BORON SORPTION ON CALCAREOUS SOILS AND REFERENCE CALCITES

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Boron sorption on two calcareous soils, one noncalcareous soil, and two reference calcites was investigated in batch systems both as a function of solution pH (5.5–12) and as a function of initial B concentration (1–250 g B m^{-3}). Boron sorption was investigated on untreated soil samples, and soil samples treated with dilute acid to remove soil calcite. Boron sorption on the soil samples increased from pH 5.5 to 9, exhibited a peak near pH 9.5, and decreased from pH 10 to 11.5. Boron sorption on the two reference calcites exhibited an adsorption envelope with maximum sorption occurring near pH 9.5. The magnitude of the B adsorption maximum was significantly lower for the soil samples treated for calcite removal than for the untreated soil samples. This result indicates that calcite plays an important role in B sorption by calcareous soils. Boron sorption as a function of equilibrium B concentration could be described by both the Freundlich and Langmuir adsorption isotherms over the entire concentration range studied on all materials. Goodness of fit of the Langmuir adsorption isotherm equation was much improved over linear transformations by using the program ISOTHERM with its nonlinear least squares optimization routine.

As an essential element in plant nutrition, B is required by plants in small amounts. The concentration range in which the plant is sufficient is narrow. Boron produces toxicity symptoms and marked yield reductions at concentrations above the sufficiency range. In arid areas toxicity of B occurs due to high levels of water-soluble B in the soils or due to additions of B via irrigation waters (Keren and Bingham 1985). Since plants respond only to the B activity in soil solution, the B sorption capacity of the soil is an important sink for attenuating phytotoxic concentrations of B in irrigation water (Keren et al. 1985).

Boron sorption in soils has been investigated

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previously by various researchers (Bingham et al. 1971, Mezuman and Keren 1981, Elrashidi and O'Connor 1982, and Goldberg and Glaubig 1986a). Amount of sorbed B was significantly positively correlated with Al oxide content of Mexican and Hawaiian soils (Bingham et al. 1971) and Fe oxide and clay content of New Mexico soils (Elrashidi and O'Connor 1982).

The B sorbing mineral constituents of soils are considered to be Al and Fe oxides and clay minerals. Sorption of B on Al and Fe oxides increased at low pH, exhibited a peak in the pH range 7–8, and decreased at high pH (Goldberg and Glaubig 1985). Sorption of B on the clay minerals kaolinite, montmorillonite, and illite exhibited similar pH dependence, but the pH range of the adsorption peak was shifted to pH 8–10 (Goldberg and Glaubig 1986b).

Boron sorption has been observed as not significantly correlated with soil CaCO$_3$ content (Elrashidi and O'Connor 1982). These researchers did, however, find the greatest amount of sorbed B on the soils with the highest CaCO$_3$ content. Hingston (1964) found that the presence of 2% CaCO$_3$ depressed the B sorption capacity of illite at pH 7.5 and 8.3. However, B sorption in the presence of CaCO$_3$ at pH 9.5 was almost as great as on the untreated illite at pH 8.5. Kitano et al. (1978) studied B coprecipitation with calcite, found it to be about 3.5 ppm, and concluded that it was favored by increasing salinity. Ichikuni and Kikuchi (1972) discussed three possible sorption mechanisms for B on CaCO$_3$: 1) precipitation of sparingly soluble calcium borates with CaCO$_3$; 2) substitution of B for carbon in CaCO$_3$; and 3) adsorption of B on CaCO$_3$. These authors concluded that retention of B on CaCO$_3$ occurred through adsorption. Clearly, the importance of calcite in B sorption is still uncertain and must be established.

In the present study, in order to pinpoint the role of calcite, the sorption behavior of B on two calcareous soils from the Imperial Valley of California was investigated before and after removal of carbonates. Previous investigations on one of the soils have shown that carbonates play a major role in sorption of the anions selenite and arsenate at high pH (Goldberg and Glaubig 1988a,b). The sorption behavior of B on a non-

calcareous soil was studied to determine the effect of the carbonate removal treatment. Boron sorption on two reference calcites was also investigated.

