

INFLUENCE OF ANION COMPETITION ON BORON ADSORPTION BY CLAYS AND SOILS

Sabine Goldberg, H. S. Forster, S. M. Lesch, and E. L. Heick¹

Boron adsorption on the clay minerals, kaolinite and montmorillonite, and two arid zone soils was investigated as a function of solution pH (3-12) and presence of competing anions (nitrate, sulfate, molybdate, and phosphate) after 2 h of reaction time. Boron adsorption on all materials increased from pH 3 to 8, exhibited a peak at pH 8 to 10, and decreased from pH 10 to 12. Boron adsorption was greatest using a NaNO₃ background electrolyte. The competitive anion effects on B adsorption increased in the order sulfate < molybdate < phosphate. The competitive effect on B adsorption was small even for the strongly adsorbing anion, phosphate. Our results suggest that B-adsorbing sites are, generally, specific to B and act independently of competing anions. This result will simplify the description of B transport in that changes in solution concentration of competing anions may not have to be considered.

BORON is an element essential for the growth of higher plants. The solution B concentration range, where crop plants exhibit neither deficiency nor toxicity symptoms, is narrow. Plants respond only to solution B concentrations. Adsorption sites on soil surfaces act as sources and sinks for B. In the eastern United States, under conditions of abundant rainfall, B fertilization is necessary. However, in the arid southwestern U.S., solution B levels can reach phytotoxic concentrations through application of irrigation water. In both situations, the adsorption reactions of B on soil surfaces are significant.

Clay minerals are an important source of B-adsorbing surfaces in soils (Keren and Mezuman 1981; Goldberg and Glaubig 1986). It has been suggested that the mechanism of B adsorption on clay minerals is ligand exchange with reactive surface hydroxyl groups on the broken edges (Keren and Talpaz 1984). Boron adsorption reactions on clay minerals and soils have generally been studied in single anion solution systems. Some previous research has evaluated the effect of competing chloride, nitrate, sulfate, phosphate (Jasmund and Lindner 1973), and silicate (Goldberg and Glaubig 1986) concentrations on B adsorption by kaolinite, montmorillonite, and illite. Chloride, nitrate, and sulfate concentrations equimolar to B concentrations had little effect

on B adsorption on clays; however, equimolar phosphate concentrations reduced B adsorption appreciably (Jasmund and Lindner 1973). Boron adsorption on kaolinite was reduced slightly whereas B adsorption on montmorillonite was unaffected by competing silicate concentrations (Goldberg and Glaubig 1986). It was suggested that silicate adsorbs on a set of adsorption sites unavailable to B and that the majority of B adsorption sites are specific to B (Goldberg and Glaubig 1986). Boron adsorption on an allophanic soil was unaffected by the presence of competing sulfate and phosphate ions (Bingham and Page 1971). These authors suggested that B adsorption sites are more or less specific and independent of the presence of competing anions.

In natural systems, B adsorption occurs in the presence of competing anions. The purpose of this study is to evaluate the effect of nitrate, sulfate, molybdate, and phosphate on B adsorption on the clay minerals kaolinite and montmorillonite and on two arid zone soils.

MATERIALS AND METHODS

Boron adsorption was studied as a function of solution pH. Samples of kaolinite (KGa-2, poorly crystallized kaolinite) and Na-montmorillonite (SWy-1, Wyoming bentonite) were obtained from the Clay Minerals Society's Source Clays Repository and used in the adsorption study without pretreatment. Subsurface (25-51 cm) samples of the Arlington (coarse-loamy,

¹ USDA-ARS, U.S. Salinity Laboratory, 450 W. Big Springs, Rd., Riverside, CA 92507. Dr. Goldberg is corresponding author. E-mail: SGoldberg@ussl.ars.usda.gov

Received June 30, 1995; accepted Nov. 11, 1995

mixed, thermic Haplic Durixeralf) and Bonsall (fine, montmorillonitic, thermic Natric Palexeralf) soil series had been sieved to contain the <2-mm fraction. Although the Bonsall soil is classified as montmorillonitic, the clay mineralogy of the particular subsample used in the study was dominantly kaolinitic. These adsorbent materials were used in an earlier study of B adsorption as a function of temperature (Goldberg et al. 1993). Clay content and organic carbon contents were determined on the soils as described by Goldberg et al. (1993).

