Constant Capacitance Model Computation of Boron Speciation for Varying Soil Water Content

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ABSTRACT

This work considered the aqueous speciation of B between a soil solution containing B and the tetrahedral surface B species (SH$_3$ BOH$_4^-$ during drying of the soil. The aqueous B species were boric acid (H$_3$BO$_3$) and the borate anion B(OH)$_4^-$. A computer program was written to calculate solution speciation of major ions using a matrix-type numerical solution including cation exchange and dissolution–precipitation of calcite. The B speciation was calculated separately but utilized the H$^+$ concentration as determined in the major ion speciation. Numerical simulations of soil drying were performed for 20 hypothetical soil textures with clay contents ranging from 10 to 60% and three solution compositions representing saline, saline-sodic, and sodic soils. The effective K_d (SH$_3$BOH$_4^-$/total solution B) decreased with gravimetric water content (θ_g) for the range $\theta_g = 1.5$ to 0.05. A decrease in H$^+$ concentration caused decreasing K_d consistent with earlier experimental work showing decreasing fractional adsorbed B with decreasing pH in the range 7 to 9. K_d varied from 2.5 to 4.7 at $\theta_g = 1.5$ because of variation of the equilibrium constants in the constant capacitance model (K^- and K^+) with varying soil texture. K_d increased with increasing sodicity of the soil water. An application of this program would be prediction of adsorbed and solution B concentrations at field water content on the basis of experimental determinations of adsorbed and solution B concentration for saturated paste extracts. Such predictions would be useful to generate initial conditions for solute transport modeling and for determining whether solution B concentrations at field water contents would be beneficial or harmful to plants.

THE OCCURRENCE AND TRANSPORT of B in the vadose zone has long been of interest due to environmental concerns and its agroeconomic importance. Considering transport, the relevant forms of B are soil solution species and sorbed B on surfaces of various minerals and organic matter (Goldberg, 1997). The objective of our work was to develop a method for calculating the speciation of B for varying soil water content. This is relevant to further understanding of the phytotoxicity of B and to developing a method for extrapolating the determination of soil B concentration in saturation paste extracts to lower water contents characteristic of field conditions. Such extrapolations could be applied to specification of initial conditions for modeling transport of B in soils. In the interest of generality, the program we have developed for B speciation can also be used to calculate the water content dependence of the concentration of other chemical species that are commonly present in soils.

The toxic effect of soil B on plants operates through the soil solution, as determined by experiments with varying soil solution B content at "field capacity" water content (Keren et al., 1985). The range of tolerance for both sensitive and tolerant plants to soil solution B concentration is 0.028 to 1.39 mmol L^{-1}. Plants are not sensitive to adsorbed B. Adsorption of B on clay minerals, calcite, and organic matter in soil reduces B in soil solution and, therefore, its availability to plants. As pH is increased, the adsorption of B by soils increases. Conversely, the lowering of soil pH in the range 7 to 9 increases the availability of B, potentially inducing B toxicity effects in plants (Goldberg, 1997; Keren et al., 1985; Goldberg and Glaubig, 1986; Bingham et al., 1971). Adsorption–desorption reactions are primarily responsible for controlling soil B concentrations, as compared with other types of chemical reactions involving B (Goldberg, 1997).

Boron adsorption and desorption reactions have been modeled by several tools, including the Langmuir and Freundlich isotherms (Rhoades et al., 1970; Fleet, 1965), the Keren equation (Keren and Mezuman, 1981), and the constant capacitance model (Goldberg, 1997). Nonequilibrium models describing hysteresis in the adsorption–desorption reactions include characterization of the kinetics of B desorption (Griffin and Burau, 1974) and evaluation of adsorption–desorption rate constants (Keren and Sparks, 1994). Boron adsorption–desorption reactions in hysteretic soils were modeled by separate sets of Freundlich parameters for each type of reaction (Elrashidi and O'Connor, 1982). Drying of montmorillonite suspensions substantially increased adsorption of B at a fixed pH compared with nondried systems (Keren and Gast, 1981). Keren and Gast also found decreases in adsorption of B on montmorillonite with decreasing pH in the range 7 to 9.

