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Recommended Citation

Ali Rashid, Namik M., "A Comparative Study of Boron Adsorption By a Calcareous and an Acid Soil" (1971). *All Graduate Theses and Dissertations*. 2984.
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A COMPARATIVE STUDY OF BORON ADSORPTION BY A CALCAREOUS AND AN ACID SOIL

by

Namik M. Ali Rashid

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Soil Chemistry

Approved:

UTAH STATE UNIVERSITY
Logan, Utah

1971

ACKNOWLEDGMENTS

I wish to express my deep and sincere appreciation to my Major Professor, Dr. J. J. Jurinak for his direction and patient guidance. I also express appreciation to Dr. R. L. Smith, Head of the Department of Soils and Meteorology, and to the third member of my committee, Dr. H. B. Peterson.

I also wish to express my thanks to Bob Griffin, a graduate student in the Department of Soils and Meteorology, for his help and cooperation in the lab; and to Richard Jones, a graduate student in the Geology Department for running the X-ray defraction analyses.

I acknowledge the Iraqi Government and United Nations (UNESCO) for making funds available for this study.

Namik M. Ali Rashid

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ABSTRACT

A Comparative Study of Boron Adsorption
By a Calcareous and an Acid Soil

by

Namik M. Ali Rashid, Master of Science

Utah State University, 1971

Major Professor: Dr. Jerome J. Jurinak
Department: Soils and Meteorology

The adsorption of boron by Aiken clay loam and Vernal sandy loam was studied in the boron equilibrium concentration range of 0 to 40 ppm. Adsorption data were obtained at 11, 20 and 30° C. The data were analyzed by the application of the Langmuir adsorption isotherm. It was concluded that, in both soils, the adsorption of boron occurred on three distinct sites or regions.

The acid ferrigenous Aiken soil had a higher adsorption capacity for boron than the calcareous Vernal soil when compared on a unit mass basis. On the unit area basis, however, the Vernal soil adsorbed more boron than the Aiken soil. The isoteric heat of adsorption showed that boron reacted more energetically with the Vernal soil. The calculated ΔH values were -7.6 K cal/M and -3.3 K cal/M for Vernal and Aiken soils, respectively.

The capacity of both soils to adsorb phosphorus was higher than their capacity to adsorb boron. The presence of adsorbed phosphate did not greatly reduce the amount of boron adsorbed by either soil studied. In the Vernal soil, phosphate was three times more efficient in replacing boron than in the Aiken soil. Also, chloride was found to desorb more boron from the Aiken soil than phosphate. However, neither phosphate nor chloride was found to be effective in reducing to any great extent the adsorption of boron by the two soils studied.

(68 pages)

INTRODUCTION

Boron is present in trace amounts in all soils (Gale, 1964). It is considered to be the essential element in the structure of rock-forming silicate mineral like tourmaline and datolite. Tourmaline, $Na(Mg,Fe)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$, is a complex of aluminosilicate and is considered to be the most abundant source of boron. The earth's crust is estimated to contain 0.001 percent of boron (Gale, 1964). Boron is present in igneous rocks, soils derived from volcanic ash, and it is present in granite and granite gniss.

Boron is an essential trace element and is required in small amounts by all plants (Eaton, 1935). However, it is highly toxic to most vegetation if it exceeds a concentration of more than a few parts per million (ppm) in the soil solution. Because of its dual role of essentiality and toxicity to plant growth, the chemistry of boron in the soil is of interest. Arid zone soils frequently have amounts of indigenous boron which require extensive reclamation before agriculture can flourish (Doneen et al., 1968). In addition, both surface and well waters used for irrigation often have boron concentrations which could lead to toxic levels in soils if proper management is not used.

Many factors have been reported to influence boron retention by soil. They are as follows (Griffin, 1966):

1. pH of the system
2. Type of clay minerals
3. Amount of clay
4. Type of exchangeable ions

5. Amount of organic matter
6. Moisture content (wetting and drying)
7. Time the soil is in contact with the soil solution
8. Temperature
9. Sesquioxides
10. Salinity.

The effect of pH on boron adsorption and its availability have been studied by Berger and Truog (1945), Olsen and Berger (1946), and Wear and Patterson (1961).

Berger and Truog (1945) showed that soils increased in available boron in the pH range, 4.7 to 6.7, and decreased in available boron in the pH range, 7.1 to 8.1. They demonstrated by partial correlation coefficient analysis that the available boron tends to decrease with an increase in pH.

At pH above 7, Olsen and Berger (1946) found good correlation between the amount of boron fixed and the pH of the system. Below pH 7, there was no significant correlation between boron fixation and pH of the soil.

The sensitivity of boron adsorption to the change of pH is described by Hingston (1964). He reported an increase in boron adsorption as the pH was increased from 5 to 9. Sims and Bingham (1968b) found the retention of boron by Fe and Al-coated kaolinite was pH dependent, and adsorption reached its maximum value at ph 8-9.

Doneen et al. (1968) reported a decrease in soluble boron in the soil solution with an increase of the pH of the soil. They also reported an increase in fixed boron in the soil with an increase of pH.

The affect of organic matter on boron availability has been studied by Berger and Truog (1945), Olsen and Berger (1946), and Parks and White (1952).

Berger and Truog (1945) reported a greater influence of organic matter in acid soils on boron availability than the pH. Olsen and Berger (1946) found a significant release of available boron when organic matter is oxidized by hydrogen peroxide, and the fixation capacity of the soil for boron is reduced upon treatment by hydrogen peroxide. Parks and White (1952) reported that humus materials have a chemical affinity for boron, and calcium-saturated humus retained less boron than hydrogen-saturated humus.

Several investigators, Eaton (1935), Wear and Patterson (1961), and Kubota and Berger (1948) have studied the effect of soil texture on boron retention and its movement in the soil.

Eaton (1935) established the fact that soils are not the same in their capacity to fix boron. Fine textured soils have a greater capacity to fix boron than coarse-textured soils. He found that the plants grown in fine textured soils induce boron injury much slower than plants grown in coarse-textured soils. Wear and Patterson (1961) reported more boron was required to correct boron deficiency in fine-textured soils than in coarse textured soils.

Few studies have been done on the effect of temperature on boron adsorption. Biggar and Fireman (1960) and Doneen et al. (1968) were in agreement that the increase in temperature resulted in a decrease in boron retention by soils. Biggar and Fireman (1960) found that boron adsorption equilibrated with soil is temperature dependent. They expressed the equilibrium reaction for boron at different temperatures by the following equation:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \text{Constant}$$

where

K = the equilibrium constant

R = the mole gas constant

T = the absolute temperature

and ΔH° = the heat of adsorption when the reactants and products are in their standard states.

Doneen et al. (1968) recommended the reclamation of lands affected by boron in summer, because more soluble boron is present in soil solution during this season. The results of Couch and Grim (1968) are in contradiction with the results of Biggar and Fireman (1960), and Doneen et al. (1968). Couch and Grim (1968) reported an increase in boron uptake by illite up to a temperature of 205 C.

Fleet (1965) found an increase in boron adsorption by illite with an increase in the salinity of the system. According to the dissociation of boric acid the presence of neutral salts, especially highly hydrated salts, are found to increase the dissociated boric acid hence, increasing the concentration of adsorbable species. Furthermore, Fleet (1965) concluded that the presences of electrolytes were expected to change the surface charges of the clay minerals.

Hingston (1964), Fleet (1965), and Harder (1961) were in agreement that illite is the best sorbent for boron among the clay minerals. The effects of exchangeable ions on boron adsorption have been studied by

Cook and Miller (1939), Wolf (1940), Parks and Show (1941), Hatcher et al. (1967), and Sims and Bingham (1967, 1968a,b).

Cook and Miller (1939) found good correlation between the presence of active calcium in the soil and boron deficiency symptoms (heart rot) in sugar beets. Carbonates and sulfates of calcium and magnesium were more effective in reducing boron toxicity than sodium carbonate. Wolf (1940) reported a greater effect of calcium and magnesium hydroxide on boron deficiency than sodium and potassium hydroxides, and the effect was greater with magnesium hydroxide.

Parks and Show (1961) demonstrated that the presence of calcium with Al in the system was more significant in boron precipitation than the presence of Al alone with boron. They reported more boron adsorption by aluminum and silicon being present individually in the system than their presence together with boron.

Sims and Bingham (1967) contend that the retention of boron by layer silicates minerals is due mainly to hydroxy iron and aluminum compounds present in the soils as impurities. Hatcher et al. (1967) are in agreement with Sims and Bingham (1967) that hydroxy-Al has a great affinity for boron. Boron retained by hydroxy aluminum material was greater than boron retained by hydroxy iron materials. This may be due to the presence of a greater amount of hydroxy groups present in the aluminum material than present in the hydroxy iron material, which may exist primarily as Fe_2O_3 (Sims and Bingham 1968b).

The effect of wetting and drying on boron fixation has been studied by Eaton and Wilcox (1939), Parks and White (1952), Biggar and Fireman (1960), and Doneen et al. (1968).

