ from those presented in the earlier figures in that in this instance we fixed the solution pH in the columns to 6.00, 7.00, 8.00, and 9.00. In contrast, our model predictions of the

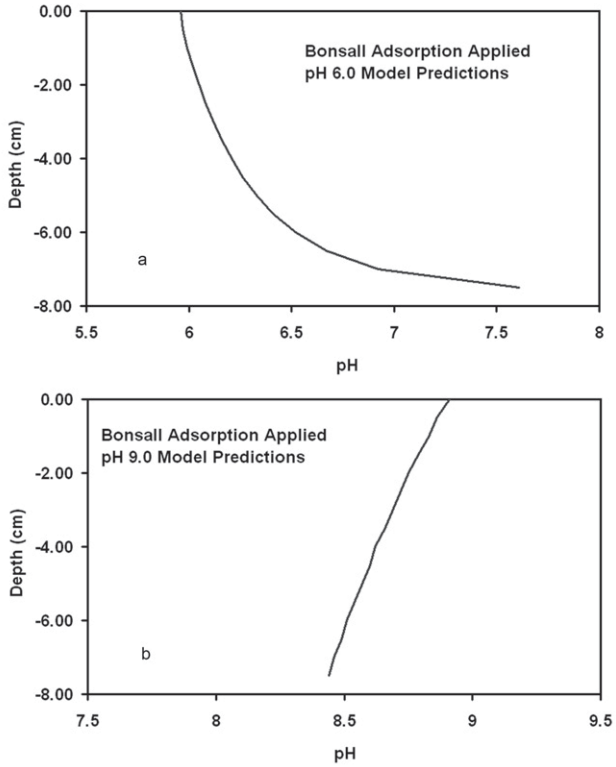


Fig. 6. Predicted pH within the Bonsall soil column for adsorption experiment at (a) pH 6.0 input water and (b) pH 9.0 input water. The pH predictions were generated from input alkalinity and CO_2 at upper and lower boundaries of the column.

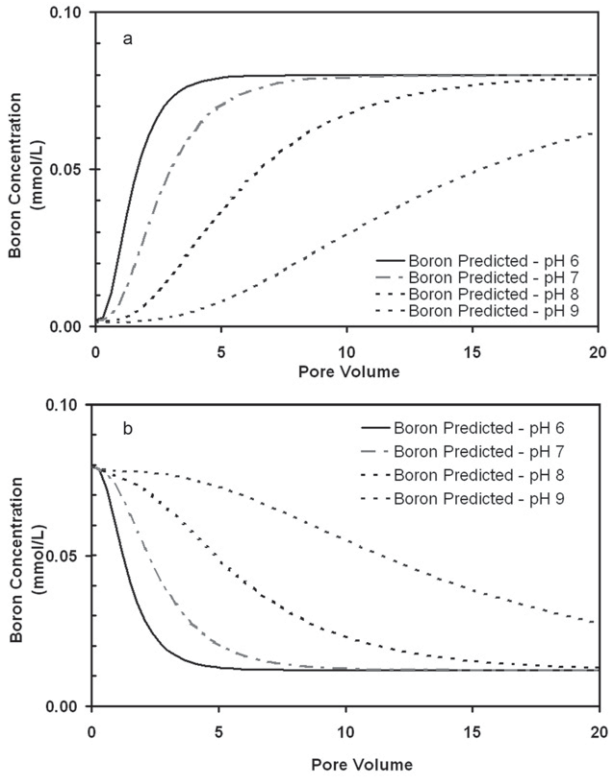


Fig. 7. The predicted pH dependence of (a) B adsorption and (b) B desorption on Bonsall soil, assuming constant pH in the soil and using the constant capacitance model constants derived from soil properties in Table 1 and Eq. [5–7].

BTC considered that the effluent pH was substantially greater for the pH 6.0 experiments (up to 1.6 pH units) and approximately 0.6 pH units lower for the pH 9.0 experiments. In predictions shown in Fig. 7 we utilized the specific parameters calculated for Bonsall soil. At pH 7 the results for desorption are comparable to the simplifying assumption that it takes two to three times as much water to leach B as it does to leach salt (Hoffman, 1980), but this simplification would be in gross error for other pH values and also depends on soil characteristics.

The model simulations reveal the large sensitivity of B transport to pH. The effect of this is evident in Fig. 7. Comparison of the results for the three soils show that they behave in relatively similar fashion, especially at pH 6. Nonetheless the data clearly show, especially at elevated pH, that the use of the soil-specific parameters with the CCM improves prediction of B transport as compared to the generalized parameters. It is likely that the errors seen in the modeling simulation (as compared to the column experimental data) can be explained by the uncertainties in the pH within the column. The changes in the pH in the columns from input to effluent were substantial for the pH 6 experiments and relatively less for pH 9; however, the errors associated with a pH error of 0.5 is much greater at pH 9 than at pH 6 or 7, as shown by Fig. 7. The results of these simulations indicate that B transport cannot be predicted in the absence of accurate pH data.