Variation in soil water B concentration with varying water content was calculated using a nonreacting model and an adsorption model (Mezuman and Keren, 1981). The nonreacting model merely displayed the concentrating effect of water removal, whereas the adsorption model indicated substantial adsorption of B and only a minor increase in solution B concentration. These calculations relied on the assumptions of equilibrium and constant solution pH. The equilibrium assumption can be considered reasonable for nonhysteretic soils, but the constant pH assumption may not be valid during drying of most soils. We examine a soil drying simulation in which pH is calculated by a generalized speciation model to evaluate the combined effects of varying pH and dilution on prediction of B speciation by the constant capacitance model.

P.J. Vaughan and D.L. Suarez, George E. Brown, Jr. Salinity Laboratory, USDA-ARS, 450 W. Big Springs Road, Riverside, CA 92507. Received 16 Sept. 2002. Original Research Paper. *Corresponding author (pvaughan@ussl.ars.usda.gov).
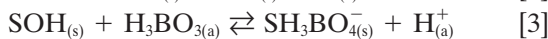
METHODS

A computer program was prepared to calculate the speciation of B under varying water content. This program utilized a matrix-type solution for major species that included solution speciation, dissolution–precipitation of calcite, and cation exchange for Ca^{2+}, Mg^{2+}, Na^+, and K^+ (Vaughan, 2001). Cation exchange was calculated using Gapon selectivity coefficients (Robbins et al., 1980; Vaughan, 2001). The selectivity coefficient values were $K_1 = 0.63$, $K_2 = 2.4$, and $K_3 = 0.36$, utilizing the coefficient definitions: $K_1 = (Ca)^{1/2}X_{1/2Mg}/[(Mg)^{1/2}X_{1/2Ca}]$, $K_2 = (Na)X_{1/2Ca}/[(Ca)^{1/2}X_{Na}]$, $K_3 = (K)X_{1/2Ca}/[(Ca)^{1/2}X_K]$ (Robbins et al., 1980). All calculations were made with a fixed partial pressure of CO_2 set to 3.65×10^{-5} MPa representing atmospheric conditions.

Activity coefficients were calculated by the Pitzer equations (Pitzer, 1979). The program first calculated the bulk composition and, subsequently, concentration of all soil solution and exchange species for the current water content. Water content reduction occurred by drying (removal of water without removal of any dissolved component). Successive iteration between the calcite dissolution–precipitation routine and the main speciation routine was continued until the ratio of the ion activity product for calcite in solution to the calcite solubility product was unity within a tolerance of 10^{-5}.

Boron speciation was calculated separately utilizing the constant capacitance model (Goldberg et al., 2000; Schindler et al., 1976). The adsorption of B is known to control B solubility in the soil because other sources of B are either too inert, as in the mineral tourmaline, or have very high solubility (Goldberg, 1997). The B species presumed present in solution were boric acid (H_3BO_3) and the tetrahedral borate anion [$B(OH)_4^-$].

Characterization of the B surface species for soils is less certain than the solution species. Both trigonal and tetrahedral coordination have been identified for B sorbed on allophane (Su and Suarez, 1997). A statistical study of 32 arid-zone soils indicated that representing sorbed B with exclusively tetrahedral coordination provided an adequate optimization of the reaction constants (Goldberg et al., 2000). In contrast, the representation of sorbed B in the trigonal form only provided adequate optimization of the reaction constants for two out of the 32 soils. Furthermore, no improvement of the fit was obtained when optimization was performed for both forms as compared with solely for the tetrahedral form. Thus, for these 32 soils, the sorbed B was best represented as the tetrahedral surface species $SH_3BOH_4^-$ (Goldberg et al., 2000). On this basis a numerical solution was developed to calculate equilibrium between $SH_3BOH_4^-$ and solution species $B(OH)_4^-$ and H_3BO_3 using the constant capacitance model.