Eaton and Wilcox (1939) reported an increase in boron fixation upon wetting and drying. They found wetting and drying had a greater effect on coarse-textured soils than in the fine textured soils. They showed that the increase in boron fixation upon drying resulted in a decrease in boron solubility. Biggar and Fireman (1960) reported an increase in the capacity of the Aiken and Yolo soils for boron fixation when the number of wetting and drying cycles increased and the increase in boron fixation was more pronounced with high boron solution concentrations.

Doneen et al. (1968) observed a decrease in soluble boron concentration continuously when the number of wetting and drying cycles increased from 1 to 15 cycles.

Olsen and Berger (1946) are in agreement with Midgley and Dunklee (1940) that the boron deficiency in over-limed soils is undoubtedly due to the alkalinity produced by the lime and not due to the lime itself. The adsorption capacity of Aiken soil is doubled, as reported by Hatcher et al. (1967) when equilibrated with 1 percent $CaCO_3$.

Hatcher and Bower (1958) described boron adsorption by soils by the Langmuir isotherm equation. They expressed the reaction for two ranges of concentration, 0-8, and 8-32 ppm of boron by using two best-fit linear isotherms. Griffin (1966) in a leaching experiment suggested that the boron was adsorbed on more than two sites of clay minerals fraction. His evidence for this was based on the sharp break exhibited in desorption curve, each part apparently followed the Langmuir isotherm. He reported the desorption of boron below 2 ppm was extracted from the layer silicate lattice. Biggar and Fireman (1960) reported that the adsorbed boron followed the Langmuir equation up to certain boron concentrations. Hingston (1964) reported the deviation of boron adsorption from the Langmuir equation at concentrations higher than 10 ppm boron solution concentration. Singh (1964) also found the Langmuir adsorption equation to be valid over ranges of limited boron concentration. When all concentrations were considered, however, the relationship seems to follow a quadratic curve which could finally be treated with the B. E. T. form of adsorption isotherm.

Objectives of the Study

This study was directed toward studying the factors which affect boron adsorption by soils. The objectives are as follows:

1. To study the adsorption of boron by two distinctly different soils.
    - a) Aiken clay loam, an acid soil of pH 5.8 that contains 13-15 percent iron oxide.
    - b) Vernal sandy loam, an alkaline soil of pH 7.7 that contains 10-15 percent calcium carbonate.
2. To relate the adsorption capacity of these soils to their specific surface areas and to express adsorption data on both the unit mass and unit area basis.
3. To verify the existence of several types of adsorption sites for boron in these soils by the application of the Langmuir adsorption isotherm.
4. To study the effect of soil temperature in boron adsorption.
5. To study the competative adsorption of boron in the presence of other anions, i.e., chloride and phosphate.

MATERIALS AND METHODS

Two soils were studied. Aiken clay loam is a weathered soil from the Sierra Nevadas. The pH of the soil is 5.8 and it contains approximately 13 percent iron oxides. Aiken clay loam had an extractable boron content of 0.1 ppm.

Vernal sandy loam from Vernal, Utah, is a calcareous soil with a pH of 7.7. The carbonate content is from 10 to 15 percent. The extractable boron content is 0.5 ppm. Both soils were air dried, passed through a 2 mm sieve and stored in plastic containers prior to use in the adsorption studies. Boron solutions of appropriate concentrations were prepared by dissolving boric acid (H_3BO_3) in redistilled water. The concentration range used was 0-50 ppm B.

Phosphate solutions were prepared by dissolving a given amount of KH_2PO_4 in redistilled water and chloride solutions were prepared using KCl dissolved in redistilled water.

Boron in solution was analyzed by the carmine dye method (Hatcher and Wilcox, 1950). Phosphate concentrations were measured by the ascorbic acid method of Watanabe and Olsen (1965). Chloride was determined potentiometrically by the method of Skoog and West (1963). No significant pH change occurred in the soil systems when in contact (24 hours) with the solutions of boron, phosphate and chloride.

Boron adsorption studies were conducted at 11, 20 and 30° C (± .5° C). Preliminary studies indicated equilibrium between the soils studied and boron in solution was reached in about 1 hour. However, all adsorption isotherms were collected after 24 hours of reaction.

Ten grams of soil were added to plastic bottles and 25 ml of boron solution (various concentrations) were added. The bottles were placed in a shaking water bath and after 24 hours of reaction time the bottles were removed. The samples were immediately centrifuged in a constant temperature at high speed centrifuge. The supernatent liquid was then analyzed for boron. The difference between the amount of boron added to each sample and the amount analyzed after reaction represented the amount of boron adsorbed per 10 grams of soil.

Adsorption data were analyzed by use of the Langmuir adsorption isotherm, that is

$$X = \frac{X_m KC}{1 + KC} \qquad [1]$$

where X = micrograms of B adsorbed/gram of soil

X_m = maximum adsorption capacity in ppm B per gram of soil

C = equilibrium concentration of B (ppm) in solution

K = constant related to the energy of adsorption and the equilibrium constant of the reaction.

Equation [1] in linear form is

$$\frac{C}{X} = \frac{1}{KX_m} + \frac{C}{X_m} \qquad [2]$$

If C/X is plotted against C, then the slope represents $1/X_m$ and K is equal to the slope divided by the intercept.

The heat of reaction (ΔH) is calculated from the Clausius-Clapeyron relation

$$\log\left(\frac{C_{T2}}{C_{T1}}\right)_\theta = \frac{\Delta H}{2.3R}\left(\frac{T_2 - T_1}{T_2 T_1}\right) \qquad [3]$$

where C_{T2} and C_{T1} represent the equilibrium boron concentration at temperatures T_2 and T_1, required to maintain the same constant surface coverage θ of boron.

For this study, T_1 = 284° K, T_2 = 303° K, R = 2.987 cal/deg - mole, $\theta = X/X_m$ and ΔH = the isosteric (differential) heat of adsorption in K calories/mole.

The effect of anions (chloride and phosphate) on boron adsorption was studied at 11, 20 and 30° C. Variable amounts of anion solution were added to the soil samples on which was adsorbed a known amount of boron. The amount of boron desorbed and amount of chloride or phosphate adsorbed was calculated. The reaction time for the competative adsorption studies was 24 hours after which the suspension was centrifuged at constant temperature and the supernatent liquid analyzed for boron and the appropriate anion. The surface area of the soils were measured by the ethylene glycol method of Bower and Gschwend (1952).

Aiken clay loam and Vernal sandy loam had a specific surface area of 96.7 and 46.8 m^2/g, respectively. To avoid boron contamination from glass, teflon and plastic ware were used throughout the study.

X-ray diffraction analyses showed that Vernal sandy loam contained the clay minerals, illite, smectite and kaolinite. In the Aiken clay loam the only clay mineral found was kaolinite.

RESULTS AND DISCUSSION

Boron adsorption and the Langmuir isotherm

The results of the boron adsorption studies by Aiken clay and Vernal sandy loam at three temperatures are shown in Figures 1 through 4. The experimental data are shown in the Appendix (Tables 2a, 2b, 2c, 3a, 3b, and 3c). The adsorption isotherms (Figures 1 and 3) are shown for only two temperatures, whereas the Langmuir isotherm analysis (Figures 2 and 4) show the adsorption data for three temperatures. Figures 1 and 3 show that in the B concentration range studied, the adsorption isotherm is not a smooth curve but appears rather erratic. This situation is somewhat clarified when the data are plotted according to the Langmuir isotherm (Figures 2 and 4). It appears that boron adsorption by these soils exhibits three linear regions and hence can be interpreted to mean adsorption is occurring on three distinct sites, each with its own capacity to adsorb boron. It becomes apparent why the previous workers have had limited success in applying the Langmuir equation to boron adsorption in soils. Hatcher and Bower (1958), Biggar and Fireman (1960), Singh (1964), and Hingston (1964) all used the Langmuir plot and generally concluded the Langmuir isotherm was only valid for equilibrium B concentrations of less than 10 ppm. The data from this study infer that these workers were only studying the adsorption in a one-site region and they did not extend their B concentration range sufficiently to obtain a complete picture. The curves indicate that a large number of data points are necessary to separate possible experimental error from the actual reaction curve. These data support