Impurities in the clay minerals were determined using X-ray diffraction powder mounts. Dominant clay minerals in the soils were determined by converting X-ray diffraction peak areas obtained with oriented mounts directly to clay mineral contents as described in Goldberg et al. (1993). Specific surface areas of all materials were determined using N_2 gas adsorption, and points of zero charge (PZC) were determined from electrophoretic mobility measurements as described by Goldberg et al. (1993). The N_2 gas adsorption method measures only the external specific surface area of expanding clay minerals. For montmorillonite and the soils, the PZC is below 2 because the electrostatic charge consists of permanent negative charge associated with the planar surfaces as a result of isomorphous substitution and pH-dependent charge associated with the particle edges. The net charge of the soils and clays used in the study was negative, providing an indication for the specific nature of B adsorption. Table 1 provides impurities for the clay minerals, organic carbon content and dominant mineralogy for the soils, and surface areas and PZC for the materials.

Boron adsorption envelopes (amount of B adsorbed as a function of solution pH per fixed total B concentration) were determined on all

materials in batch systems. Samples of adsorbent (0.75 g for montmorillonite, 2.5 g for kaolinite, and 5.0 g for soils) were added to 50-ml polypropylene centrifuge tubes and equilibrated with 25-ml aliquots of a 0.1 M NaCl or 0.1 M $NaNO_3$ solution by shaking for 2 h on a reciprocating shaker. The equilibrating solution contained 0.462 or 0.925 mmol B L^{-1} from boric acid and had been adjusted to the desired pH values using 1 M HCl, 1 M HNO_3 , or 1 M NaOH additions that changed the total volume by less than 2%. The samples were centrifuged for 20 min in a Servall Superspeed Centrifuge at 7800 RCF (10,000 rpm). The decantates were analyzed for pH, filtered through a 0.45- μm Whatman filter, and analyzed for B concentration on a Technicon Auto Analyzer II using the Azomethine-H method described by Bingham (1982).

To investigate the effect of competing anions, B adsorption was studied in the presence of equimolar and two times equimolar added anion concentration under conditions identical to those above. The background electrolyte for the anion competition studies was 0.1 M $NaNO_3$. Concentrations of the competing anions, sulfate (SO_4^{2-}), molybdate ($HMoO_4^-$, MoO_4^{2-}), and phosphate ($H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-}) were determined using inductively coupled plasma (ICP) emission spectrometry. Anion adsorption was determined by difference.

Adsorbed B levels obtained under various levels of anion addition were compared with the 0.1 M $NaNO_3$ control. To determine the replicability of the control treatments, multiple experimental runs were conducted using each adsorbent. The number of replications were three for kaolinite, four for montmorillonite, and two for the soils. Third order polynomial regression equations relating adsorbed B to pH were used to model the adsorbed B levels obtained for the 0.1 M $NaNO_3$ treatments for each adsorbent. Each

TABLE 1
Characterization of adsorbent materials

Reference minerals	Impurities	Organic carbon (%)	Surface area ($m^2 g^{-1}$)	PZC
kaolinite	chlorite		19.3	3.3
montmorillonite	mica		18.6	< 2.0
Soils	Dominant minerals			
Arlington	montmorillonite, vermiculite, kaolinite	0.15	13.7	< 2.0
Bonsall	kaolinite, illite, montmorillonite	0.21	22.2	< 2.0

regression equation was fit only to data within a restricted 4-pH unit range. The range was centered approximately ± 2 pH units around the pH level of maximum B adsorption. The fitted regression model was used to estimate both the mean regression Line (MRL) and the 95% prediction interval (PI) across the 4-pH unit range (Myers 1986). These prediction intervals were then superimposed over the appropriate adsorbed B levels observed in the presence of competing anions to "graphically" test for any statistically significant reduction in adsorbed B over the NaNO_3 control levels.