The equations of the constant capacitance model represent the reactions:

$$SOH_{(s)} + H_{(a)}^+ \rightleftarrows SOH_{2(s)}^+ \quad [1]$$
$$SOH_{(s)} \rightleftarrows SO_{(s)}^- + H_{(a)}^+ \quad [2]$$
$$SOH_{(s)} + H_3BO_{3(a)} \rightleftarrows SH_3BO_{4(s)}^- + H_{(a)}^+ \quad [3]$$

in which "s" represents surface and "a" aqueous species The intrinsic equilibrium expressions for these reactions (Goldberg et al., 2000) are

$$K_+^i = \frac{[SOH_2^+]}{[SOH][H^+]}\exp(F\psi/RT) \quad [4]$$

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

$$K_{B-}^i = \frac{[SH_3BO_4^-][H^+]}{[SOH][H_3BO_3]}\exp(-F\psi/RT) \quad [6]$$

where F is the Faraday constant (C mol_c^{-1}), ψ is surface potential (V), R is the gas constant (J mol^{-1} K^{-1}), and T is temperature (K). These intrinsic equilibrium constants were estimated utilizing fits that were based on the presumption that the surface species was tetrahedral (Goldberg et al., 2000). All results reported here are consistent with this assumption.

Additional constraints required to solve these equations are provided by mole balance of the surface sites and B (Goldberg et al., 2000).

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + [SH_3BO_4^-] \quad [7]$$
$$[B_T] = [H_3BO_3] + [B(OH)_4^-] + [SH_3BO_4^-] \quad [8]$$

Charge balance on the surface was calculated as

$$\sigma = [SOH_2^+] - [SO^-] - [SH_3BO_4^-] \quad [9]$$

where σ is the net surface charge (mol L^{-1}). Surface potential (ψ) is related to surface charge by $\sigma = CSa\psi/F$, where C is the capacitance density (F m^{-2}), S is the specific surface area (m^2g^{-1}), and a is the suspension density (g L^{-1}). The solution speciation between H_3BO_3 and the tetrahedral borate anion, $B(OH)_4^-$, was calculated from the equilibrium expression

$$K_a = \frac{(B[OH]_4^-)(H^+)}{(H_3BO_3)(H_2O)} \quad [10]$$

Combining Eq. [4] through [10] results in a pair of nonlinear equations and two unknowns, $[SOH_2^+]$ and $[SO^-]$. These two equations were solved numerically using a modified Newton–Raphson technique with an analytical Jacobian. The related species concentrations were calculated directly from the results. The H^+ concentration, determined from the main speciation calculation, was provided as an input to the separate B speciation calculation.

The main program reduced gravimetric water content steadily from a value of 1.5 to 0.05. This minimum water content was selected as an endpoint to study the calculated speciation as the water content approached that of a very dry soil. Speciation was calculated for 85 different water contents between the two endpoints.

Three initial solution compositions representing saline, sodic, and saline-sodic soils were tested (Table 1). The cation exchange capacity (CEC, $mmol_c$ kg^{-1} soil) was calculated by the empirical expression for an Entisol:

$$CEC = 27.47 + 4.95 \times Clay + 24.13 \times OC \quad [11]$$

where Clay refers to clay content (%) and OC is the organic C (%, w/w) (Manrique et al., 1991). The soil texture was varied to provide a range of CEC values (Table 2).

RESULTS AND DISCUSSION

The concentrations of both the solution species, H_3BO_3 and $B(OH)_4^-$, and adsorbed B, $SH_3BO_4^-$, increased as the water content declined because of the concentrating effect of drying. Because we were primarily concerned with the relationships between solution B and the surface species, all relevant graphs display total solution B (mmol L^{-1}). It should be noted, however, that all calculations solved the entire B speciation problem.

Numerical Accuracy

The B speciation calculations were highly accurate, with mole balance of B accurate to 10^{-10} mmol L^{-1}. Recovery of the equilibrium constants for B speciation by calculating the equilibrium constant from the concen-

Table 1. Soil solution composition at $\theta_g = 1.5$.