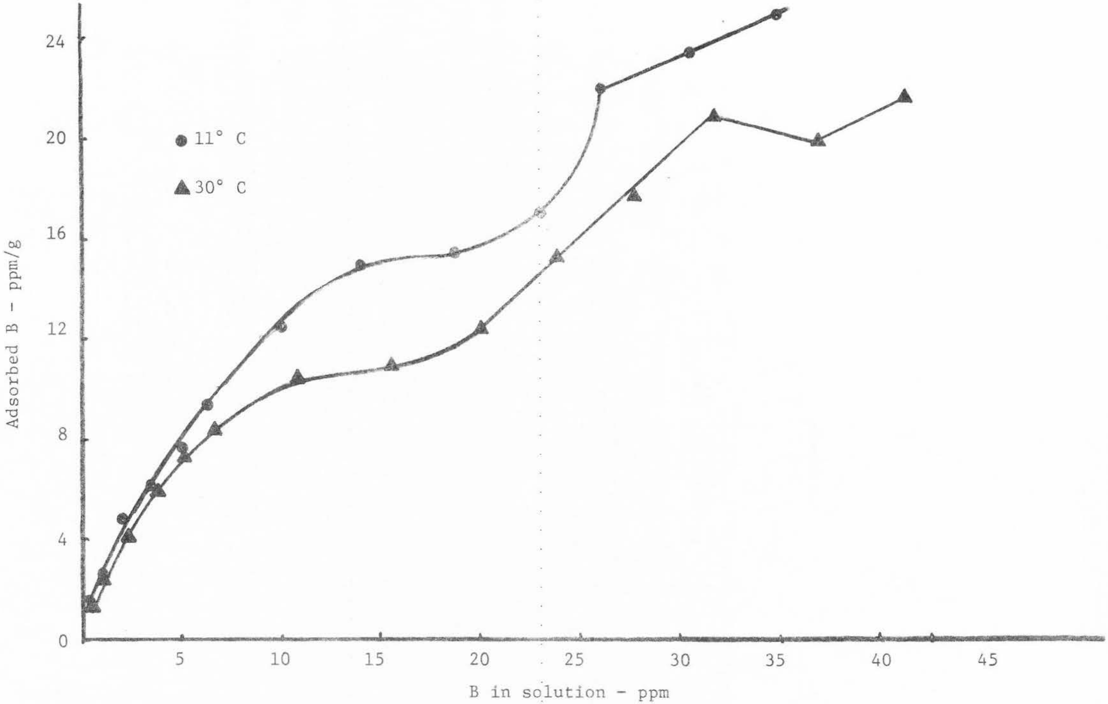

Figure 1. Boron adsorption by Aiken clay loam soil at two temperatures.

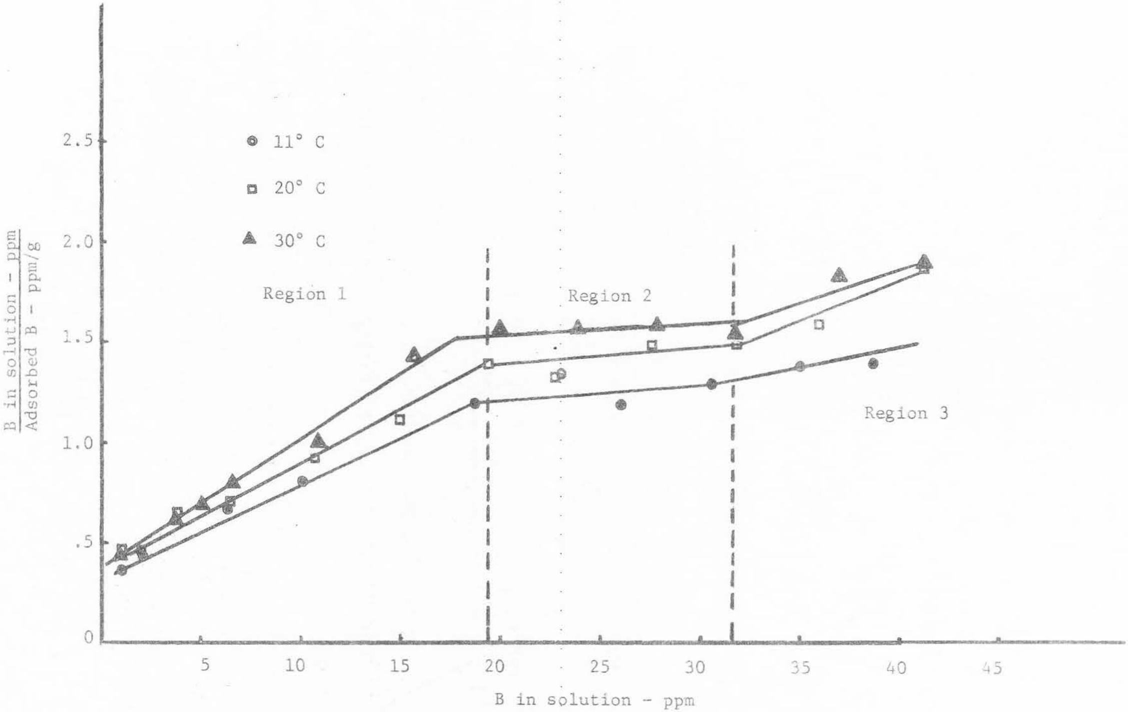

Figure 2. Boron adsorption by Aiken clay loam soil at three temperatures plotted according to the Langmuir equation.

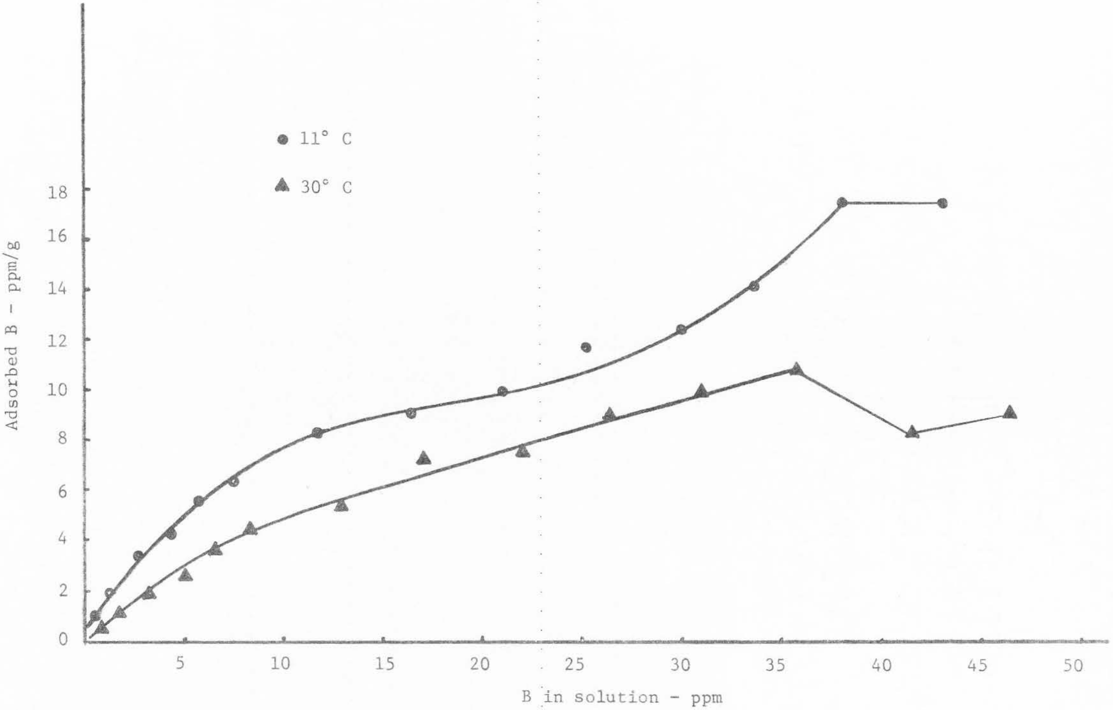

Figure 3. Boron adsorption by Vernal sandy loam at two temperatures.

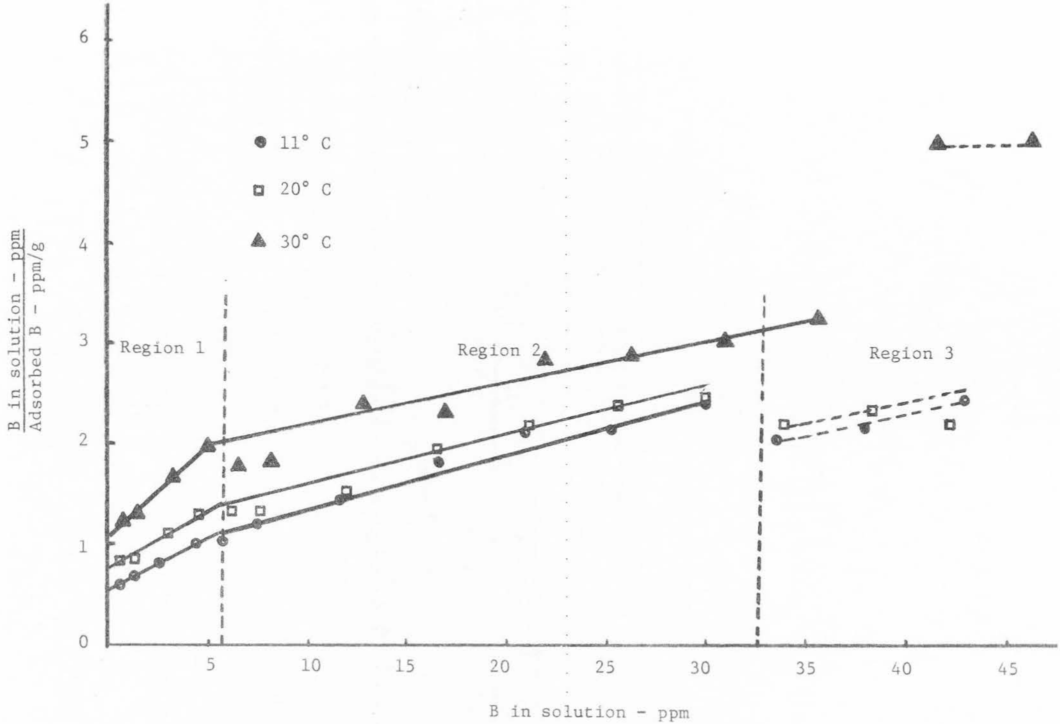

Figure 4. Boron adsorption by Vernal sandy loam at three temperatures plotted according to the Langmuir equation

the contention of Griffin (1966) who studied the desorption of boron from soils and concluded boron was adsorbed by more than two adsorption sites each of which could be described by the Langmuir isotherm.

