Boron Adsorption on California Soils[1]

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ABSTRACT

Boron adsorption on 15 arid zone soil samples was investigated both as a function of equilibrium B concentration (0–100 g m^{-3}) and as a function of solution pH (5.5–11.5). Boron adsorption as a function of equilibrium B concentration could be described by the Freundlich adsorption isotherm over the entire concentration range studied and by the Langmuir adsorption isotherm over a limited concentration range. Boron adsorption increased from pH 5.5 to 8.5, exhibited a peak in the pH range 8.5 to 10, and decreased from pH 10 to 11.5. The adsorption maximum was highly correlated with both specific surface area and clay content. It was assumed that B adsorbs by ligand exchange with hydroxyl groups at the edges of clay particles and Al and Fe oxide minerals. The constant capacitance model was able to describe B adsorption on the soil samples. While the fit was generally good, the chemical significance of one of the surface complexation constants is uncertain for a few soil samples. An average set of surface complexation constants could be used to predict B adsorption on most of the soil samples studied.

Additional Index Words: **anion adsorption, ligand exchange, surface chemistry, constant capacitance model, FITEQL.**

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Boron is an important element in plant nutrition being essential at low concentrations and producing toxicity symptoms at higher concentrations. The concentration range between plant deficiency and toxicity is narrow (Keren and Bingham, 1985). For this reason understanding of reactions affecting B availability in soils is necessary.

Boron present in soil solution or applied via irrigation water equilibrates with soil solid surfaces. The extent of this adsorption reaction is affected by clay mineral type and content, Al and Fe oxide content, organic matter content, $CaCO_3$ content, and soil pH (Keren and Bingham, 1985). Boron adsorption data on arid zone soils have been described previously with the Freundlich adsorption isotherm (Elrashidi and O'Connor, 1982). Elrashidi and O'Connor (1982) were able to describe these data over a limited concentration range using the Langmuir adsorption isotherm as well.

The adsorption behavior of B on Al and Fe oxide minerals (Sims and Bingham, 1968; McPhail et al., 1972; Choi and Chen, 1979; Goldberg and Glaubig, 1985) as well as on layer silicate clay minerals (Hingston, 1964; Sims and Bingham, 1967; Keren and Mezuman, 1981; Mattigod et al., 1985; Goldberg and Glaubig, 1986) has been investigated previously. Boron adsorption on both types of minerals exhibited strong pH dependence. Adsorption peaks for the oxide minerals occurred in the pH range 7 to 9 (Goldberg and Glaubig, 1985). For the clay minerals the range for the adsorption peaks was shifted upward to pH 8 to 10 (Goldberg and Glaubig, 1986).

The constant capacitance model (Stumm et al., 1980) was applied to describe B adsorption on Al and Fe oxides both crystalline and amorphous (Goldberg and Glaubig, 1985), and on the clay minerals: kaolinite, montmorillonite, and illite (Goldberg and Glaubig, 1986). The model is based on a ligand exchange mechanism of adsorption, considers the charge on both the adsorbent and the adsorbate, and is able to represent the experimental adsorption data under changing conditions of solution pH.

Little information about B adsorption on soil samples as a function of pH is available. Boron adsorption behavior as a function of pH for two amorphous soils from Mexico (Bingham et al., 1971) and four soils from Israel (Mezuman and Keren, 1981) was found to be similar to that for oxide and clay minerals, exhibiting an adsorption maximum near pH 9.

In this paper, the role of the pH variable in B adsorption on fifteen soil samples is investigated. The constant capacitance model is extended for the first time to B adsorption on soil samples.

MATERIALS AND METHODS

Boron adsorption was studied using 15 surface and subsurface soil samples from eight different soil series. Soil classifications are given in Table 1. The soils were chosen because of their low organic and inorganic C contents to insure that B adsorption would occur primarily on oxide mineral and clay surfaces. The soil samples used consisted of the <2-mm fraction. Particle size distributions were determined using the hydrometer method described by Day (1965). Specific surface areas were determined using ethylene glycol monoethyl ether (EGME) (Cihacek and Bremner, 1979). Inorganic and organic C analyses were determined using the method described by Nelson and Sommers (1982). Clay minerals present in the <2-μm fractions were determined by x-ray analysis (B.S. Kapoor, 1985, personal communication).