ID†	Ca	Mg	Na	K	HCO₃	SO₄	Cl	NO₃	H₃BO₃
	mmol_c L⁻¹								mmol L⁻¹
1	20.0	10.0	15.0	0.5	1.0	30.0	10.0	4.5	0.15
2	4.0	0.5	12.0	0.0	2.5	4.0	9.0	1.0	0.15
3	10.0	6.0	30.0	0.5	2.0	22.0	20.0	2.5	0.15

† 1, saline; 2, sodic; 3, saline-sodic.

trations resulted in a maximum relative error of 1×10^{-6} for K_+. The maximum relative error for either K_- or K_{B-} was $<2.4 \times 10^{-16}$. Recovery of the intrinsic equilibrium constants for the secondary species (H^+, OH^-, CO_3^{2-}, and ion pairs $CaCO_3$ and $MgCO_3$) gave a maximum relative error of 8.0×10^{-3} that occurred during simulation of sodic conditions. The Gapon selectivity coefficients were reproduced with a maximum relative error of 1×10^{-3} occurring for the Ca–Na exchange. The maximum mole balance error was 2.3×10^{-3} mmol L⁻¹. Both the selectivity coefficient and mole balance error maxima occurred in the simulation of sodic conditions.

Computed Effective K_d

The effective distribution coefficient (K_d) is defined here as the ratio $SH_3BO_4^-$/total solution B. In all numerical experiments K_d decreased with decreasing water content (Fig. 1). One factor causing this decrease was the increase in H^+ concentration as the soil dried (Fig. 2). Considering Eq. [6], effective K_d would be expected to decrease with increasing H^+ concentration. The decrease in K_d was also consistent with measurements of the B adsorption envelope for soils that show an increase in adsorbed B with increasing pH in the range 7 to 9 (Bingham et al., 1971; Mezuman and Keren, 1981; Goldberg et al., 1993a). In an actual soil there may be other reactions occurring during drying that could also affect K_d.

For the soil solution compositions utilized in this study a minimum in solution pH occurred for θ_g near 0.07

(Fig. 3). Further extrapolation of the calculation to water contents below 0.05 confirmed this minimum. The computed increase in pH with decreasing water content under very dry conditions was due to a rapidly decreasing activity coefficient. The increasing pH, however, did not cause an increase in the effective K_d because K_d was calculated using H^+ concentration as specified in Eq. [4] through [7] (Fig. 1).

If B deficiency in plants is a problem, it is more likely to occur during dry conditions in the summer (Fleming, 1980). This appears to be an anomaly considering that B desorption with increasing temperature at constant pH was found for an arid zone soil (Goldberg et al., 1993b). In addition, the current calculations indicate that increasing H^+ concentration is likely to provide increased concentration of B in soil water as soils dry out during the summer. Despite these effects, the reduction in water available to plants may be the root cause of B deficiency for these conditions because plant roots would be forced to extract water from deeper horizons where B concentrations are likely to be smaller (Fleming, 1980).

Another significant feature of the computed results was the spread in K_d values at the starting water content ($\theta_g = 1.5$). These starting K_d values were strongly correlated with the intrinsic equilibrium constant K_- (Fig. 4, $r^2 = 0.89$). They are also negatively correlated with K_+. This would be expected due to the strong negative correlation between K_- and K_+. Correlation between K_d and K_{bm} was not significant for the set of calculations

Table 2. Texture.