The adsorption on several sites has been reported previously. Reyes and Jurinak (1967) concluded molybdate was adsorbed by hematite at pH 4 on two distinct sites. Muljadi et al. (1966a) reported the existence of three adsorption regions to explain phosphate adsorption by kaolinite, gibbsite and pseudobeohmite. Phosphate adsorption by these minerals in regions I and II followed the Langmuir isotherm, whereas phosphate interaction in region III was more complex.

Figures 2 and 4 show that region or site I was more active in adsorbing boron in the acid (Aiken) soil than on the calcareous (Vernal) soil. The linear plot of the Langmuir isotherm extended to 20 ppm B in the Aiken system as compared to about 6 ppm B in the Vernal system. Region II in the Aiken soil was found in the equilibrium concentration range of 20 to 32 ppm, whereas the region II in the Vernal soil extended from 6 to 32 ppm B in the equilibrium solution.

It is noted that sites I and II were saturated when the solution concentration of boron reached about 32 ppm. This saturation concentration was the same for both soils. Region or site III in this study is not as well defined because of the limited amount of data that was collected at the higher B concentration.

The adsorption data indicate that boron adsorption by both acid and calcareous soils in exothermic, that is adsorption decreases as the temperature increases. These findings are in agreement with Biggar and Fireman (1960) and Doneen et al. (1968). It is of interest to note that the adsorption regions were uneffected by the change in temperature (Figures 2 and 4). The consistency of these data support the general conclusions of the adsorption studies.

The Langmuir constants calculated for region I and region II are shown in Table 1. With both soils the capacity of region II is greater than region I. The X_m^{II} values, however, appear inordinately large in the Aiken soil system. These values result from the extremely small slope in region II as shown in Figure 2. It is not obvious why region II exhibits this large capacity for boron in the Aiken soil. One may speculate that iron and boron interact in the Aiken soil to form "surface complexes." These complexes are essentially heavy metal-boron polymers which have been postualted to exist by Parks and Show (1941), Biggar and Fireman (1960) and Sims and Bingham (1968a and b). Although these workers investigated systems with much higher boron concentrations, a definite possibility exists than an iron oxide-boron complex serves as a sink for boron in the Aiken soil. More data is required to define the adsorption of boron by Aiken clay loam.

The X_m^I and X_m^{II} values for the calcareous Vernal soil are considerably lower. The value of X_m^I may be misleading since any indigenous boron in the Vernal soil (also in the Aiken soil) would exist on the sites in region I. Thus, the experimentally determined value may underestimate X_m^I.

The reader is cautioned that the calculated values of X_m^I and X_m^{II} are idealized in the sense that their computed values represent the case where all sites are occupied in a given region. For example, Table 1 shows that $X_m^I + X_m^{II}$ for Aiken clay loam equals about 120 ppm B/g. The data show (Figure 1) that this is an unrealistic value for the natural

Table 1. Langmuir constants for boron and phosphate adsorption by Aiken clay loam and Vernal sandy loam

	Boron			Phosphorous	
	X_m^I	X_m^{II}	ΔH	X_m	ΔH
Temp °C	ppm/g	ppm/g	K cal/M	ppm/g	K cal/M
Aiken					
11	21.0	110		789	
20	18.3	98	-3.23	796	-6.58
30	15.9	110		754	
Vernal					
11	8.5	17.2		109	
20	7.0	21.8	-7.15	107	-3.77
30	5.4	24.3		110	

system. The reason for this discrepancy is that adsorption does not usually occur in discrete steps or reaction does not occur on only one type site at a time. The Langmuir analysis of the data produces an X_m value which is valid only if the reaction were allowed to proceed to completion. It assumes no other adsorption or precipitation reaction will occur until all sites in a given adsorption region are occupied. As Figures 1 and 2 show, this assumption is not valid in nature. The interpretation of the adsorption capacity of a system with multiple site adsorption requires more development than occurs in literature.

Table 1 shows that the differential, ΔH, heat of adsorption of boron in Aiken soil is less than in the Vernal soil. Thus, although the capacity for boron is greater in the acid soil, the energy of interaction is less than in the calcareous soil. These values were calculated from data taken in region I and represent the order of magnitude of the heat of adsorption.

Boron adsorption in the presence of competing anions

Both chloride and phosphate anions were studied with regard to how they effected the adsorption of boron at various temperatures by Aiken clay loam and Vernal sandy loam. The general procedure was to add 50 ppm B to the soil then add variable amounts of the competing anion. Both the adsorption of boron and the competing ion was determined. Figures 5 through 9 show P adsorption by Aiken and Vernal soil along with the Langmuir plot of the data obtained. Figures 7 and 9 show that the Langmuir isotherm was not closely followed by either soil. The presence of several adsorption sites or regions for P adsorption is suggested, but insufficient data precludes any valid conclusions.

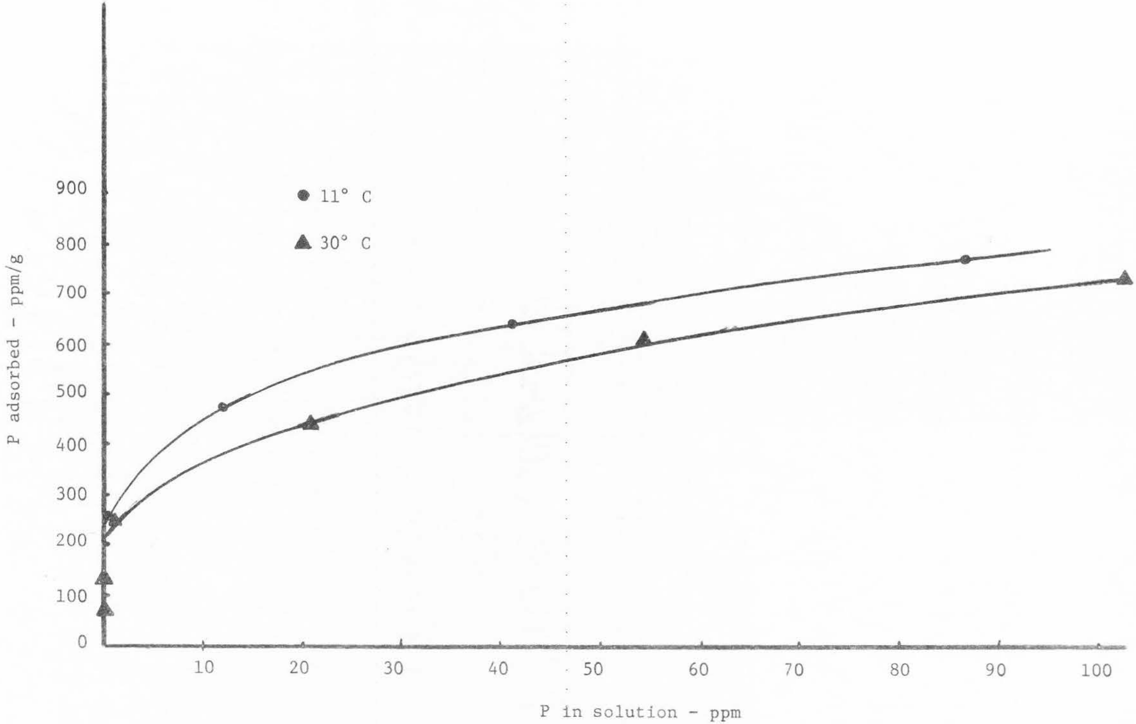

Figure 5. Phosphorous adsorption in the presence of 50 ppm B by Aiken clay loam soil at two temperatures.