Boron adsorption experiments were carried out in batch systems to determine both adsorption isotherms (amount of B adsorbed as a function of equilibrium B concentration) and adsorption envelopes (amount of B adsorbed as a function of solution pH per fixed total B concentration). Boron adsorption envelopes were determined using the identical procedure used previously by Goldberg and Glaubig (1985, 1986). The suspension density of solid was 200 kg m^{-3}. For determination of B adsorption isotherms the procedure was modified so that the equilibrating solution contained 0, 1, 2, 5, 10, 15, 25, 50, or 100 g B m^{-3} and no acid or base additions were used. The decantates were analyzed for pH, filtered, and analyzed for B concentration using a Technicon Auto Analyzer II and the Azomethine-H method described by Bingham (1982).

The constant capacitance model (Stumm et al., 1980) was used to describe the B adsorption envelopes obtained for the soil samples. The computer program FITEQL (Westall, 1982) was used to fit intrinsic surface complexation constants to the experimental data using the model assumptions and procedure described in detail by Goldberg and Sposito (1984). Surface reactions, intrinsic conditional equilibrium constants, mass balances, and charge balance were analogous to

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Table 1. Classifications and physical and chemical characterization of soils.

Soil series	Depth	Particle size Sand	 Silt	 Clay	Surface area	Inorganic carbon	Organic carbon	pH†	Clay minerals‡
	cm	%			10^4 m^2 kg^{-1}	%			
Altamont (fine, montmorillonitic, thermic Typic Chromoxererts)	0-25	40.5	36.5	23.0	10.25	<0.010	0.85	5.6	Montmorillonite, illite, mixed-layer§
	25-51	52.0	31.0	17.0	11.42	<0.010	0.65	5.5	
Arlington (coarse-loamy, mixed, thermic Haplic Durixeralfs)	0-25	40.5	42.0	17.5	6.11	0.060	0.51	7.3	Illite, montmorillonite, mixed-layer, vermiculite
	25-51	39.0	47.0	14.0	10.31	0.011	0.15	7.3	
Bonsall (fine, montmorillonitic, thermic Natric Palexeralfs)	0-25	48.5	35.0	16.5	3.29	<0.010	0.60	5.7	Kaolinite, illite, montmorillonite, mixed-layer, vermiculite
	25-51	38.5	30.6	30.9	10.57	<0.010	0.21	5.9	
Fallbrook (fine-loamy, mixed, thermic Typic Haploxeralfs)	0-25	62.0	21.0	17.0	6.83	0.020	0.38	6.8	Kaolinite, illite, mixed-layer, montmorillonite, vermiculite
	25-51	79.6	11.2	9.2	2.85	0.024	0.31	6.4	
Imperial (fine, montmorillonitic [calcareous], hyperthermic Vertic Torrifluvents)	surface clods	0.0	54.0	46.0	19.60	1.88	0.89	6.7	Montmorillonite, illite, kaolinite, mixed-layer
	0-7.6	7.0	49.0	44.0	19.14	1.76	0.83	7.4	
Pachappa (coarse-loamy, mixed, thermic Mollic Haploxeralfs)	0-25	49.0	38.0	13.0	3.63	0.010	0.49	6.8	Illite, montmorillonite, mixed-layer
	25-51	54.0	39.0	7.0	4.10	0.038	0.12	6.9	
Ramona (fine-loamy, mixed, thermic Typic Haploxeralfs)	0-25	64.5	23.5	12.0	2.79	<0.010	0.56	5.6	Illite
	25-51	64.0	23.8	12.2	3.88	0.025	0.21	6.2	
Twisselman (fine, mixed [calcareous], thermic Typic Torriorthents)	surface	24.2	42.8	33.0	18.24	0.160	0.56	7.4	Montmorillonite, illite, chlorite, mixed-layer

† Determined in the equilibrating solution containing no added boron. This was a 1:5 solution of 0.1 *M* NaCl.

‡ X-ray diffraction data of the 0-25 cm fraction from B.S. Kapoor (1985, personal communication).

§ Mixed-layer means 0.10-0.14 nm interstratification.