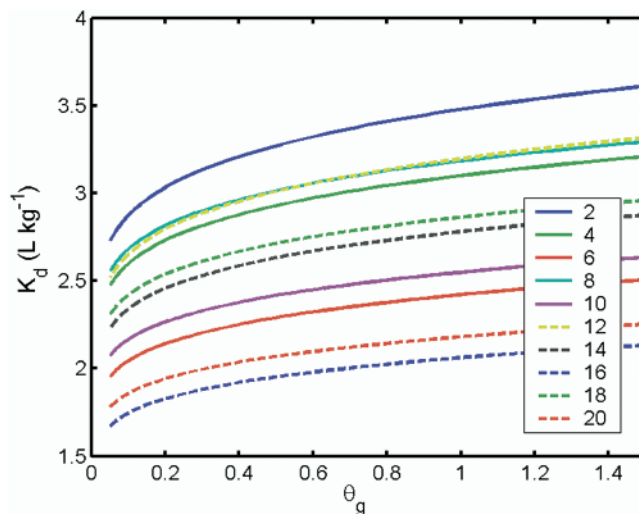| ID	Depth	Sand	Silt	Clay	CEC
	m	%			mmol_c kg⁻¹
1	0.3	10	30	60	173.0
2	0.3	20	30	50	147.0
3	0.3	30	30	40	121.0
4	0.3	40	30	30	95.0
5	0.3	50	30	20	70.0
6	0.3	60	30	10	44.0
7	0.3	50	10	40	121.0
8	0.3	60	10	30	95.0
9	0.3	70	10	20	70.0
10	0.3	80	10	10	44.0
11	1.5	10	30	60	169.0
12	1.5	20	30	50	143.0
13	1.5	30	30	40	118.0
14	1.5	40	30	30	92.0
15	1.5	50	30	20	66.0
16	1.5	60	30	10	40.0
17	1.5	50	10	40	118.0
18	1.5	60	10	30	92.0
19	1.5	70	10	20	66.0
20	1.5	80	10	10	40.0

Fig. 1. Effective K_d decreases with decreasing gravimetric water content (θ_g) for saline water composition. Numbers represent textures given in Table 2.
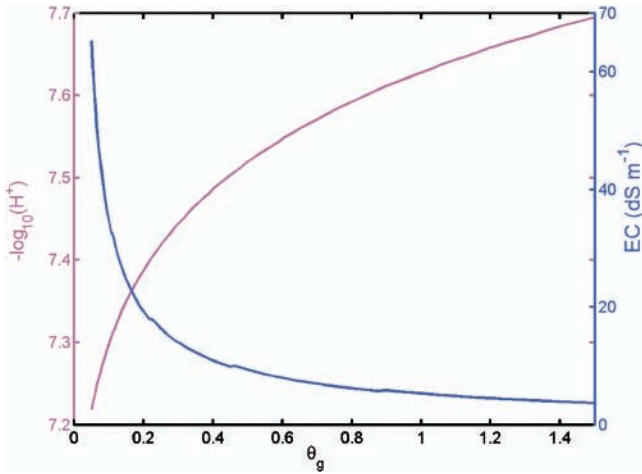
Fig. 2. Variation of H⁺ concentration and electrical conductivity (EC) with gravimetric water content (θ_g) for saline water composition. Calculated H⁺ concentration was not affected by variations in soil texture.

Fig. 4. Effective K_d at $\theta_g = 1.5$ vs. the intrinsic equilibrium constant K_-, for saline water composition.

performed here ($r^2 = 0.02$). These results suggest that improving accuracy in the estimation of K_- and K_+ would result in a greater improvement in the determination of K_d.

The maximum concentration of $SH_3BO_4^-$ approaches a fixed value that is constrained by the site density (Fig. 5). In contrast, the H_3BO_3 concentration increases continuously as θ_g approaches 0.01. Thus, the effective K_d function approaches zero as θ_g approaches zero (Fig. 6).