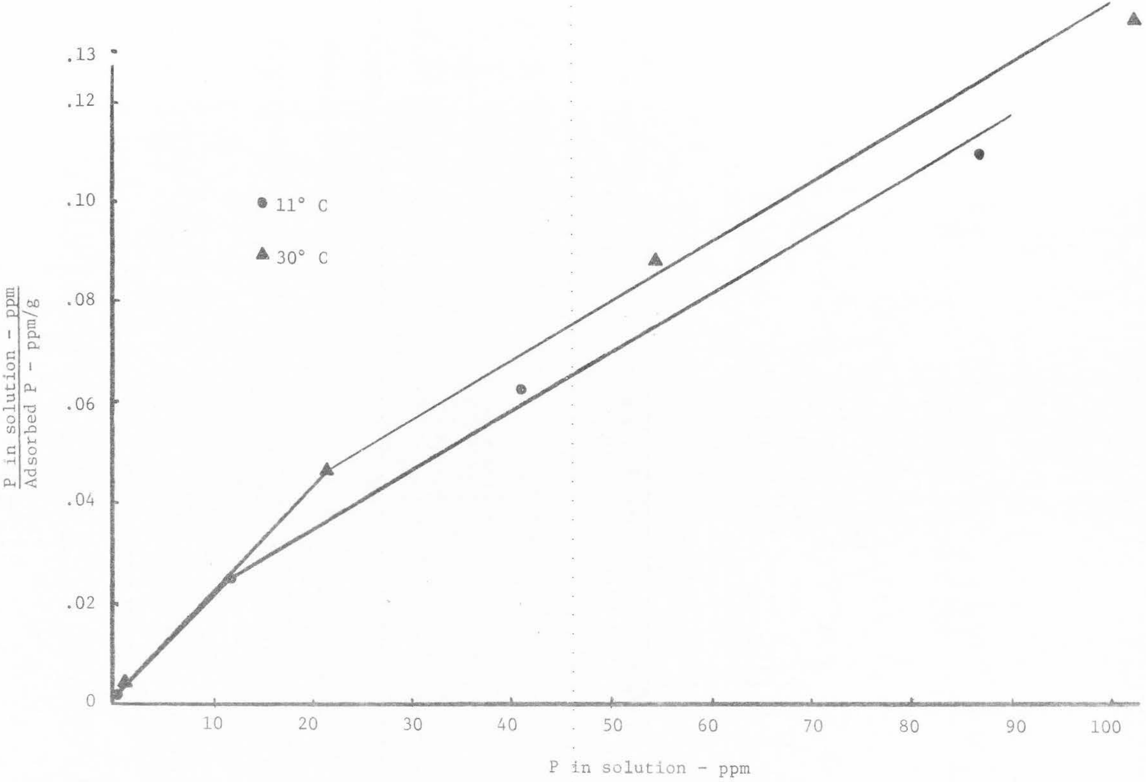

Figure 6. Phosphorous adsorption by Aiken clay loam soil at two temperatures, plotted according to the Langmuir equation.

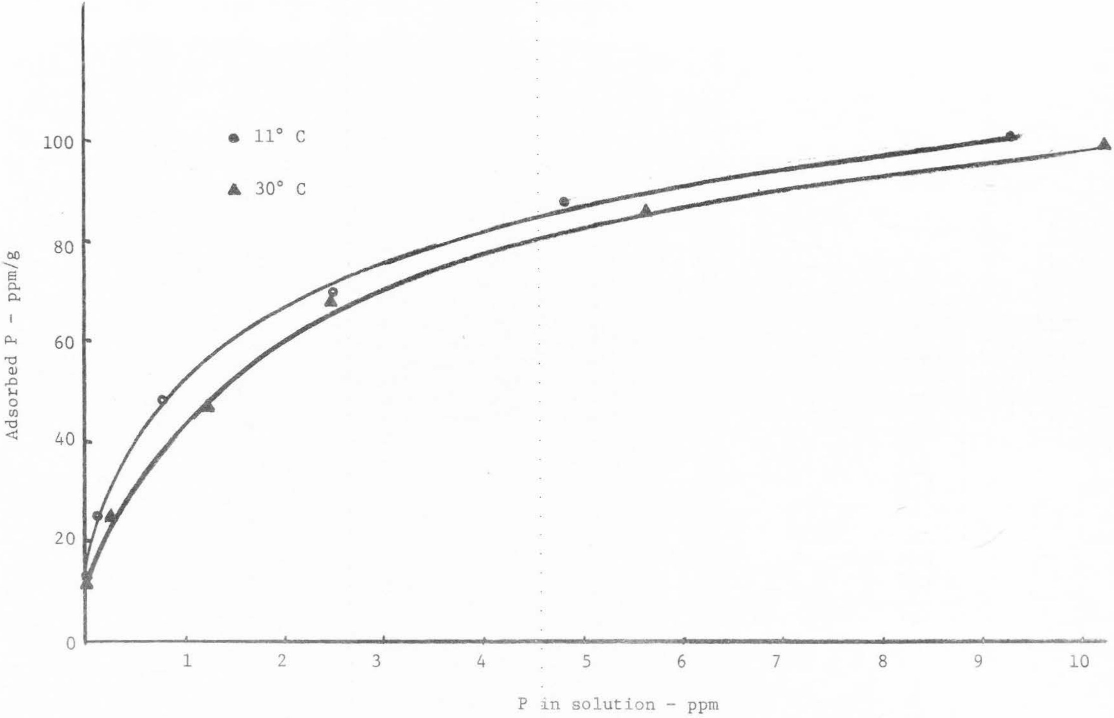

Figure 7. Phosphorous adsorption in the presence of 50 ppm B by Vernal sandy loam at two temperatures.

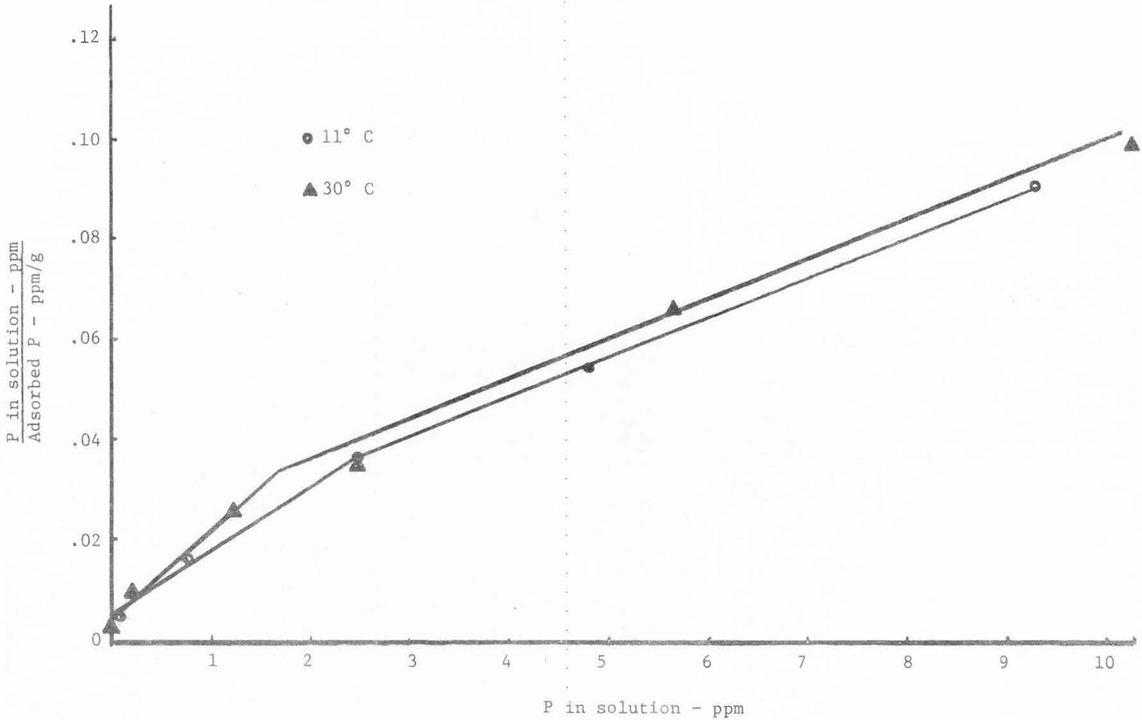

Figure 8. Phosphorous adsorption by Vernal sandy loam at two temperatures plotted according to the Langmuir equation

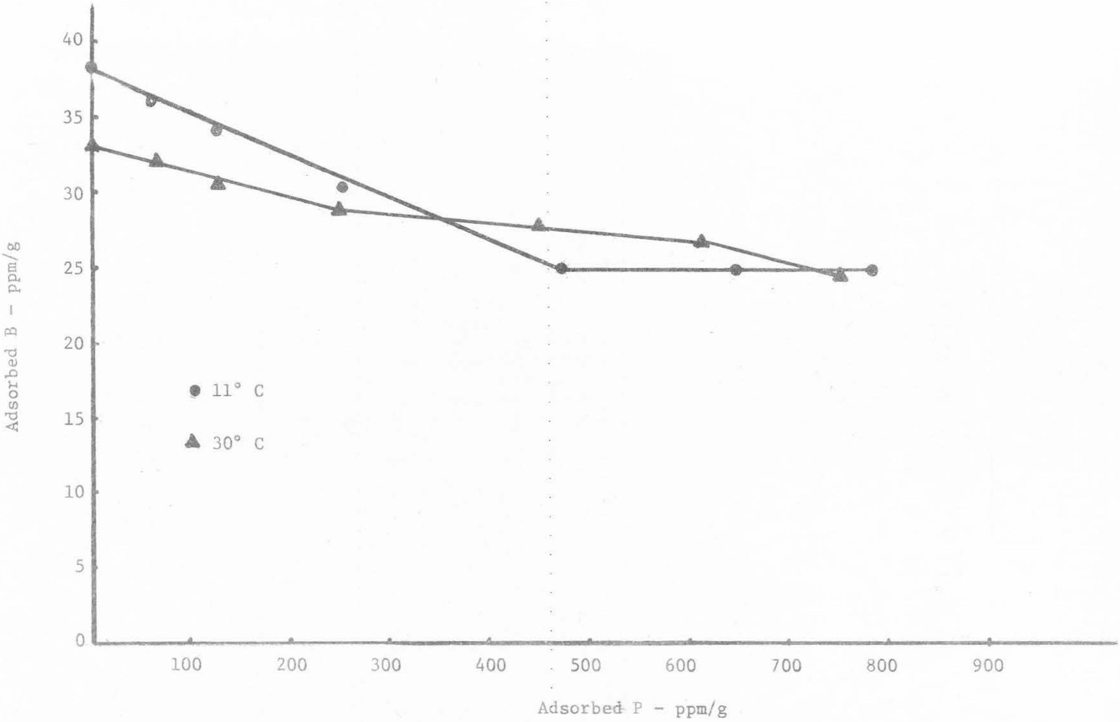

Figure 9. Effect of adsorbed P on boron adsorption in Aiken clay loam soil.

