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Mechanisms for Boron Regeneration[1]

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ABSTRACT

The ability of reclaimed natively high B soils to re-establish elevated soluble B concentrations has been termed "boron regeneration". Potential mechanisms for this phenomenon were qualitatively examined. Soil samples reclaimed in columns contained appreciable concentrations of residual, potentially reactive B and Cl$^-$. Reclamation by multiple batch extraction removed 100 percent of the Cl$^-$; however, the soils could not be completely reclaimed of B. Boron regeneration was observed in both column and batch reclamation systems, while Cl$^-$ regeneration occurred only in the column systems. The data suggest that two mechanisms may account for B regeneration. Post-reclamation release of B from residual sparingly soluble or desorbable B-containing sources is confirmed by the batch and column experimental results. The column data suggest that portions of the soil were bypassed by the leaching solution during reclamation. By analogy with Cl$^-$ behavior, post-reclamation diffusion of B from bypassed to leachable pores also contributes to the B regeneration phenomena.

Additional Index Words: **reclamation, salt-affected soils, arid zone soils.**

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RHOADES ET AL. (1970) used the B concentrations of soil column effluents to monitor the status of high B soils undergoing reclamation by leaching. Soluble B concentrations increased in the leachates following a period of post-reclamation storage. The phenomenon was termed "boron regeneration" and was attributed to the continued dissolution of sparingly soluble sources of B. Boron regeneration occurred in both natively high B and B-amended soils (Peryea et al., 1985).

The work of Hingston et al. (1974) suggests that post-reclamation desorption of B cannot be ruled out as an additional mechanism for regeneration. Dissolved B occurs primarily as uncharged B(OH)$_3^0$ molecules and B(OH)$_4^-$ anions. Boron tends to be specifically adsorbed to hydrous metal oxide-type surfaces in soils; the B(OH)$_4^-$ anion appears to be the preferred adsorbed species (Keren and Bingham, 1985). Hingston et al. (1974) demonstrated that repeated washings of such surfaces with a solution of constant pH resulted in reduced desorbability of specifically-adsorbed anions. Increased surface-anion affinity was produced through the loss of net negative surface charge or by the development of multiply-bonded coordination structures. Analogous behavior may be anticipated in soil systems subjected to long-term leaching, such as reclaimed high B soils. Changes in surface charge characteristics during post-reclamation storage could result in the release of residual surface-adsorbed B, causing soluble B levels to increase. The desorption and the dissolution mechanisms cannot be differentiated macroscopically; hence, they are combined and described as the dissolution mechanism in the ensuing discussion.

A second major mechanism is provided by considering soil voids to be composed of two behavioral classes of pores. Percolating solution derived from surface ponding will be transported primarily by a system of convectively dynamic, continuous pores. A second class of pores are those which are constrained from transporting water convectively, due to small size, discontinuity, or mobile and immobile water partitioning (Kissel et al., 1973; McMahon and Thomas, 1974; van Genùchten and Wierenga, 1977a). Native soil B will be preferentially leached from the soil volume that is accessible to the leaching solution. Using some low threshold concentration of B in the drainage water to signal the achievement of reclamation may result in a soil that is only apparently reclaimed. Considerable amounts of B may reside in the bypassed soil pores and associated surfaces. Subsequent diffusion of B from the bypassed to the leachable pores would result in elevated concentrations in the initial drainage effluents after the equilibration of reclaimed high B soils.

The goal of the current study was to qualitatively demonstrate the existence of one or both of the mechanisms proposed in the preceding paragraphs. This was accomplished in part by examining the ability of natively high B soils to regenerate B after reclamation by a multiple batch extraction procedure. This technique should effectively eliminate the contribution of the pore bypass mechanism. The pore bypass mechanism was tested by comparing the leaching and regeneration behavior of B with that of Cl$^-$ in column systems. The latter soil constituent is highly soluble and generally inert with respect to adsorption phenomena in soils. The presence of residual Cl$^-$ and the observation of Cl$^-$ regeneration should indicate pore bypass during reclamation and redistribution by diffusion during storage.

MATERIALS AND METHODS

Soils

Surface horizon samples of a Traver silt loam, Traver loam, and Twisselman clay loam were used in the study. The soils contained naturally high levels of B and Cl$^-$. They are further described in Peryea et al. (1985). The Traver soils are both classified as coarse-loamy, mixed, thermic Natric Haploxeralfs. The Twisselman clay loam is a fine, mixed (calcareous), thermic Typic Torriorthents.