Increasing sodicity of the soil solution composition caused an increase in solution K_d (Fig. 7). The exchangeable sodium percentage (ESP) at saturation paste water content was 8.8 for saline, 19.4 for sodic, and 21.9 for saline-sodic soil water. The electrical conductivity (EC) was 7.7 dS m⁻¹ for saline, 3.6 for sodic, and 9.7 saline-sodic soil water. The combination of high ESP and low EC in the sodic soil water resulted, consistently, in the highest K_d values of the three soil water compositions.
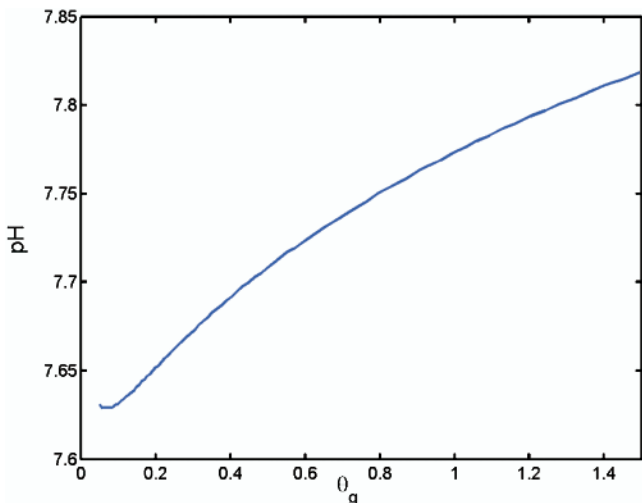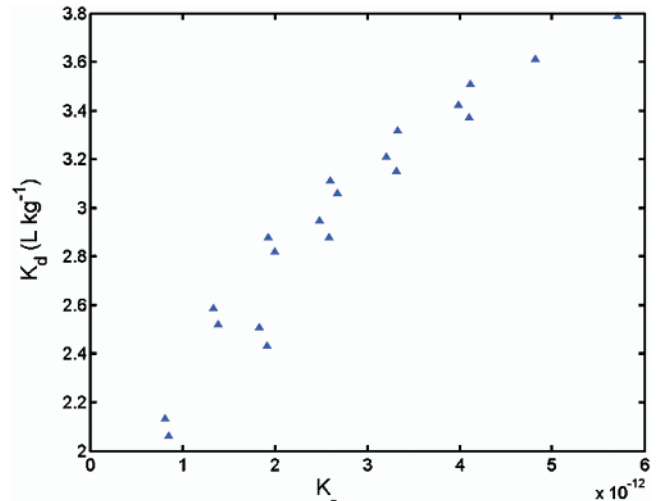
The results reported here concern how adsorbed and

solution B concentrations vary with changing water content as predicted by the constant capacitance model. This model is an equilibrium model and may not adequately represent adsorption–desorption of B in situations where hysteresis in the adsorption and desorption reactions is significant. Furthermore, other processes may be occurring during drying of a soil that would not be represented by the model.

Application

A computer program was developed to predict chemical speciation for B at varying water content on the basis of the constant capacitance model. As an example of how a prediction of this kind might be applied, consider a chemical transport model for B to be applied to a field data set. All transport models require either data or an assumption concerning the initial conditions. The initial conditions for B consist of concentrations of adsorbed ($SH_3BO_4^-$) and solution B (H_3BO_3 and $B(OH)_4^-$)
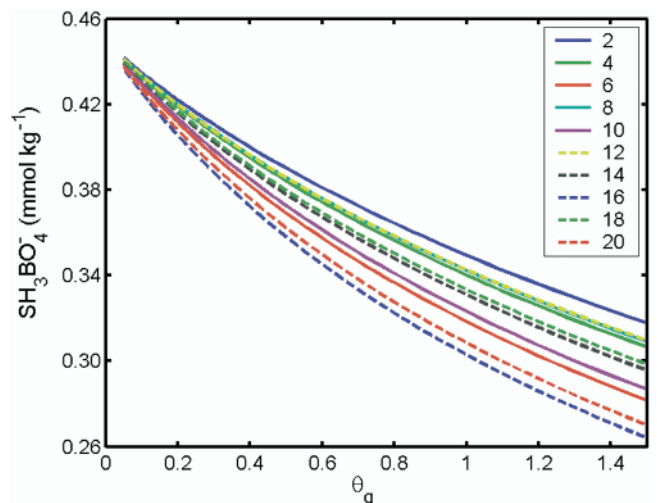

Fig. 3. Variation of pH with gravimetric water content (θ_g) for saline water composition.