Table 1 shows that X_m for phosphate was considerably higher than for boron in both soils. These values were calculated by drawing the best straight line through the data shown in Figures 6 and 8. Data for the studies at 20° are not shown however, the values obtained were intermediate to the 11 and 30° C data. The reaction time for both P and Cl adsorption studies was 24 hours. No attempt was made to verify that equilibrium occurred in this time interval. From our data, however, it seems likely the equilibrium was established during 24 hours. Muljadi et al. (1966a) and Olsen and Watanabe (1957) reported 24 hours as the equilibrium time for phosphorous adsorption with different adsorbents.

Figures 5 through 9 show that the adsorption of P in the presence of 50 ppm B was exothermic, i.e., adsorption decreased with an increase in temperature. These data are in disagreement with Low and Black (1950) and Muljadi et al. (1966c). Both these workers reported P adsorption is endothermic. Hunter and Alexander (1963) considered the results of Low and Black (1950) as an artifact. Figures 10 and 11 show that the adsorption of phosphate did not have a dramatic effect on boron retention by the soils. Figure 10 shows that after 700 ppm P was adsorbed by Aiken soil only about 10 ppm B was released to solution. Correspondingly, after 100 ppm P was adsorbed by the Vernal soil only about 5 ppm B was released. These data show definitely that P is not competitive for B adsorption sites in the soils studied. This study also shows the great difference between the two soils in their affinity for P (Table 1). Aiken soil has an adsorption maximum for P about 7 times greater than the Vernal soil. The indigeneous P levels in these soils were not determined, however, it is highly probable that it was very low.

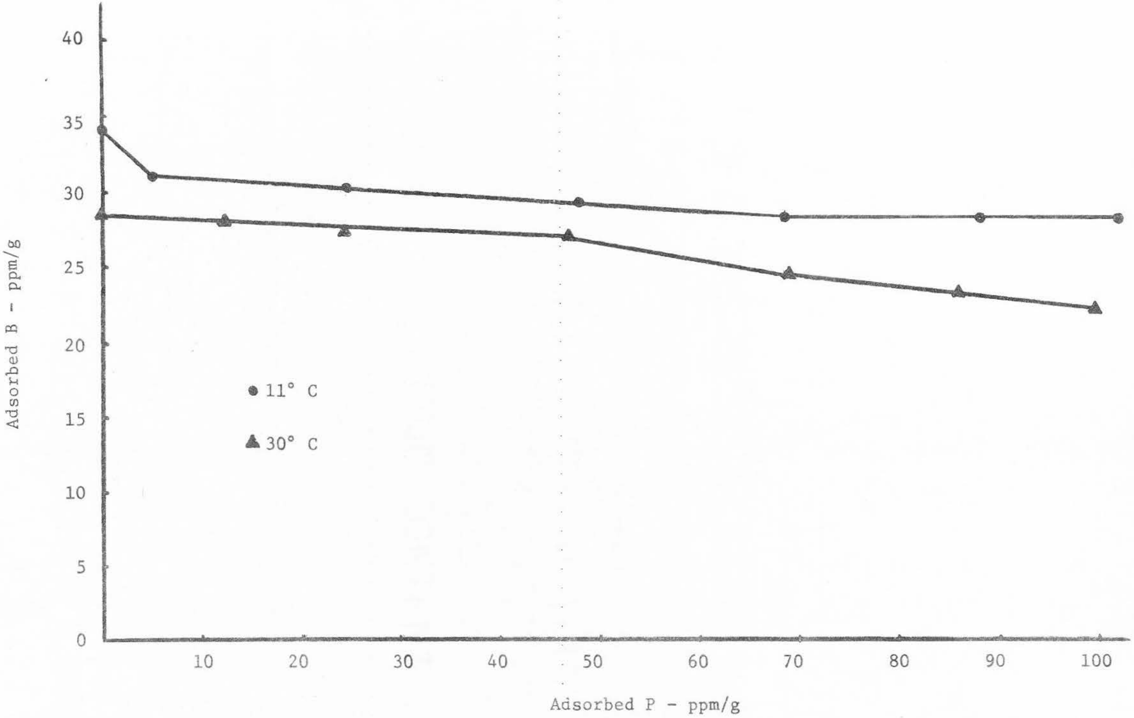

Figure 10. Effect of adsorbed P on boron adsorption in Vernal sandy loam soil at two temperatures.

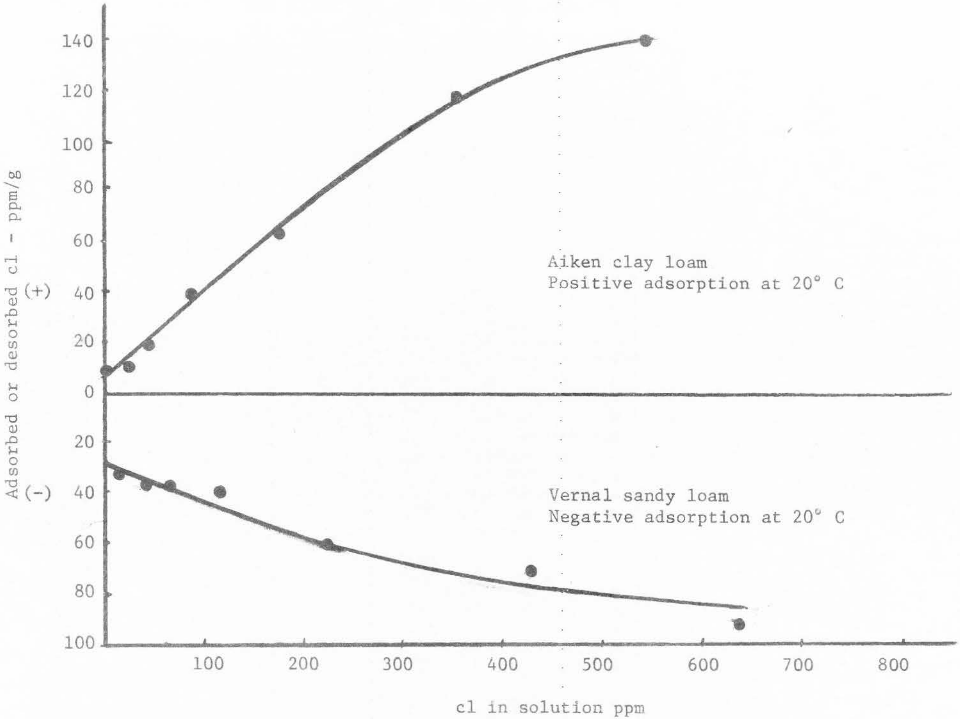

Figure 11. Positive and negative adsorption of chloride in the presence of 50 ppm B by Aiken and Vernal soils.

The differential heat of adsorption (Table 1) for phosphate shows Aiken soil interacts more energetically with phosphate than with boron. The reverse is true of Vernal soil. These data show the difference that exists between the two soils in regard to anion interaction. This data supports the contention that phosphate interaction differs fundamentally from boron in the soils studied. The ΔH values were calculated for $\theta = 0.5$ using the X_m values for 11° and 30° C.

Figure 12 shows the adsorption data of chloride ion in the presence of 50 ppm B for both Vernal and Aiken soils.

The Aiken soil shows a definite capacity to interact with chloride. This is expected since it is highly probable that positive changes exist in this soil. This condition is enhanced both by its high iron oxide and kaolinite content (Schofield and Samson, 1954; and Quirk, 1960). The indigenous chloride content of Aiken clay loam as measured was negligible.

The interaction of chloride with Vernal soil is dramatically different than with the Aiken soil. In the presence of 50 ppm B and no chloride added (Table 9b, Appendix) 33.65 ppm Cl was desorbed from the soil. This data indicates a substantial amount of soluble salts in this soil. As increasing amounts of chloride was added to the soil the amount of chloride desorbed was almost linear (see Figure 12). The data in Figure 12 are of interest because they show a fundamental electrochemical difference between the two soils.