Batch Studies

The air-dry equivalent of 20.00 g of oven-dry soil per tube was placed into acid-washed, 40 ml, polypropylene, Oak Ridge-type centrifuge tubes (18 tubes per soil). Sufficient deionized water was added to each tube to bring the total solution volume to 20.00 ml. The tubes were sealed with

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screw-on caps and paraffin film and were placed on a wrist-action shaker. After shaking for selected time periods up to 30 d, two replicates of each soil were centrifuged and the supernatants collected following filtration. Boron, Cl^-, and pH were measured in the supernatants.

The air-dry equivalent of 3.00 g of oven-dry soil per tube was placed into a second set of centrifuge tubes (3 replications per soil). These were extracted with 10 consecutive, 48-h, 1:10 [solid/0.033 *M* $Ca(NO_3)_2$] extractions. Following each reaction period, the solids were spun down using a high-speed centrifuge fitted with an anglehead rotor (RCF=42850 for 15 min). Ninety percent of the supernatant was removed by gentle suction and replaced with fresh extractant. Following the 10th extraction, the soils were resuspended and equilibrated while sealed for 30 d at 298 K. The solids were gently resuspended manually on a daily basis. The supernatants were subsequently recovered by centrifugation. Boron, Cl^-, and pH were analyzed in all supernatants following filtration. Boron was measured by the method of John et al. (1975), modified by using a higher azomethine-H concentration to enhance sensitivity, and Cl^- was analyzed using a Cl-titrator.

Column Studies

The air-dry equivalent of 2.50 g of oven-dry soil per column was uniformily packed in chromatography columns, producing four replications per soil. The soils were continuously leached with 0.033 *M* $Ca(NO_3)_2$ under saturated flow conditions until 40 pore volume displacements were collected. The saturated columns were sealed and stored for 30 days at 298 K. The columns were leached with 10 additional pore volumes. The effluents were analyzed for B, Cl^- and pH. Details of the procedure appear in Peryea et al. (1985).

RESULTS AND DISCUSSION

In the 1:1 batch reaction experiment, Cl^- achieved 100% of its 30-d supernatant concentration in < 15 min for the Traver loam and Twisselman soils and by 30 min for the Traver silt loam. The respective $c(Cl^-)$ values were 498.4, 28.61, and 11.67 mol m^{-3}. Boron, on the other hand, was continuing to solubilize at rates of 0.001 to 0.30 mol m^{-3} d^{-1} after 30 d of reaction. At this point, supernatant B concentrations for the three soils were 6.96, 3.50, and 0.88 mol m^{-3}, respectively. These data indicate that the sources of reactive B in the soils were found at lower concentrations and in less readily soluble states than were sources of Cl^-.

The results of the multiple, 1:10, batch extraction series are presented in Table 1. The term "new" constituent refers to the supernatant concentration of that constituent corrected for the previous extraction, i.e.,

$$S_i = \{C_i(V_i/M_i) - C_{i-1}\,[(V_{i-1} - V^r_{i-1})/M_{i-1}]\}\,, \quad [1]$$

where, for extraction *i*, *S* is the freshly solubilized gravimetric concentration of the constituent (mmol kg^{-1}), *C* is the supernatant concentration (mol m^{-3}), *V* is the volume of the supernatant (m^3), V^r is the volume of the supernatant removed following centrifugation (m^3), and *M* represents the oven-dry mass of soil (kg). The cumulative gravimetric concentrations of B (S^t_B) and Cl^- (S^t_{Cl}) extracted by the 1:10 batch series were used to estimate the reactive fraction of each constituent originally present in the soils, where

$$S^t = \sum_{i=1}^{11} S_i\,. \quad [2]$$

The reactive class of compounds are those subject to relatively rapid transformations and translocations. They would roughly correspond to the total diffusible (Sulaiman and Kay, 1972) or the leachable (Rhoades et al., 1970) components found in the soils.

Table 1 indicates that freshly dissolved B was present in the supernatant of each extraction. The elevated B concentrations found after the 30-d regeneration phase demonstrate that equilibrium was not attained in the 48-h reaction period used in the extraction procedure. The supernatant pH also increased during the regeneration phase. This may have resulted in a regenerated B concentration that under-reflects the B release rate, due to possible readsorption by pH-dependent sites (Keren and Bingham, 1985).

Each extraction of the 1:10 batch procedure can be considered a separate, 48-h regeneration opportunity, with the sum of the previous extractions representing the effects of reclamation. The average rate of post-reclamation B dissolution is inversely related to the cumulative amount of B removed by preceding extractions. This may be due to exhaustion of the reactive B content and subsequent changes in the rates of approach to the equilibrium concentration value, alteration of surface and solution properties which

Table 1. Newly released B and Cl^- and supernatant pH in successive extractions of three natively high B soils.