RESULTS AND DISCUSSION

Boron adsorption in the presence of a 0.1 M NaCl and NaNO_3 background electrolyte as a function of solution pH is depicted in Fig. 1. For all materials B adsorption increases with increasing pH until a peak of adsorption is reached. The increase in B adsorption is attributable to the ionization of boric acid. Above this peak, B adsorption decreases as pH continues to

increase. The fitted regression models were highly significant ($P < 0.0001$) for all materials. The B adsorption peak occurs near pH 8 for kaolinite, pH 10 for montmorillonite, and pH 9-10 for soils. Boron adsorption at high pH is depressed both because of increasing competition from hydroxyl ions and increasing negative charge on the clay edges. The influence of the negative permanent charge on B adsorption on the particle edges is less in kaolinite than in montmorillonite (Keren and Mezuman 1981). There is virtually no difference in B adsorption on all materials in the presence of either background electrolyte. Preliminary results on the soils had indicated that B adsorption was greater in the presence of NaNO_3 than of NaCl in the pH range 6 to 9. This result would suggest that NO_3^- is less competitive with B than Cl^- . Parfitt (1978) has previously suggested that Cl^- adsorbs on soils more strongly than NO_3^- . For this reason, all subsequent experiments were carried out in the presence of a 0.1 M NaNO_3 back-

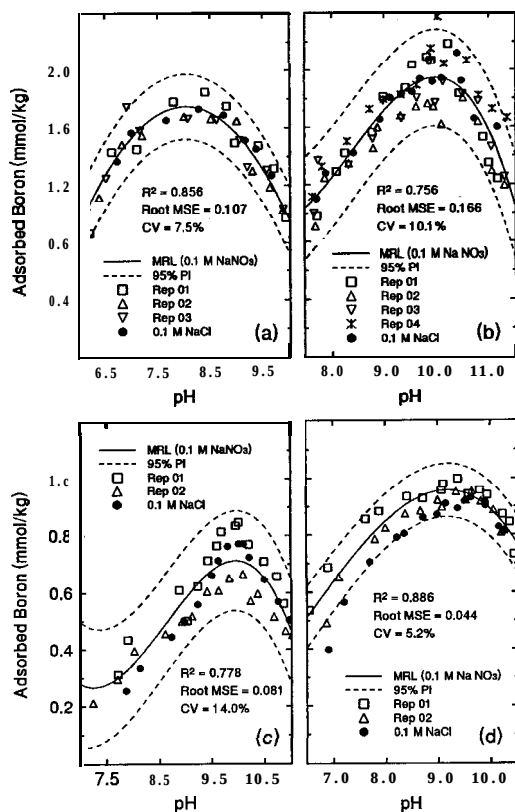


Fig. 1. Boron adsorption as a function of pH in 0.1 M NaCl and 0.1 M NaNO_3 solution: (a) kaolinite, (b) montmorillonite, (c) Arlington soil, (d) Bonsall soil.

