Influence of Soil Solution Cation Composition on Boron Adsorption by Soils

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Abstract: Boron (B) adsorption on five arid-zone soil samples from California was investigated as a function of solution pH (4–10) and cation composition (Na^+, Ca^{2+}, or Mg^{2+}). Boron adsorption was also determined on KGa-1b kaolinite as a function of solution pH in the presence of K^+ or Ca^{2+}. Boron adsorption increased with increasing solution pH, reached an adsorption maximum near pH 9, and decreased with further increases in pH. Boron adsorption as a function of solution pH was independent of solution cation composition from pH 4 to 8.5. At pH values greater than 8.5, increased B loss from solution was found for the magnesium systems. Chemical speciation calculations indicated supersaturation with respect to the Mg silicate minerals, chrysotile and sepiolite, at pH values greater than 7.8, suggesting that B is removed from solution by either adsorbing to or coprecipitating with these minerals. For the purposes of describing B transport under agricultural conditions (pH 4–8.5), it is advantageous that B adsorption can be described without consideration of changes in solution cation composition.

Key words: Sodium, calcium, magnesium, kaolinite, borate ion pairs.

B oron (B) is an essential element for plant growth that is required in trace amounts. Plants respond only to the B concentration in solution and have a narrow range between deficient and toxic concentrations. Under conditions of plentiful rainfall, B fertilization is often needed; whereas in arid areas, soil solution B levels can reach phytotoxic concentrations through application of irrigation water. Adsorption sites on soil surfaces act as sources and sinks for B, necessitating the careful quantification of adsorption reactions. Detailed knowledge of the factors that influence B availability is required both to optimize plant B nutrition and for management of irrigation waters with elevated B concentrations.

The magnitude of B adsorption on clay minerals is affected by both the cation composition of the reacting solution (Jasmund and Lindner, 1973; Mattigod et al., 1985) and the exchangeable cation composition of the surface (Keren and Gast, 1981; Keren and O'Connor, 1982; Keren and Talpaz, 1984). Jasmund and Lindner (1973) investigated the clay minerals kaolinite, illite, muscovite, and montmorillonite and observed a 2 % to 10 % increase in B adsorption in a divalent background electrolyte of $CaCl_2$ compared with monovalent background electrolytes of KCl and NaCl. The solution pH values, although not provided, were most likely in the neutral range because no acid or base additions were mentioned. At pH values greater than

8.5, B adsorption on kaolinite was increased in the presence of $Ca(ClO_4)_2$ as compared with $KClO_4$ and attributed to the formation and adsorption of the calcium borate ion pair, $CaB(OH)_4^+$ (Mattigod et al., 1985). Increased B adsorption was found on Ca-saturated montmorillonite and illite, over Na-saturated clays in the pH range of 7 to 10 (Keren and Gast, 1981; Keren and O'Connor, 1982). This result was attributed to reductions in the extent of the diffuse double layer and negative electric field of 2:1 Ca clays because of tactoid formation. This phenomenon would make the edge sites of Ca clays more accessible to B adsorption than those of Na clays that exist in solution as single particles (Keren and Gast, 1981).

The effect of solution cation composition on B adsorption by soils has been investigated only indirectly. Boron adsorption on two Hawaiian soils was found to be greater when pH was adjusted using a saturated $Ca(OH)_2$ solution as opposed to 0.1 M NaOH (Okazaki and Chao, 1968). At pH values greater than 9, B adsorption from a solution having electrical conductivity = 7.9 dS m^{-1} and Ca concentration = 5 mmol L^{-1} was greater than from a solution of electrical conductivity = 0.32 dS m^{-1} and Ca = 1.5 mmol L^{-1} (Goldberg et al., 2008).

In natural systems, adsorption takes place from solutions of mixed electrolytes having variable cation compositions. The purposes of this study were (1) to evaluate the effect of sodium, calcium, and magnesium on B adsorption by five arid-zone soils as a function of solution pH and (2) to evaluate the necessity to consider $CaB(OH)_4^+$ as an adsorbing species. Cation concentrations were chosen to be representative for saline soils (see table 5, U.S. Salinity Laboratory Staff, 1954).