Conclusions

Overall, B transport during adsorption and desorption in flowing columns from three arid-land soils was very well predicted based on soil-specific parameters and the CCM. The major exception was a poor prediction of adsorption of B on Bonsall soil at pH 9.0. Since desorption was well predicted in all instances, we attribute this failure to the inability to simulate the pH changes in the soil column, especially on initial application of a high pH water (during adsorption). The predictions using the generalized parameters were satisfactory at pH 6.0 but not at elevated pH. The predictions of B transport by the model were similar to the strong dependence on pH observed in the experimental data. Model predictions are considered adequate for field transport studies, without the need to determine the individual adsorption isotherms and envelopes for each soil type or sample. It appears, at least for these soils, that the influence and uncertainty in soil pH on B transport is more important than the specific soil properties of each individual soil. The limiting factor in improving prediction of B transport is accurate prediction of pH, as relatively accurate characterization of the B transport is demonstrated, based on adsorption, from soil parameters and the CCM model of the soil examined.

References

Communar, G., and R. Keren. 2006. Rate-limited boron transport in soils: The effect of soil texture and solution pH. Soil Sci. Soc. Am. J. 70:882–892. doi:10.2136/sssaj2005.0259

Corwin, D.L., S. Goldberg, and A. David. 1999. Evaluation of a functional model for simulating boron transport in soil. Soil Sci. 164:697–717. doi:10.1097/00010694-199910000-00001

Elrashidi, M.A., and G.A. O'Connor. 1982. Boron sorption and desorption in soils. Soil Sci. Soc. Am. J. 46:27–31. doi:10.2136/sssaj1982.03615995004600010005x

Goldberg, S., and H. Forster. 1991. Boron adsorption on calcareous soils and reference calcites. Soil Sci. 152:304–310. doi:10.1097/00010694-199110000-00009

Goldberg, S.R., and R.A. Glaubig. 1985. Boron adsorption on aluminum and iron oxide minerals. Soil Sci. Soc. Am. J. 49:1374–1379. doi:10.2136/sssaj1985.03615995004900060009x

Goldberg, S.R., and R.A. Glaubig. 1986. Boron adsorption on California soils. Soil Sci. Soc. Am. J. 50:1173–1176. doi:10.2136/sssaj1986.03615995005000050016x

Goldberg, S.R., S.M. Lesch, and D.L. Suarez. 2000. Predicting boron adsorption by soils using the soil chemical parameters in the constant capacitance model. Soil Sci. Soc. Am. J. 64:1356–1363. doi:10.2136/sssaj2000.6441356x

Grieve, C.M., S.R. Grattan, and E.V. Mass. 2012. Plant salt tolerance. In: W.W. Wallender and K.K. Tanji, editors, Agricultural salinity assessment and management. 2nd edition. ASCE Manual and Reports on Engineering Practice 71. ASCE, Reston VA. p. 405–459.

Hoffman, G.J. 1980. Guidelines for the reclamation of salt-affected soils. In: G.A. O'Connor, editor, 2nd Inter-American Conference on Salinity and Water Management Technology, Juarez, Mexico. 11–12 Dec. 1980. p. 49–64.

Herbelin, A.L., and J.C. Westall. 1996. FITEQL: A computer program for determination of the chemical equilibrium constants from experimental data. Rep. 96-01, Ver. 3.2. Dep. of Chemistry, Oregon State Univ. Corvallis, OR.

Keren, R., and G. Communar. 2009. Boron transport in soils as affected by dissolved organic matter in treated sewage effluent. Soil Sci. Soc. Am. J. 73:1988–1994. doi:10.2136/sssaj2009.0103

Mahmood-Ul-Hassan, M., M.S. Akhtar, and G. Nabi. 2008. Boron and zinc transport through intact columns of calcareous soils. Pedosphere 18:524–532. doi:10.1016/S1002-0160(08)60043-0

Marti, V.C., and C.E. Arozarena. 1981. Automated colorimetric determination of bromide in water. Paper 734. In: Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ.

Mezuman, U., and R. Keren. 1981. Boron adsorption by soils using phenomenological adsorption equation. Soil Sci. Soc. Am. J. 45:722–726. doi:10.2136/sssaj1981.03615995004500040009x

Schindler, P.W., B. Furst, R. Dick, and P.U. Wolf. 1976. Ligand properties of surface silanol groups. I. Surface complex formation with Fe2+, Cu2+, Cd2+, and Pb2+. J. Colloid Interface Sci. 55:469–475. doi:10.1016/0021-9797(76)90057-6

Sposito, G. 1983. Foundations of surface complexation models of the oxide-aqueous solution interface. J. Colloid Interface Sci. 91:329–340. doi:10.1016/0021-9797(83)90345-4

Stumm, W., R. Kummert, and L. Sigg. 1980. A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces. Croat. Chem. Acta 53:291–312.

Su, C., and D.L. Suarez. 1995. Coordination of adsorbed boron: A FTIR spectroscopic study. Environ. Sci. Technol. 29:302–311. doi:10.1021/es00002a005

Suarez, D.L., and H. Frenkel. 1981. Cation release from sodium and calcium-saturated clay size soil fractions. Soil Sci. Soc. Am. J. 45:716–722. doi:10.2136/sssaj1981.03615995004500040008x

Suarez, D.L., and J. Simunek. 1992. UNSATCHEM code for simulating one-dimensional variably-saturated water flow, heat transport, carbon dioxide production and transport, and multi component solute transport with major ion equilibrium and kinetic chemistry. Tech. Rep. 129. U.S. Salinity Lab., Riverside, CA.

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. doi:10.2136/sssaj1997.03615995006100060014x