	New constituent extracted								
	Traver sil			Traver l			Twisselman cl		
Extraction	B	Cl^-	pH	B	Cl^-	pH	B	Cl^-	pH
	mmol kg^{-1}			mmol kg^{-1}			mmol kg^{-1}		
1†	1.26	11.89	7.66	10.55	503.56	8.34	5.52	26.53	7.81
2	0.27	0.41	7.35	2.04	0.15	7.98	1.05	0.00	7.48
3	0.17	0.00	7.23	1.03	0.00	7.48	0.60	0.00	7.26
4	0.09	0.00	7.10	0.61	0.05	7.33	0.35	0.00	7.22
5	0.06	0.00	7.02	0.39	0.00	7.01	0.23	0.00	7.03
6	0.05	0.00	6.93	0.25	0.00	6.91	0.16	0.00	6.95
7	0.04	0.00	6.84	0.18	0.00	6.88	0.13	0.00	6.90
8	0.04	0.00	6.76	0.17	0.00	6.83	0.10	0.00	6.93
9	0.03	0.00	6.74	0.12	0.00	6.82	0.08	0.00	6.83
10	0.03	0.00	6.67	0.11	0.00	6.73	0.06	0.00	6.72
REGEN	0.11	0.00	7.23	0.35	0.00	7.14	0.23	0.00	7.40
Σ‡	2.16 ± 0.01	12.29 ± 0.12		15.81 ± 0.14	503.74 ± 3.58		8.50 ± 0.10	26.57 ± 0.21	

† Extraction 1 to 10—48 h at 1:10 (soil:0.033 *M* $Ca(NO_3)_2$). Regeneration extraction: 720 h at 1:10 (soil:0.033 *M* $Ca(NO_3)_2$).

‡ Gravimetric concentration of reactive constituent (S^t).

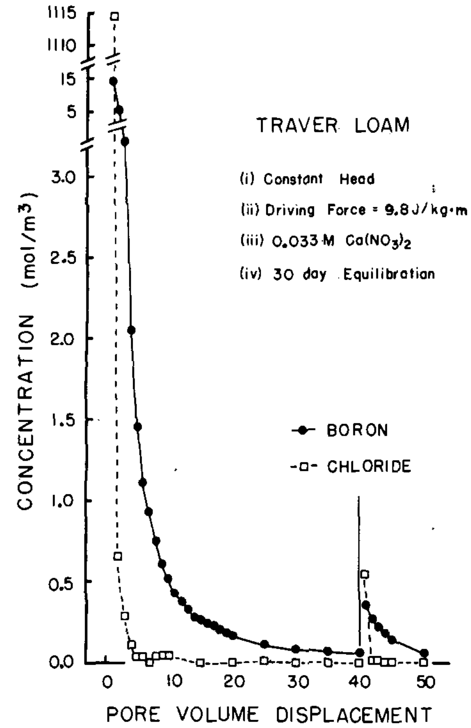

Fig. 1. Boron and Cl⁻ concentrations in successive pore volume displacements (PVD) of the Traver loam soil. The solid vertical line at PVD = 40 indicates an intervening 30-d, saturated storage period.

would enhance the energy of association of B with solid phase materials (Hingston et al., 1974), or removal of soluble B-containing solids with the kinetics of solubility controlled by more recalcitrant forms (Griffin and Burau, 1974). The data in Table 1 imply that the capability of a soil to regenerate B will be a function of the extraction history of the soil and the time scale over which the phenomenon is observed.

Table 1 also indicates that essentially 100% of the Cl^- content of each soil was dissolved in the first 48-h extraction. No Cl^- was found to come into solution during the 30-d regeneration phase. These observations point out that the Cl^- sources in the soils are readily soluble and that these highly saline soils can be completely reclaimed of Cl^-, but not B, if the reclamation solution is not restricted from interaction with all of the solid phase components. This conclusion provides strong qualitative support for the post-reclamation dissolution mechanism for B regeneration.

Figure 1 shows the column leachate data for the Traver loam soil. As in the batch extraction, even in the presence of considerable native constituent, the effluent concentrations of Cl^- rapidly dropped to nondetectible levels. The values for key points along the leaching curves for all three soils are in Table 2. In each case, the behavior of Cl^- and B in the drainage water was qualitatively similar to the 1:10 batch extraction results. The important exception is that both Cl^- and B regenerated in the column systems. Although no Cl^- was apparent in the drainage water of any of the soils by the 40th pore volume displacement, from one to 10% of the original Cl^- content was calculated to still be present. The observation of Cl^- regeneration qualitatively supports the existence of the pore bypass mechanism in soils that are reclaimed by leaching.

Table 2. Selected properties of key pore volume displacements (PVD) of soils leached and equilibrated in columns.