MATERIALS AND METHODS

Boron adsorption was investigated using three surface and two subsurface soil samples from California. Soil physical and chemical characteristics and classifications are provided in Table 1. Surface areas were measured using ethylene glycol monoethyl ether adsorption (Cihacek and Bremner, 1979). Free Fe and Al oxides were extracted with a citrate/citric acid buffer and hydrosulfite (Coffin, 1963); concentrations of Fe and Al were determined using inductively coupled plasma–optical emission spectrometry (ICP-OES). Carbon content was determined coulometrically; total carbon by combustion at 950°C, inorganic carbon using an acidification module and heating, and organic carbon by difference. Clay content was obtained from a complete particle size distribution (Gee and Bauder, 1986).

Boron adsorption experiments were carried out on the soils in batch systems to determine adsorption envelopes (amount of B adsorbed as a function of solution pH per fixed total B concentration). Five grams of soil was added to 50-mL polypropylene centrifuge tubes and equilibrated with 25 mL of a mixed electrolyte solution for 20 h on a reciprocating shaker. This solution consisted of 0.1 M KCl and 0.05 M NaCl, 0.0167 M $CaCl_2$, or 0.0167 M $MgCl_2$ to fix the ionic strength at 0.15 M. The mixed electrolyte solution also contained 0.463 mmol B L^{-1} and had been adjusted to the desired pH range using 0.5 mL of varying proportions of 1 M HCl, 1 M KCl, or 1 M KOH. In this

TABLE 1. Chemical and Physical Characteristics and Classification of Soils[1]

Soil Series	Depth	Clay	CEC	SA	IOC	OC	Fe	Al
	cm	%	$mmol_c\ kg^{-1}$	$m^2\ g^{-1}$		$------\ g\ kg^{-1}\ ------$		
Arlington (coarse-loamy, mixed thermic Haplic Durixeralf)	0–25	17.5	107	41.9	0.30	4.7	8.2	0.48
	25–51	14.0	190	64.0	0.16	2.8	10.1	0.60
Pachappa (coarse-loamy, mixed, thermic Mollic Haploxeralf)	0–25	13.0	39	17.2	0.026	3.8	7.6	0.67
	25–51	7.0	52	20.9	0.014	1.1	7.2	0.35
Ramona (fine-loamy, mixed, thermic Mollic Haploxeralf)	0–25	12.0	66	14.3	0.02	4.4	4.5	0.42

[1]Excerpted from Goldberg (2008).

manner, the solutions were not significantly diluted during pH adjustment (2 % change in volume). The reaction temperature was 23.9°C ± 0.1°C. After the reaction, the samples were centrifuged, and the decantates were analyzed for pH, passed through 0.45-μm filters, and analyzed for B, K, and Ca or Mg concentrations using ICP-OES. Sodium concentrations were analyzed using atomic absorption spectrometry.

Five grams of KGa-1b kaolinite were added to 50-mL polypropylene centrifuge tubes and equilibrated with an electrolyte solution for 20 h on a reciprocating shaker. This solution consisted of 0.1 *M* KCl or 0.033 *M* CaCl₂ to fix the ionic strength at 0.1 *M* as well as 0.463 mmol B L⁻¹. The solution pH was adjusted to the desired pH range using varying amounts of 0.1 *M* HCl, 0.1 *M* KOH, or saturated 0.013 *M* Ca(OH)₂ to replicate the procedure used by Mattigod et al. (1985). The reaction temperature was 24.2 °C ± 0.3 °C. After the reaction, the samples were centrifuged, and the decantates were analyzed for pH, passed through 0.45-μm filters, and analyzed for B concentration using ICP-OES.

For the Mg treatment on Arlington surface and Pachappa subsurface soils, solution Si concentrations were also measured in the filtered decantates using ICP-OES. Chemical speciation calculations were carried out on these solutions to check for supersaturation with silica and magnesium silicate minerals using the program MINEQL+ (Schecher and McAvoy, 2003).

The thermodynamic data in MINEQL+ were derived from the MINTEQA2 thermodynamic database (Allison et al., 1991), which originated from WATEQ4F (Ball and Nordstrom, 1991). In this database, two sepiolite solubility values are listed. The more soluble one was chosen because it was derived from precipitation experiments (Wollast et al., 1968).