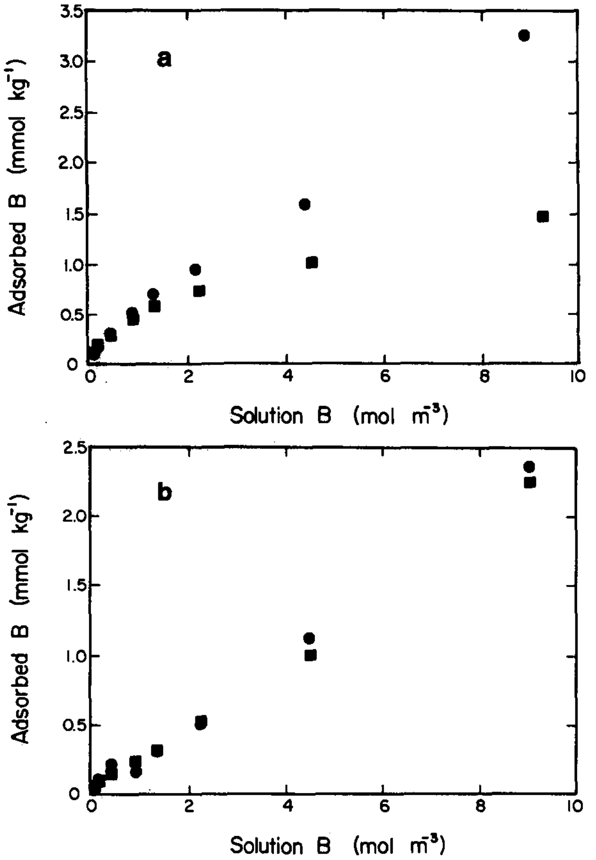

Fig. 1. Boron adsorption isotherms on arid zone soil samples: (a) Arlington; (b) Pachappa. The 0- to 25-cm samples are represented by squares, 25- to 51-cm samples are represented by circles.

those for the application of the model to B adsorption on Al and Fe oxides and layer silicate clay minerals (Goldberg and Glaubig, 1985, 1986). The intrinsic protonation-dissociation constants $K_+(\mathrm{int})$ and $K_-(\mathrm{int})$ were fit simultaneously with the B surface complexation constant $K_B(\mathrm{int})$ using FITEQL in identical fashion as in the clay mineral study (Goldberg and Glaubig, 1986). The value of the capacitance was fixed at $C = 1.06$ F m^{-2} as in the oxide and clay mineral studies. In previous studies the value of the specific surface area, *S*, of the adsorbent had been determined using N_2 adsorption (Goldberg and Glaubig, 1985; 1986). However, due to the extreme slowness of the N_2 method (four samples per week) and the insensitivity of the model to the surface area parameter, the EGME method was used in this study.

RESULTS AND DISCUSSION

Boron adsorption isotherms for two representative soils are shown in Fig. 1. Boron adsorption on the 15 soil samples could be described by the Langmuir adsorption isotherm over a limited equilibrium B concentration range. For most soils, the data deviated from linear Langmuir behavior at initial B concentrations of 50 g m^{-3} or higher. Boron adsorption on all soil samples could be adequately described over the entire concentration range studied using the Freundlich adsorption isotherm. The fit of this equation to the data was acceptable in that all linear relations were significant at the 99% level of confidence. Our results are in excellent agreement with those previously obtained by Elrashidi and O'Connor (1982) in their application of the isotherm equations to 10 soils from New Mexico. However, the limitations of the above adsorption isotherm equations (summarized by Goldberg and Sposito, 1984) are such that their use reduces essentially to curve-fitting.

Boron adsorption envelopes are shown in Fig. 2 for two representative soil samples studied. The shapes of the adsorption envelopes for all soil samples are quite similar, showing adsorption peaks in the pH range 8.5 to 10. The shapes of the adsorption envelopes and the location of the maxima are similar to those of silicate clay minerals (Goldberg and Glaubig, 1986). This is not surprising as these materials are expected to constitute the majority of B reactive surfaces in these arid zone soils. There was a highly significant correlation ($r = 0.96$) between the specific

Table 2. Constant capacitance model parameters.

Soil series	Depth (cm)	Maximum adsorption density (mol m^{-3})	Log K_+ (int)	Log K_- (int)	Log K_B (int)
Altamont	0–25	0.121	8.72	−8.94	5.57
	25–51	0.143	8.45	−10.07	5.45
Arlington	0–25	0.108	9.74	−11.69	5.67
	25–51	0.166	10.61	−11.30	5.93
Bonsall	0–25	0.0842	8.70	−10.51	4.88
	25–51	0.193	8.90	−11.66	5.29
Fallbrook	0–25	0.116	9.62	†	5.56
	25–51	0.0685	8.78	†	5.14
Imperial	surface clods	0.219	10.37	−10.42	6.05
	0–7.6	0.228	10.39	−9.93	6.08
Pachappa	0–25	0.0897	8.72	†	4.97
	25–51	0.0648	9.99	−11.50	6.06
Ramona	0–25	0.0796	8.59	−10.39	5.04
	25–51	0.0851	9.22	†	5.00
	Average Log K (int)		9.34	−10.64	5.48
	Standard deviation		0.76	0.89	0.44

† Indicates that this constant is insignificantly small (−30.95).
All intrinsic surface constants were obtained using concentrations in mol L^{-1}.