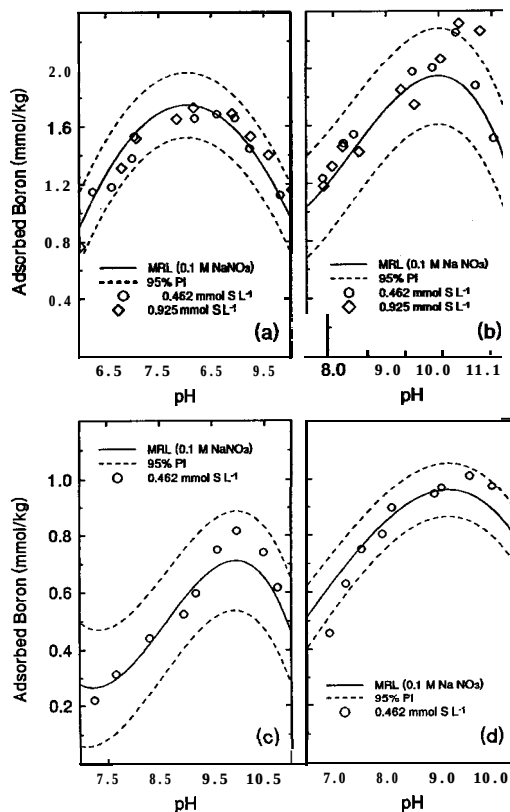


Fig. 2. Boron adsorption as a function of pH and sulfate concentration in 0.1 M NaNO_3 solution: (a) kaolinite, (b) montmorillonite, (c) Arlington soil, (d) Bonsall soil.

ground electrolyte using 0.1 M NaNO₃ as the control treatment. Based on the PZCs of the materials, competition with NO₃⁻ and Cl⁻ would not be expected.

The effect of equimolar and twice equimolar sulfate concentrations on B adsorption is indicated in Fig. 2. The competitive effect of sulfate on B adsorption is negligible. Nearly all data points in the sulfate system fall within the 95% prediction interval indicating no statistically significant effect of sulfate on B adsorption. Sulfate adsorption on the materials appeared to be insignificant although this was difficult to determine as sulfate was released in small amounts from the soils and in amounts approximately equimolar to B from the clays even in the non-competitive systems (data not shown).

Figure 3 shows the effect of equimolar and twice equimolar concentrations of molybdate on B adsorption. Some reduction in B adsorption attributable to molybdate competition is seen on most of the materials. However, this effect does

not appear to be statistically significant except, possibly, on kaolinite and Bonsall soil below pH 8 for twice equimolar additions. Molybdate adsorption on the materials was significant only at pH values less than 7 (data not shown). The lack of competitive effect of molybdate on B adsorption may thus result because the pH regions of dominant adsorption do not appreciably overlap for these two anions.

Boron adsorption as affected by equimolar and twice equimolar phosphate concentrations is presented in Fig. 4. As for molybdate, some reduction in B adsorption is seen on nearly all materials. Statistically significant reductions of B adsorption are seen only on kaolinite and possibly Bonsall soil below pH 8. On kaolinite, B adsorption is reduced to a greater extent in the presence of phosphate than in the presence of molybdate. Phosphate adsorption was significant on all materials and greatest on kaolinite, indicating some competitive effect of phosphate on B adsorption (data not shown).

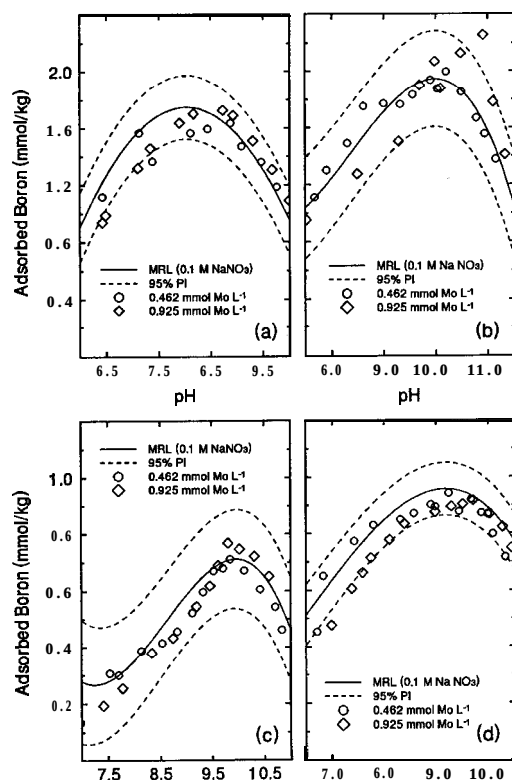


Fig. 3. Boron adsorption as a function of pH and molybdate concentration in 0.1 M NaNO₃ solution: (a) kaolinite, (b) montmorillonite, (c) Arlington soil, (d) Bonsall soil.