RESULTS AND DISCUSSION

Boron adsorption as a function of solution pH is presented in Figs. 1 to 3 for three representative arid-zone soils (Arlington, Pachappa, and Ramona soil samples). Boron adsorption increased with increasing solution pH, reached an adsorption maximum around pH 9, and decreased with further increases in solution pH. The effect of solution cation composition on B adsorption was not evident in the pH range 4 to 8.5.

Greater adsorption was observed in the presence of the divalent cations as compared with sodium at pH values greater than 8.5 for all three soils. Greater B adsorption in the Ca system over the Na system below pH 8.5 was important in only one of the five soil samples studied (Ramona). Because this effect was not observed for all soils, it is likely caused by experimental variability (or perhaps calcite precipitation at high pH) rather than to the formation and adsorption of a calcium-borate ion pair.
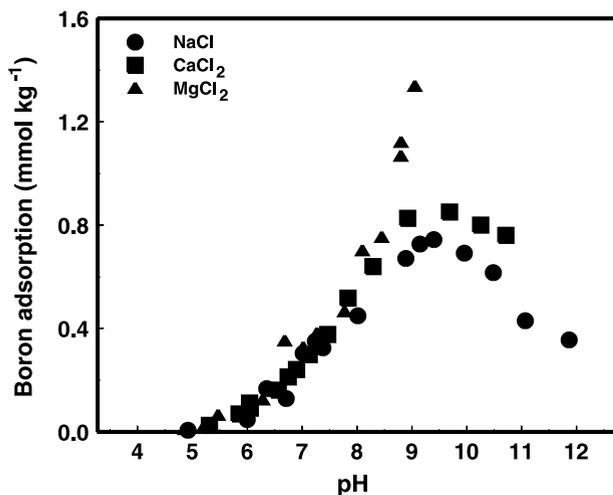

FIG. 1. Boron adsorption as a function of solution pH in 0.1 *M* KCl and 0.05 *M* NaCl, 0.0167 *M* CaCl₂, or 0.0167 *M* MgCl₂ on Arlington surface soil (0–25 cm). Total ionic strength for all systems = 0.15 *M*.
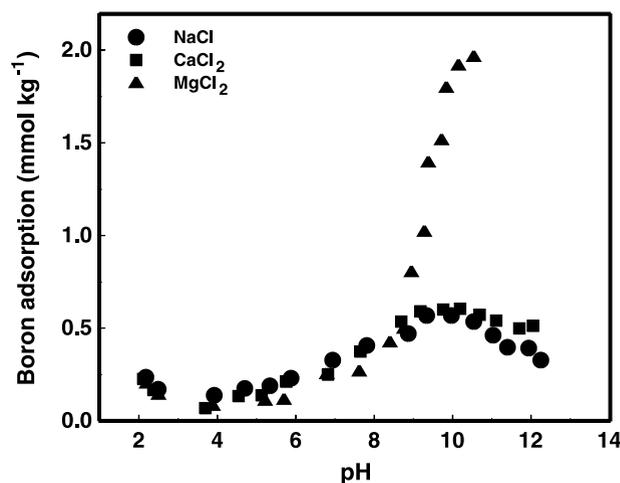

FIG. 2. Boron adsorption as a function of solution pH in 0.1 *M* KCl and 0.05 *M* NaCl, 0.0167 *M* CaCl₂, or 0.0167 *M* MgCl₂ on Pachappa subsurface soil (25–51 cm). Total ionic strength for all systems = 0.15 *M*.
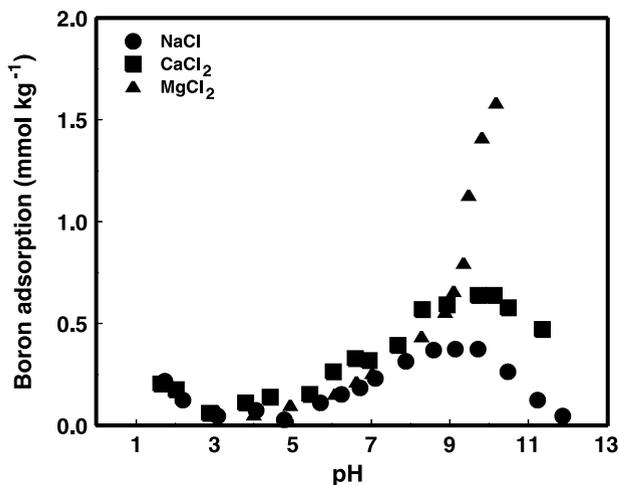
FIG. 3. Boron adsorption as a function of solution pH in 0.1 *M* KCl and 0.05 *M* NaCl, 0.0167 *M* CaCl$_2$, or 0.0167 *M* MgCl$_2$ on Ramona surface soil (0–25 cm). Total ionic strength for all systems = 0.15 *M*.