MATERIALS AND METHODS

Boron sorption was studied using the ≤2-mm particle size fractions of a surface (0–7.6 cm) sample of the Imperial soil series [fine, montmorillonitic (calcareous), hyperthermic Vertic Torrifluvent], a subsurface (61–76 cm) sample of the Holtville soil series [clayey over loamy, montmorillonitic (calcareous), hyperthermic Typic Torrifluvent], and a surface (0–25 cm) sample of the Bonsall soil series (fine, montmorillonitic, thermic Natric Palexeralf). The $CaCO_3$ equivalent on the Imperial soil and organic C content on the Imperial and Bonsall soils were determined by wet combustion using the method of Nelson and Sommers (1982). Organic C content on the Holtville soil and $CaCO_3$ equivalent on the Holtville and Bonsall soils were obtained using a UIC Full Carbon System 150 with a C coulometer (UIC, Inc., Joliet, IL). Organic C was determined directly by furnace combustion at 375°C; inorganic C was determined using an acidification module and heating. Organic C was found to be 0.83%, 0.10%, and 0.60% and the $CaCO_3$ equivalent 14.7%, 13.3%, and 0.004% for the Imperial, Holtville, and Bonsall soils, respectively.

Boron sorption was studied on two reference calcites. Purecal U $CaCO_3$ was obtained from the Wyandotte Chemical Co. (Wyandotte, MI), and Multifex $CaCO_3$ was obtained from Pfizer Inc. (New York, NY). The calcites had been identified as such using x-ray diffraction analysis (Purecal U per J. J. Jurinak 1987 and Multifex per Z. R. Hinedi 1988, personal communications). The calcites were used without pretreatment.

Specific surface areas were determined using a single point BET N_2 adsorption isotherm obtained with a Quantachrome Quantasorb Jr. surface area analyzer (Quantachrome Corp., Syosset, NY). The values were 36.1, 36.4, 11.7, 13.2, 6.81, 6.02, 12.1, and 22.0 $m^2 \cdot g^{-1}$ for the Imperial soil, treated Imperial soil, Holtville soil, treated Holtville soil, Bonsall soil, treated Bonsall soil, Purecal U calcite, and Multifex calcite, respectively. This gas adsorption method measures only the external specific surface area of expanding clay minerals. The removal of carbon-

ates did not significantly change the soil surface areas, suggesting that carbonates are present as coatings on soil minerals.

Boron sorption experiments were carried out in batch systems to determine both sorption isotherms (amount of B sorbed as a function of equilibrium B concentration) and sorption envelopes (amount of B sorbed as a function of solution pH). Samples of solid (5 g for untreated Imperial and Holtville soils and Multifex calcite, 4.3 g for Bonsall soil and treated Holtville soil, 4.2 g for treated Imperial soil, and 1.25 g for Purecal U calcite) were added to 50-mL polypropylene centrifuge tubes and equilibrated with 25 mL of a 0.1 M NaCl solution by shaking for 2 h on a reciprocating shaker. For B sorption envelopes, the equilibrating solution contained 5 g B m^{-3} and had been adjusted to the desired pH values using 4 M HCl or 4 M NaOH. For B sorption isotherms, the equilibrating solution contained 1, 2, 5, 10, 15, 25, 50, 100, 150, 200, or 250 g B m^{-3}, and no acid or base additions were used. Equilibrating solutions were prepared by dissolving either boric acid or borax. These solids yield monomeric solutions of $B(OH)_3$ and $B(OH)_4^-$ at concentrations ≤0.025 M (Cotton and Wilkinson 1980). Fourier transform infrared spectra for the 250 g B m^{-3} solutions of boric acid and borax were virtually identical (data not shown). The samples were centrifuged for 20 minutes at 7800 RCF (10,000 rpm) in a Servall superspeed centrifuge. The decantates were analyzed for pH. They were then filtered through a 0.45-μm Whatman filter and analyzed for B concentration using a Technicon Auto Analyzer II and the Azomethine-H method described by Bingham (1982).

To evaluate their importance in B sorption, carbonates were removed from the Imperial and Holtville soils using a modification of the procedure described by Kunze and Dixon (1986). The soils were washed three times with a 0.5 M Na acetate solution which had been adjusted to pH 5 by the addition of glacial acetic acid, washed twice with deionized water, air dried, and passed through a 2-mm sieve. Boron sorption on the treated soils was determined under identical conditions as described above. To evaluate possible artifacts resulting from the carbonate removal treatment, B sorption was determined on the noncalcareous Bonsall soil using both treated and untreated soil samples.

The B sorption isotherms were described using the linear form of the Freundlich absorption

isotherm equation:

$$\log x = b \log c + \log K$$

where x = sorbed B (mg B g^{-1} solid), c = equilibrium B concentration (g B m^{-3}), and b and K are empirical parameters.