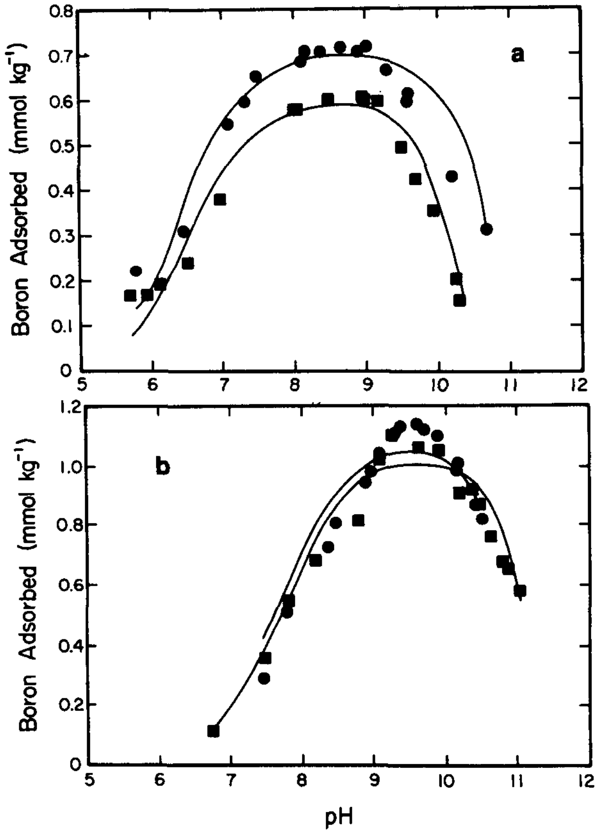

Fig. 2. Boron adsorption envelopes on arid zone soil samples: (a) Altamont; 0- to 25-cm sample represented by squares, 25- to 51-cm sample represented by circles. (b) Imperial: surface clods represented by squares; 0- to 7.6-cm sample represented by circles. Model results are represented by solid lines. B_T = 5.0 g m^{-3}.

surface area and the B adsorption maximum. A highly significant correlation (r = 0.94) also was found between the clay content and the B adsorption maximum. Similar correlations between B adsorption and these two variables have been observed previously (Elrashidi and O'Connor, 1982).

Table 2 lists the surface complexation constants obtained from the application of the constant capacitance model to the experimental data using FITEQL. Values were obtained by optimizing all three surface constants simultaneously. Optimization of solely the B surface complexation constant gave extremely poor fits. This behavior had been observed previously in the modeling of B adsorption on montmorillonite and illite minerals (Goldberg and Glaubig, 1986).

The constant capacitance model is well able to describe B adsorption on most soil samples, fitting a smooth curve through the experimental data (Fig. 2). The model is unable to fit closely the very pointed shape of two of the adsorption envelopes. Because of the high amount of B released to solution, the constant capacitance model was not applied to the adsorption envelope of the Twisselman soil. While fits to the data were in general very good, the optimized value of log K_-(int) for four soil samples was −30.95. This result suggests that this constant is virtually unnecessary and implies that the surface functional group, SOH, is not dissociating. This is a chemically unrealistic situation. It thus appears that while the model fit is good, chemical significance of at least one of the surface complexation constants is uncertain in these cases.

Averages of log K_+(int), log K_-(int), and log K_B(int) values are given in Table 2 and were obtained by excluding values of log K_-(int) = −30.95. The ability of the constant capacitance model to predict B adsorption data on each soil sample was tested using the set of average surface complexation constants (Table 2). The resulting predictions of B adsorption were comparable to the fits shown in Fig. 2 for nine of the 14 soils (data not shown). For the five remaining soil samples the model at least was able to predict B adsorption over the portion of the pH range near the maximum. Use of an average set of surface complexation constants to predict B adsorption on arid zone soils appears promising especially if the soil data set were expanded to include additional calcareous soil samples.

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