Adjustment of pH with saturated Ca(OH)$_2$ requires a much larger volume than pH adjustment with 0.1 *M* NaOH or KOH to achieve the same final solution pH. This dilution effect will result in both lower B concentration in solution and lower B adsorption. If the data are not corrected for the change in volume, then B adsorption in the Ca system will appear to be much greater than in monovalent systems. Shown in Fig. 4A are the pH-dependent adsorption data that we obtained with KGa-1b kaolinite. These data are similar to the data presented by Mattigod et al. (1985) for B adsorption on KGa-1a kaolinite also titrated with 0.1 *M* KCl or saturated Ca(OH)$_2$. As shown in Fig. 4B, when our KGa-1b kaolinite data are subsequently corrected for dilution effects on solution B concentration, B adsorption in the Ca system is roughly comparable in magnitude to that in the K system. Boron adsorption in the Ca system is somewhat less at lower pH and somewhat greater at higher pH (Fig. 4B), with a shift of the B adsorption maximum to pH 9.2 in the Ca system as compared with pH 8 for the K system. The increase in pH of the B adsorption maximum to higher pH value is consistent with a measured increase in zeta potential to a less negative value observed in the Ca system caused by specific adsorption of calcium ions on kaolinite (data not shown). Not only are Ca-borate ion pairs a very minor percentage of solution B (<10 % at pH 8.8), but we did not need to correct the solution for the presence of Ca-borate ion pairs, as they constituted a minor component of the total solution species. Thus, adsorption of Ca-borate ion pairs does not need to be invoked for these dilution-corrected data. This dilution effect caused by titrating with saturated Ca(OH)$_2$ also provides an explanation for the greater B adsorption observed in the Ca systems of Okazaki and Chao (1968) and Mattigod et al. (1985), again without the need to invoke adsorption of borate ion pairs. These authors did not address the need for dilution corrections when adding saturated Ca(OH)$_2$ for pH control.

Greater B adsorption in the Mg system over the Na system was clearly observed for the Arlington surface soil at pH values greater than 8.6 (Fig. 1) and for the Pachappa subsurface and Ramona surface soils at pH values greater than 8.8 (Figs. 2 and 3). The value of the formation constant for the magnesium-borate ion pair, MgB(OH)$_4^+$ (log *K* = 1.62), is very similar to that of the calcium-borate ion pair (log *K* = 1.80) (Reardon, 1976).

Calculations using MINEQL+ found the Ca-borate ion pair to constitute less than 10 % and the Mg-borate ion pair less than 6 % of the B in solution at pH 8.8. It thus seems unlikely that the much greater loss of B from solution at high pH observed in the Mg system was caused by Mg-borate ion pair adsorption. An alternative explanation relates to precipitation of a B-containing Mg phase.