Figure 13 shows how boron adsorption is effected by the addition of chloride. No boron is released by Aiken clay loam until the equilibrium chloride concentration reaches 83 ppm. About 7 ppm B is released as the equilibrium concentration approaches 600 ppm Cl. Chloride has

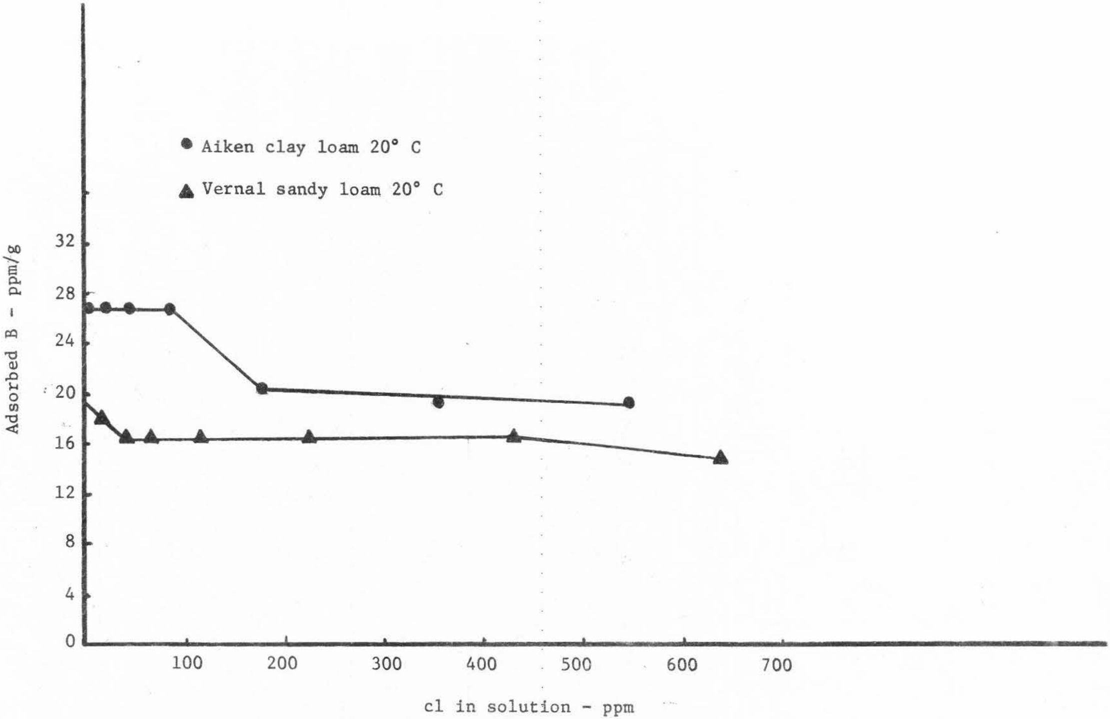

Figure 12. Effect of adsorbed chloride on boron adsorption.

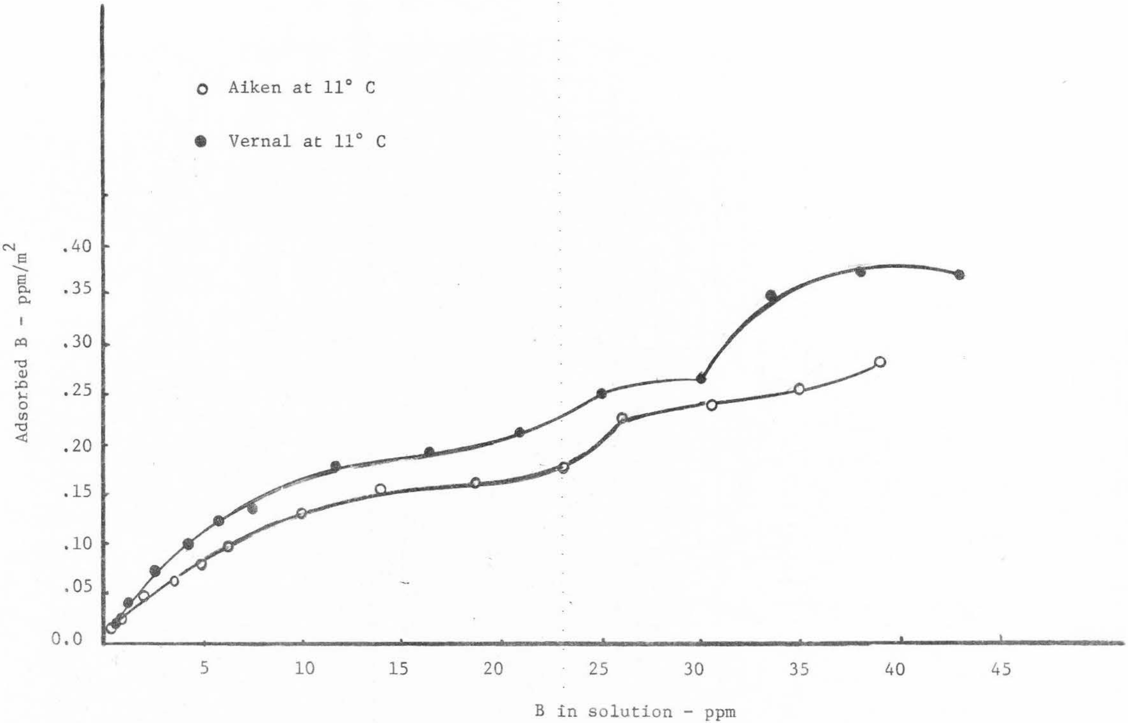

Figure 13. Amount of B adsorbed per (m^2) plotted against equilibrium B concentration.

essentially no effect on boron retention in the Vernal soil, only 2-3 ppm B is released as the equilibrium chloride reaches 600 ppm.

The experimental data concerning the effect of both P and Cl on boron are given in the appendix, Tables 4 through 9.

Adsorption of boron and phosphate on the unit area basis

Figure 13 shows the adsorption of boron on the unit area basis comparing both Aiken and Vernal soil at one adsorption temperature. On the area basis, Vernal soil adsorbs more boron than Aiken soil which is the reverse of the situation when adsorption is considered on the mass basis (see Figures 1 and 3). Thus, the calcareous soil has more surface activity than the high iron soil. This conclusion is supported by the higher ΔH of adsorption for boron exhibited by the Vernal soil when compared to the Aiken soil (Table 1).

Figure 14 shows the adsorption of phosphate by Vernal and Aiken soil compared on an unit area basis. Because of the much greater capacity of Aiken soil to adsorb phosphate (Table 1) on the mass basis, removal of the surface bias from the data does not affect the general statement that Aiken soil has a greater capacity to interact with phosphate than Vernal soil. These data support the contention that boron and phosphate react by totally different mechanisms which appears to be a function of the soil studied.

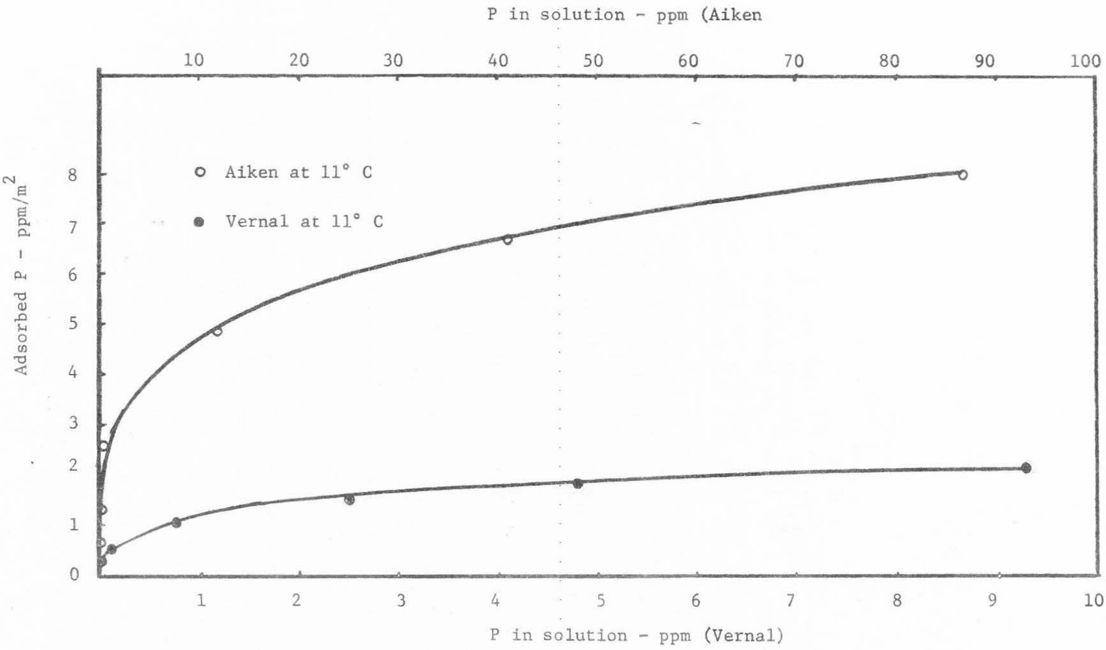

Figure 14. Amount of phosphorous adsorbed per (m^2) plotted against equilibrium P concentration

CONCLUSION

The adsorption of boron by Aiken clay loam and Vernal sandy loam was studied in the equilibrium boron concentration range of 0 to 40 ppm. The adsorption process was studied at three temperatures, 11, 20 and 30° C. The Langmuir adsorption isotherm equation was applied to the data. The results inferred that boron adsorption was occurring on multiple sites. Three adsorption regions were delineated however, only two regions could be positively identified by the Langmuir linear equation. Each adsorption region is assumed to consist of one type of adsorption site. This study suggests that much of the inconsistency in the literature regarding the application of the Langmuir isotherm to boron adsorption is the result of not obtaining a sufficient amount of data and assuming a simple Langmuir model instead of multiple adsorption sites.