Soil	Condition†	Associated PVD	PVD properties Cl⁻	PVD properties B	PVD properties pH
			mol m⁻³ (%)‡		
Traver sil	Nat	1	28.92 (90.3)	1.26 (23.3)	8.35
	Rec	40	0.00 (90.5)	0.01 (76.2)	7.60
	Reg§	41	0.14 (91.0)	0.12 (78.4)	7.85
Traver l	Nat	1	1149. (99.6)	14.29 (36.2)	8.35
	Rec	40	0.00 (99.7)	0.06 (90.3)	7.90
	Reg§	41	0.41 (99.7)	0.32 (91.3)	7.95
Twisselman cl	Nat	1	62.64 (95.4)	6.42 (30.4)	7.95
	Rec	40	0.00 (95.4)	0.03 (87.8)	7.70
	Reg§	41	0.15 (95.6)	0.18 (88.6)	7.95

† Nat = native; Rec = reclaimed; Reg = regenerated.
‡ Percent of reactive constituent (S^t) leached by indicated PVD.
§ First PVD after 30-d of saturated storage.

The simultaneous presence of potentially regenerable sources of B in the leached soil volumes (i.e., dissolution mechanism) is also suggested by the column effluent data. Chloride located in the bypassed soil regions appears to be effectively isolated from the leaching solution. It is reasonable, therefore, to presume that B in the bypassed regions is similarly constrained from interaction. Since B was always present in the column effluent, the contribution of a source of regenerable B located external to the bypassed soil volume is indicated.

The 1:10 batch extraction and the column leachate data indicate the existence of appreciable quantities of potentially reactive B residing in natively high B soils after reclamation. The phenomenon of B regeneration appears to be generated by at least two processes: dissolution of residual sparingly soluble/desorbable B sources and post-reclamation redistribution of B by diffusion from bypassed to leachable soil pore regions. Although the experiment was not designed to quantify the relative contributions of the two mechanisms or to recreate field behavior, it does show that the causes of B regeneration are more complex than originally proposed and that quantitative mechanistic models of B reclamation should incorporate components describing pore bypass and slow dissolution effects. The relative contribution of each mechanism will be a complex function of the nature and rates of surface exchange and solid solubilization, inter- and intra-aggregate diffusion rates, pore water velocity, and soil and pore water characteristics (Tanji, 1970; van Genuchten et al., 1977b; Rao et al., 1980).

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REFERENCES

Griffin, R.A., and R.G. Burau. 1974. Kinetic and equilibrium studies of boron desorption from soil. Soil Sci. Soc. Am. Proc. 38:892–897.

Hingston, F.J., A.M. Posner, and J.P. Quirk. 1974. Anion adsorption by goethite and gibbsite: II. Desorption of anions from hydrous oxide surfaces. J. Soil Sci. 25:16–26.

John, M.K., H.H. Chuah, and J.H. Neufeld. 1975. Application of improved azomethine-H method to the determination of boron in soils and plants. Anal. Letters 8:559–568.

Keren, R., and F.T. Bingham. 1985. Boron in water, soils and plants. Adv. Soil Sci. 1:229–276.

Kissel, D.E., J.T. Ritchie, and E. Burnett. 1973. Chloride movement in undisturbed swelling clay soil. Soil Sci. Soc. Am. Proc. 37:21–24.

McMahon, M.A., and G.W. Thomas. 1974. Chloride and tritiated water flow in disturbed and undisturbed soil cores. Soil Sci. Soc. Am. Proc. 38:727–732.

Peryea, F.J., F.T. Bingham, and J.D. Rhoades. 1985. Regeneration of soluble boron by reclaimed high boron soils. Soil Sci. Soc. Am. J. 49:313–316.

Rao, P.S.C., D.E. Rolston, R.E. Jessup, and J.M. Davidson. 1980. Solute transport in aggregated porous media: theoretical and experimental evaluation. Soil Sci. Soc. Am. J. 44:1139–1146.

Rhoades, J.D., R.D. Ingvalson, and J.T. Hatcher. 1970. Laboratory determination of leachable soil boron. Soil Sci. Soc. Am. Proc. 34:871–874.

Sulaiman, W., and B.D. Kay. 1972. Measurement of the diffusion coefficient of boron in soil using a single cell technique. Soil Sci. Soc. Am. Proc. 36:746–752.

Tanji, K.K. 1970. A computer analysis on the leaching of boron from stratified soil columns. Soil Sci. 11:44–51.

van Genuchten, M.Th., and P.J. Wierenga. 1977a. Mass transfer studies in sorbing porous media: II. Experimental evaluation with tritium (^3H_2O). Soil Sci. Soc. Am. J. 41:272–278.

van Genuchten, M.Th., P.J. Wierenga, and G.A. O'Connor. 1977b. Mass transfer studies in sorbing porous media; III. experimental evaluation with 2,4,5-T. Soil Sci. Soc. Am. J. 41:278–285.