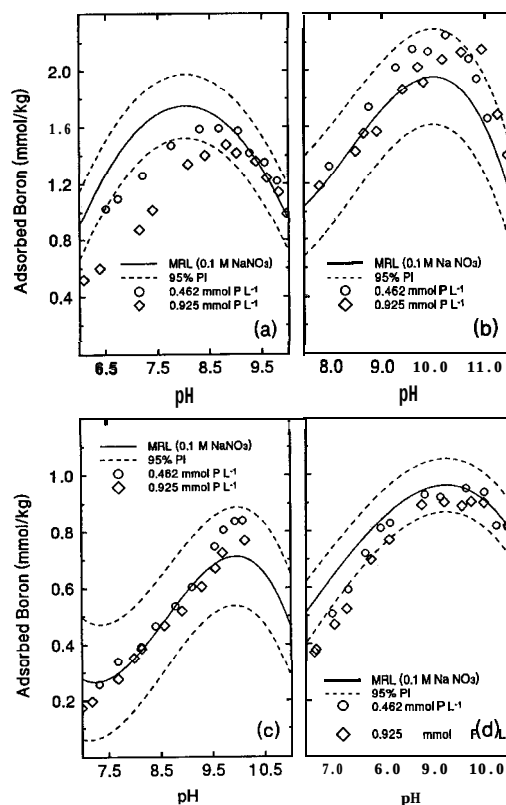


Fig. 4. Boron adsorption as a function of pH and phosphate concentration in 0.1 M NaNO₃ solution: (a) kaolinite, (b) montmorillonite, (c) Arlington soil, (d) Bonsall soil.

Parfitt (1978) considered the order of anion adsorption by soil to be phosphate > molybdate > sulfate. Our results on the competitive anion effects-phosphate > molybdate > sulfate-are in agreement with this finding. Our results show little competitive effect on B adsorption even by the strongly adsorbing anion, phosphate. Thus, our results are in agreement with previous results on clays (Goldberg and Glaubig 1986) and soil (Bingham and Page 1971) that B adsorbing sites are essentially specific to B and act independently of competing anions. However, in order to study agriculturally realistic systems we did not achieve site saturation in our experiments. Thus, it is certainly possible that greater competition might be observed at greater surface coverages. For the purpose of describing the transport of B in soils under agricultural conditions, our results are advantageous as they suggest that B adsorption can be described without consideration of changes in the solution concentration of competing anions.

ACKNOWLEDGMENT

Gratitude is expressed to Dr. J. D. Rhoades for providing the soil samples.

REFERENCES

- Bingham, F.T. 1982. Boron. In *Methods of soil analysis*, 2nd Ed., part 2. A. L. Page (ed.). Agronomy 9:431-447.
- Bingham, F.T., and A. L. Page. 1971. **Specific character of boron adsorption by an amorphous soil.** *Soil Sci. Soc. Am. Proc.* 35:892-893.
- Goldberg, S., H. S. Forster, and E. L. Heick. 1993. Temperature effects on boron adsorption by reference minerals and soils. *Soil Sci.* 156:316-321.
- Goldberg, S., and R. A. Glaubig. 1986. **Boron adsorption and silicon release by the clay minerals kaolinite, montmorillonite, and illite.** *Soil Sci. Soc. Am. J.* 50:1442-1448.
- Jasmund, K., and B. Lindner. 1973. **Experiments on the fixation of boron by clay minerals.** *Proc. Int. Clay Conf* 1972:399-412.
- Keren, R., and Mezuman. 1981. **Boron adsorption by clay minerals using a phenomenological equation.** *Clays Clay Miner.* 29: 198-204.
- Keren, R., and H. Talpaz. 1984. **Boron adsorption by montmorillonite as affected by particle size.** *Soil Sci. Soc. Am. J.* 48:555-559.
- Myers, R. H. 1986. *Classical and modern regression with application.* Duxbury Press, Boston, MA.
- Parfitt, R. L. 1978. **Anion adsorption by soils and soil materials.** *Adv Agron.* 30:1-50