Two linear forms of the Langmuir adsorption isotherm equation were used to describe the data, the reciprocal Langmuir:

$$c/x = 1/(Kx_m) + c/x_m,$$

where x_m = maximum B sorption (mg B g^{-1} solid), is the linear form most commonly used by soil scientists, and the Eadie-Hofstee:

$$x = x_m - x/(Kc)$$

is the linear form that provides the most precise value of maximum sorption x_m. Langmuir and Freundlich isotherms were also fit to the B sorption data using the nonlinear least squares optimization program ISOTHERM (Kinniburgh 1985), eliminating the need for linearization.

RESULTS AND DISCUSSION

Boron sorption on the Imperial soil as a function of pH is shown in Fig. 1 before and after calcite removal. Both sorption curves show in-

FIG. 1. Boron sorption envelopes on untreated Imperial soil (squares) and on Imperial soil treated to remove calcite and corrected for weight of calcite removed (circles). B_T = 5.0 g·m^{-3} from boric acid.

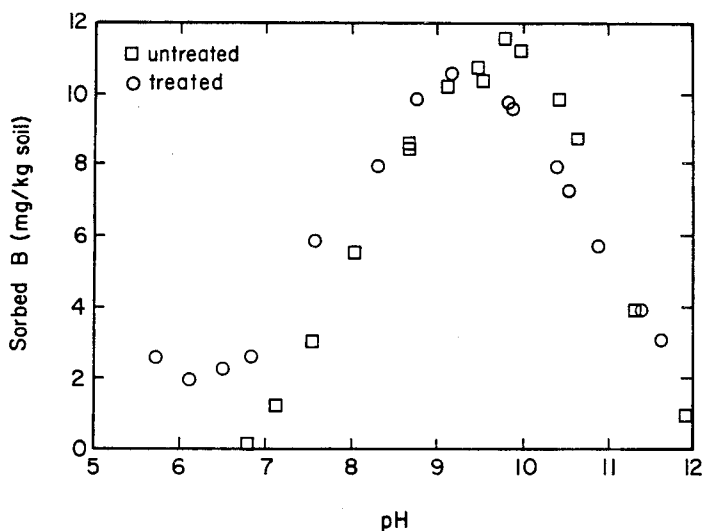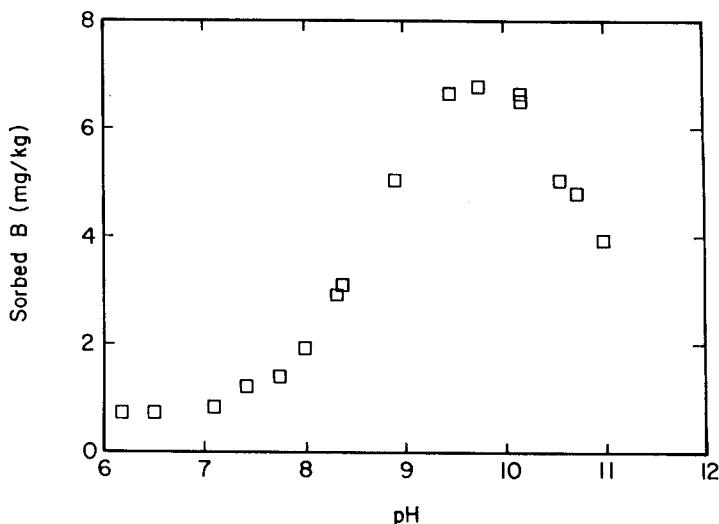FIG. 2. Boron sorption envelope on Multifex calcite. B_T = 5.0 g·m^{-3} from boric acid.

creases at low pH, sorption peaks near pH 9, and declines at high pH. The sorption maximum per gram of soil decreased by approximately 10% upon calcite removal. Boron sorption as a function of pH for reference calcite exhibits behavior similar to that of the soil (Fig. 2). Boron sorption on calcite increases at low pH, exhibits a peak near pH 9.5, and decreases at higher pH. The similarity in shape of the sorption envelopes suggests that soil calcite is responsible for a fraction of the B sorption in calcareous soils.