Fig. 5. Tetrahedral surface B species ($SH_3BO_4^-$) vs. θ_g for saline water composition. Numbers represent textures given in Table 2.
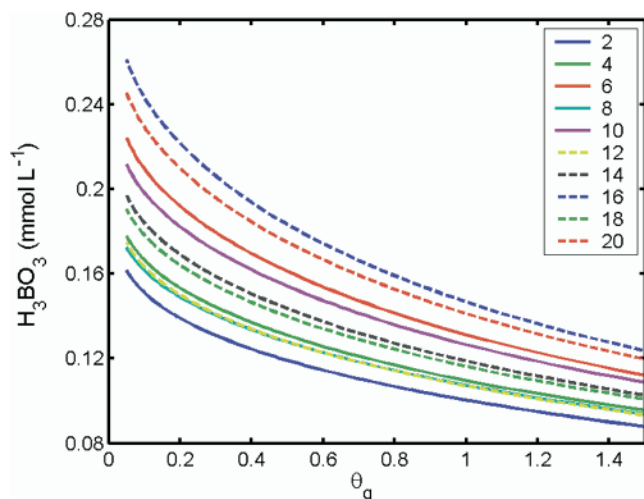
Fig. 6. Total solution B represented as H₃BO₃ vs. θ_g for saline water composition. Numbers represent textures given in Table 2.

at the initial water content. Most laboratory analyses of solution B are, however, conducted on saturation paste extract or some other extract taken at substantially higher water content than that of field conditions. Thus, a useful application of this model would be the recalculation of adsorbed and solution B concentrations for field water content to estimate initial adsorbed and solution B concentrations.

CONCLUSIONS

The speciation of B can be calculated from the constant capacitance model. A computer program to conduct this calculation for varying water content was developed and applied to a range of hypothetical soil textures and soil water compositions. The effective K_d ($K_d = \text{SH}_3\text{BO}_4^-/\text{solution B}$) for B decreases nonlinearly with decreasing gravimetric water content. The calculations indicate that, as a soil dries, the H$^+$ concentration

in the soil solution increases and contributes to the decrease in K_d. At the gravimetric water content, $\theta_g = 1.5$, which was the starting water content for these calculations, there was a substantial spread of values for K_d. The K_d values were positively correlated with the K_- equilibrium constant and CEC. This correlation reflects the dependence of both CEC and K_- on the clay content. A high ESP of the soil water coupled with low electrical conductivity (sodic soil conditions) resulted in the highest effective K_d of the three water compositions.

The computer program was developed to calculate the effect of varying soil water content on B speciation. An application of this program would be prediction of solution and adsorbed B concentrations at field water content. Predictions of this kind are useful because there is strong evidence that plants respond to soil solution B rather than adsorbed or total B. Thus it may be possible to make more accurate predictions of whether a particular soil solution might cause B deficiency or B toxicity in plants. Another application would be prediction of initial conditions for B as would be required by a solute transport model.

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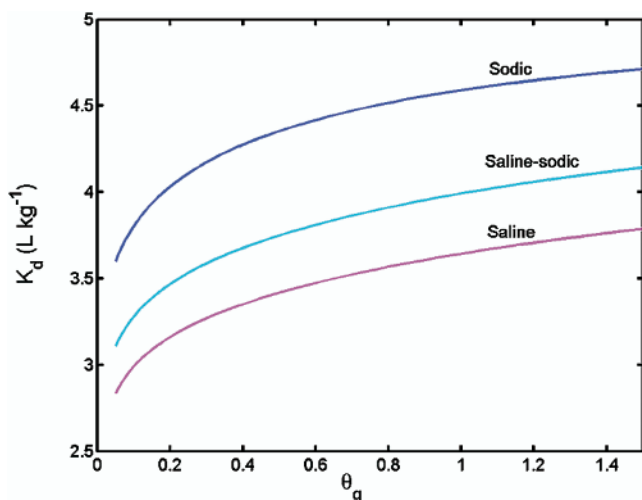Manrique, L.A., C.A. Jones, and P.T. Dyke. 1991. Predicting cation-

Fig. 7. Effective K_d vs. θ_g for Soil Texture 1, 60% clay. The three lines represent three different water compositions but identical initial total B.

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