Chemical speciation calculations on the Mg systems found supersaturation with the Mg silicate mineral, chrysotile, at pH values greater than 7.8 for the Arlington soil, and pH values greater than 8.4 for the Pachappa soil. However, we do not expect that chrysotile will precipitate in these short-term experiments, and we do not see evidence for Mg depletion from solution at pH values less than 8.5. More importantly, we determined supersaturation or equilibrium with respect to sepiolite (database WATEQ4F), a Mg silicate that can readily precipitate within the 1-day time frame of these adsorption experiments. Solutions were supersaturated or at equilibrium with respect to sepiolite at pH values greater than 8.8 for both the Arlington and the Pachappa soils. Further evidence for the precipitation
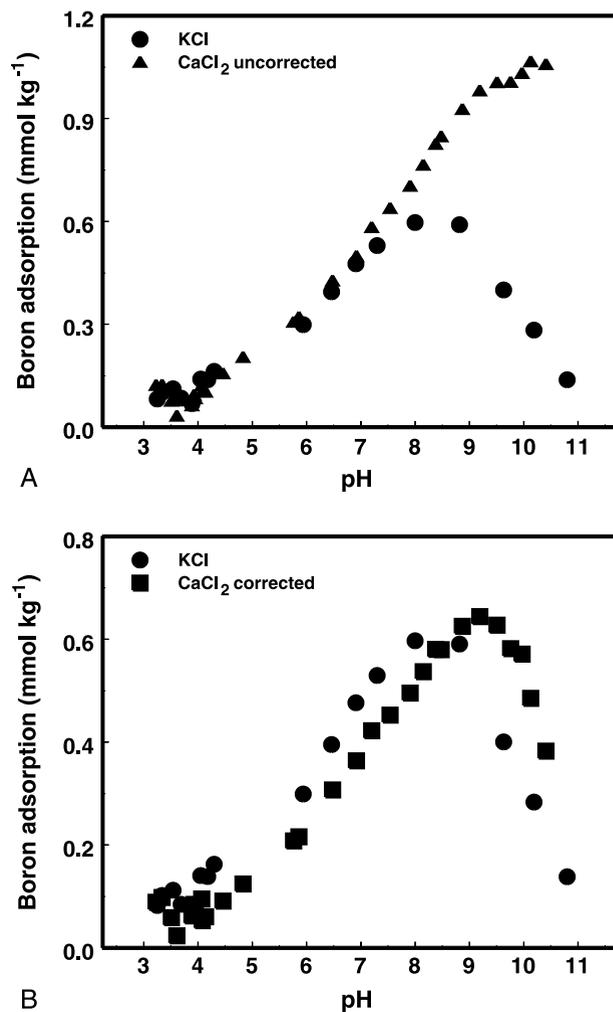

FIG. 4. Boron adsorption as a function of solution pH in 0.1 *M* KCl or 0.033 *M* CaCl$_2$ on KGa-1b kaolinite. Solution pH was adjusted using 0.1 *M* KOH or saturated 0.013 *M* Ca(OH)$_2$. Data were not corrected (A) or corrected (B) for the effect of dilution upon base addition.

of a Mg-containing solid phase is the decrease in Mg solution concentration at pH values greater than 8.8.

Magnesium silicates have been found to contain larger amounts of adsorbed B than other silicate minerals (Rhoades et al., 1970). Sepiolite exhibits the capacity to adsorb B (Ozturk and Kavak, 2004; Karahan et al., 2007). These results suggest that B removal from solutions with high Mg concentrations at elevated pH is caused by either adsorption on or coprecipitation into a freshly precipitated magnesium silicate mineral, most likely sepiolite.

The adsorption experiments in the Ca systems showed some loss of Ca at elevated pH values. Differences in the Ca system compared with the Na system at high pH may be related to B adsorption on freshly precipitated calcite. Calculations with MINEQL+ found supersaturation with respect to calcite at pH values greater than 7.8 for the Altamont soil and at pH values greater than 7.7 for the Pachappa subsoil.

Boron adsorption over most of the agriculturally important pH range of 4 to 8.5 was found to be independent of the major cation composition of the soil solution. At pH values greater than 8.5, solution B concentrations in Mg-dominated soil systems decreased dramatically, apparently because of increased B sorption, *via* either coprecipitation with or adsorption onto Mg-silicate minerals. This increased adsorption in the presence of high Mg concentrations would not necessarily be detrimental to plant growth because excessive, rather than deficient, B concentrations are often found in arid-zone soils. The slightly greater B adsorption in the Ca system at elevated pH is likely caused by B adsorption onto freshly precipitated $CaCO_3$. These data indicate that adsorption studies need to consider not only the confounding effects of potential precipitation of the adsorbing ion, but also the potential effect of precipitation of any other solution species. These effects, in addition to dilution, likely explain most of the differences in B adsorption related to cation composition.

ACKNOWLEDGMENTS

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