Boron sorption on both the Imperial and the Holtville soil was decreased by the calcite removal treatment. Solution pH in the treated Holtville soil decreased by approximately half a pH unit, while it was virtually treatment invar-

iant for the Imperial soil. For this reason, our analysis will emphasize the experimental results for the Imperial soil. Boron sorption on the noncalcareous Bonsall soil showed no significant differences between treated and untreated soil samples. The nonlinear Langmuir adsorption maxima for the Bonsall soil were not significantly different at the 95% level of confidence with or without calcite removal for both boric acid and borax systems (data not shown). This result indicates that removal of carbonates using weak acetic acid treatment does not lead to artifacts in sorption behavior.

Boron sorption isotherms on the Imperial soil before and after calcite removal are shown in Fig. 3. The pH value was 7.72 ± 0.15 and 8.22 ±
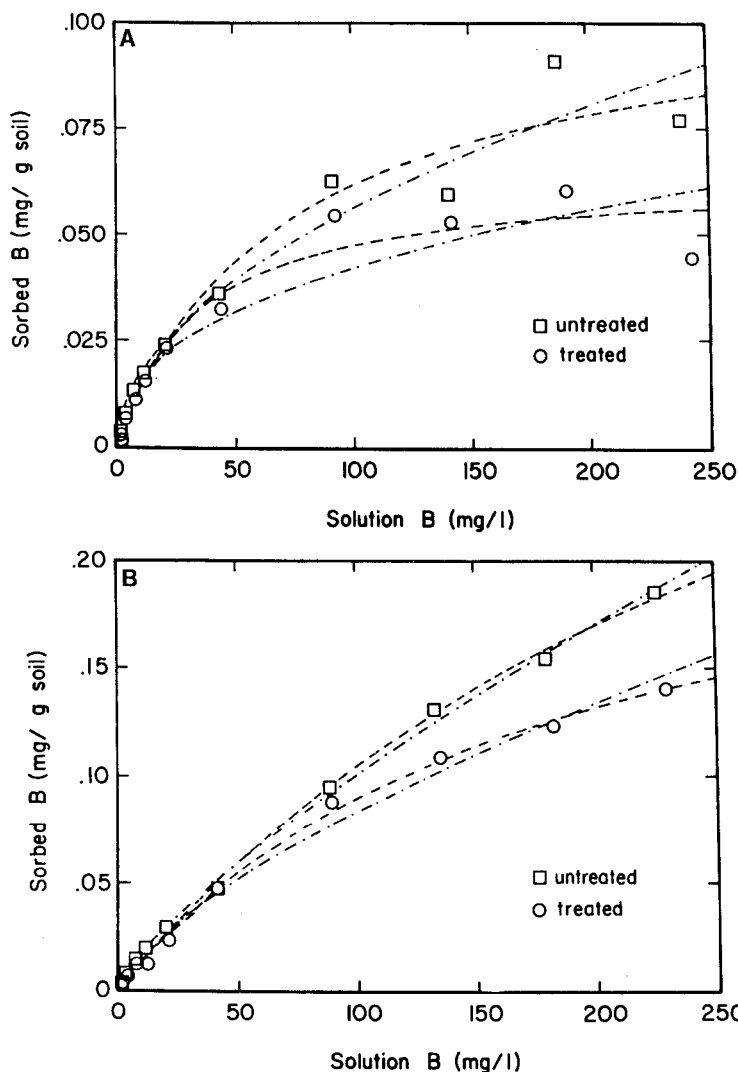

FIG. 3. Boron sorption isotherms on untreated Imperial soil (squares) and on Imperial soil treated to remove calcite and corrected for weight of calcite removed (circles): a) boron from boric acid, b) boron from borax. Dashed line represents nonlinear Langmuir fit. Dashed-dotted line represents nonlinear Freundlich fit.

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TABLE 1

Absorption isotherm parameters

	Imperial soil—boric acid					
	Untreated			Treated		
Freundlich	K	b	R^2	K	b	R^2
Linear	0.00203	0.734	0.940**[a]	0.00149	0.746	0.894**
Nonlinear	0.00493	0.526	0.953**	0.00607	0.418	0.879**
Langmuir	K	x_m	R^2	K	x_m	R^2
Eadie-Hofstee	0.0239	0.0807	0.675**	0.0282	0.0570	0.576**
Reciprocal	0.0148	0.103	0.917**	0.0215	0.0628	0.866**
Nonlinear	0.0132	0.108	0.962**	0.0276	0.0639	0.948**

	Imperial soil—borax					
	Untreated			Treated		
Freundlich	K	b	R^2	K	b	R^2
Linear	0.00179	0.882	0.983**	0.00121	0.924	0.967**
Nonlinear	0.00290	0.768	0.998**	0.00342	0.691	0.989**
Langmuir	K	x_m	R^2	K	x_m	R^2
Eadie-Hofstee	0.00821	0.223	0.608**	0.0112	0.142	0.360
Reciprocal	0.00425	0.361	0.751**	0.00319	0.346	0.370*
Nonlinear	0.00292	0.459	0.998**	0.00548	0.251	0.997**

	Holtville soil—boric acid					
	Untreated			Treated		
Freundlich	K	b	R^2	K	b	R^2
Linear	0.0000000571	0.817	0.984**	0.000000131	0.617	0.957**
Nonlinear	0.000270	0.972	0.973**	0.00000833	0.568	0.827**
Langmuir	K	x_m	R^2	K	x_m	R^2
Eadie-Hofstee	0.0113	0.0596	0.413*	0.0325	0.0243	0.555**
Reciprocal	0.00406	0.119	0.465*	0.0189	0.0293	0.699**
Nonlinear	0.0000445	6.64	0.973**	0.00911	0.0407	0.816**

	Holtville soil—borax					
	Untreated			Treated		
Freundlich	K	b	R^2	K	b	R^2
Linear	0.0000000253	0.932	0.967**	0.0000000827	0.832	0.988**
Nonlinear	0.000437	1.09	0.991**	0.000116	0.734	0.947**
Langmuir	K	x_m	R^2	K	x_m	R^2
Eadie-Hofstee	0.0145	0.0551	0.170	0.00872	0.0876	0.684**
Reciprocal	0.00143	0.297	0.100	0.00604	0.112	0.810**
Nonlinear	0.00000000756	45800	0.989**	0.00319	0.164	0.949**

	Purecal U calcite—boric acid		
Freundlich	K	b	R^2
Nonlinear	0.00686	0.573	0.862**
Langmuir	K	x_m	R^2
Nonlinear	0.0100	0.215	0.904**

	Purecal U calcite—borax		
Freundlich	K	b	R^2
Nonlinear	0.00172	0.861	0.926**
Langmuir	K	x_m	R^2
Nonlinear	0.00125	0.834	0.926**

[a] * and ** indicate significance at the 0.05 and 0.01% levels, respectively.

0.45 when boric acid and borax, respectively, were used for the equilibrating solution. Despite its frequent use as a pH buffer, borax was less successful in maintaining a constant pH value than boric acid. As predicted from the Imperial soil sorption envelope (Fig. 1), B sorption was very pH dependent. Sorption at pH 8.2 was much greater than at pH 7.7. Boron sorption per gram of Imperial soil was reduced approximately 25% by calcite removal at both pH values. Boron sorption per gram of Holtville soil was reduced an average of approximately 35% by calcite removal (data not shown). Since calcite constituted only 15% of the Imperial soil and 13% of the Holtville soil by weight, it is clear that both soils sorbed significant amounts of B. These results indicate that calcite plays an important role in B sorption of calcareous soils.

Boron sorption on the soil samples and the reference calcite was adequately described over the entire concentration range studied using the Reciprocal Langmuir and the Eadie-Hofstee forms of the Langmuir isotherm as well as the Freundlich isotherm. Isotherm parameter values and the coefficient of determination R^2, a goodness-of-fit statistic, are provided in Table 1. Linear transformations of isotherm equations often result in changes in error distribution and biased parameters. These difficulties can be avoided by use of a nonlinear least squares routine (Kinniburgh 1985). The computer program ISOTHERM (Kinniburgh 1985) contains such a routine and was used to fit the Langmuir and Freundlich isotherm equations to our sorption data. Goodness-of-fit for the Langmuir isotherm, as evidenced by the increase in R^2 (Table 1), was much improved over the linear transformations by using the nonlinear least squares routine. The fits of the nonlinear adsorption isotherm equations to B sorption on the Imperial soil are indicated in Fig. 3. The Langmuir adsorption maxima from these equations with and without calcite removal were statistically different at the 95% level of confidence, indicating a significant sink for B sorption on soil calcite.

CONCLUSIONS

Boron sorption on calcareous soils and on reference calcite was very similar, increasing at low pH, exhibiting a peak near pH 9.5, and decreasing at high pH. Upon treatment for removal of soil carbonates, the magnitude of the

B adsorption maximum was significantly reduced over that for untreated soil samples. These two results provide evidence that soil calcite acts as an important sink for B in calcareous soils. Soil carbonates may play an important role in attenuating phytotoxic B concentrations from irrigation waters.

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