The ferrigenous acid soil (Aiken) had a higher adsorption capacity for boron both in regions I and II than the calcareous (Vernal) soil. The higher capacity of the ferrigenous Aike soil for boron is ascribed to the possible interaction of boron with iron oxide forming a polymeric surface compound with a general equation, $Fe_2O_3 \cdot 3B_2O_3 \cdot 3H_2O$, as described by Sims and Bingham (1968a, b). In the two soils studied, adsorption in region II was completed when the equilibrium concentration reached 32 ppm. Thus, the full value of X_m^{II} is not realized in the natural system (see Table 1 and Figures 2 and 4) before the interaction in region 3 proceeds and effectively overshadows the reaction occurring in region II. These data indicate that interpretation of the multiple site adsorption reaction by the Langmuir isotherm is complex and must be used with caution.

The effect of temperature on boron adsorption was the same in both soils. Adsorption was exothermic. An increase in temperature decreased adsorption. Thus, boron leaching from a field soil would be more efficient in summer than in winter for a given amount of water leached through the soil.

The differential (isosteric) heat of adsorption, ΔH, calculated from the Clausius-Clapeyron equation was -7.6 K cal/M and -3.3 K cal/M for boron adsorption by the Vernal and Aiken soils, respectively. These values represent adsorption in region I. Any indigenous boron in these soils probably occupies the high energy sites, thus the heat of adsorption is not critically defined and is of limited operational use. The data indicated that boron reacts more energetically with the Vernal soil than with the Aiken soil, although the capacity to adsorb boron is in the reverse order.

This study showed that the capacity of both soils to adsorb phosphate was considerably higher than their capacity to adsorb boron (Table 1). The adsorbed phosphate, however, was not a strong competitor for the boron adsorption site. For the Aiken soil the ratio of the moles of phosphate adsorbed to the moles of boron desorbed was about 20 to 1. In the Vernal soil, the ratio of the moles of phosphate adsorbed to the moles of boron desorbed was about 6 to 1. Thus in a calcareous soil, phosphate is about three times more efficient in replacing boron than in a ferrigenous soil. It appears that phosphate and boron adsorption by soil is not very competitive, particularly in the presence of iron oxide.

The adsorption of phosphate by Vernal and Aiken soil was not well defined by the linear Langmuir isotherm. This result is in agreement with Larsen (1967) who found a curvilinear relation, on 120 soil samples, when the linear Langmuir isotherm equation was applied. Any curved line can be interpreted in terms of a series of straight lines, thus a curvilinear plot can mean that multiple site adsorption of phosphate by soils is a rule rather than the exception. Insufficient data were collected in this study to prove or disprove this point.

The adsorption of chloride by Vernal and Aiken soil followed distinctly different trends. Positive adsorption of chloride occurred in Aiken soil, whereas negative adsorption occurred in Vernal soil. Chloride had little effect on the adsorption of boron by the Vernal soil. However, in the Aiken soil, chloride was more effective. Calculations indicate that for each 6.3 moles of chloride reacting with the soil, 1 mole of boron was desorbed. No boron was desorbed until the equilibrium concentration of chloride reached about 100 ppm or 2.8×10^{-3} moles Cl. Thus, it appears chloride is more effective in blocking boron adsorption than phosphate in Aiken soil. The reason for this anamoly is not obvious. However, neither phosphate or chloride appears to seriously limit the adsorption or interaction of boron with the soil.

When the adsorption of boron is expressed on a unit area basis, the Vernal soil has a greater adsorption capacity than the Aiken soil. These data are in line with the larger differential heats of adsorption, ΔH, calculated for the Vernal soil (Table 1). It appears the calcareous soil has more surface activity than the acidic iron soil.

The data from this study indicate that boron adsorption is not a simple process and the mechanism depends to a marked degree on the soil system studied. Considerable more date are required to explain boron chemistry in soil. This research represents a first step.

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APPENDIX

Table 2a. Equilibrium solution and adsorbed boron concentration in Aiken soil with solution containing various concentrations of boron at 11° C. Soil-water ratio = 1:2.5

Initial B soln. conc.	B in solution	B adsorbed	$\frac{\text{B in solution-ppm}}{\text{B adsorbed-ppm/g}}$
ppm	ppm	ppm/g	
1	.371	1.753	.234
2	.936	2.660	.352
4	2.064	4.840	.427
6	3.544	6.140	.577
8	4.899	7.753	.632
10	6.254	9.365	.669
15	9.990	12.525	.798
20	13.997	15.008	.933
25	18.787	15.533	1.210
30	23.140	17.150	1.349
35	26.140	22.150	1.180
40	30.590	23.525	1.300
45	34.961	25.098	1.393
50	38.928	27.680	1.406

Table 2b. Equilibrium solution and adsorbed boron concentration in Aiken soil with solution containing various concentrations of boron at 20° C. Soil-water ratio = 1:2.5

Initial B soln. conc.	B in solution	B adsorbed	B in solution-ppm / B adsorbed-ppm/g
ppm	ppm	ppm/g	
1	0.375	1.563	.240
2	1.070	2.325	.460
4	2.113	4.750	.450
6	3.720	5.700	.652
8	5.150	7.125	.723
10	6.400	9.000	.710
15	10.490	11.275	.931
20	14.916	12.709	1.174
25	19.460	13.850	1.400
30	23.044	17.391	1.325
35	27.688	18.281	1.515
40	31.750	20.622	1.540
45	36.025	22.438	1.606
50	41.637	20.909	1.991

Table 2c. Equilibrium solution and adsorbed boron concentration in Aiken soil with solution containing various concentrations of boron at 30° C. Soil-water ratio = 1:2.5

Initial B soln. conc.	B in solution	B adsorbed	$\frac{\text{B in solution-ppm}}{\text{B adsorbed-ppm/g}}$
ppm	ppm	ppm/g	
1	.448	1.380	.325
2	.980	2.550	.385
4	.233	4.175	.557
6	3.564	6.090	.585
8	5.054	7.365	.686
10	6.650	8.380	.790
15	10.800	10.500	1.030
20	15.600	11.000	1.420
25	20.000	12.500	1.600
30	23.850	15.380	1.550
35	27.850	17.880	1.550
40	31.600	21.000	1.500
45	37.000	20.000	1.850
50	4.250	21.875	1.890

Table 3a. Equilibrium solution and adsorbed boron concentration in Vernal soil with solution containing various concentrations of boron at 11° C. Soil-water ratio = 1:2.5

Initial B soln. conc.	B in solution	B adsorbed	B in solution-ppm / B adsorbed-ppm/g
ppm	ppm	ppm/g	
1	.593	1.018	.583
2	1.242	1.895	.655
4	2.635	3.413	.772
6	4.319	4.203	1.028
8	5.731	5.673	1.010
10	7.473	6.318	1.183
15	11.656	8.360	1.394
20	16.368	9.080	1.803
25	21.012	9.970	2.108
30	25.269	11.828	2.137
35	30.010	12.475	2.405
40	33.493	15.268	2.059
45	37.960	17.600	2.157
50	42.990	17.525	2.453

Table 3b. Equilibrium solution and adsorbed boron concentration in Vernal soil with solution containing various concentrations of boron at 20° C. Soil-water ratio = 1:2.5

Initial B soln conc.	B in solution	B adsorbed	B in solution-ppm / B adsorbed-ppm/g
ppm	ppm	ppm/g	
1	.673	.818	.823
2	1.349	1.628	.829
4	2.952	2.620	1.127
6	4.565	3.588	1.272
8	6.120	4.700	1.302
10	7.636	5.910	1.292
15	11.892	7.770	1.531
20	16.595	8.512	1.950
25	21.135	9.663	2.187
30	25.675	10.813	2.374
35	30.020	12.450	2.411
40	33.835	15.413	2.195
45	38.410	16.475	2.331
50	missing	missing	missing

Table 3c. Equilibrium solution and adsorbed boron concentration in Vernal soil with solution containing various concentrations of boron at 30° C. Soil water ratio = 1:2.5

Initial B soln. conc.	B in solution	B adsorbed	B in solution-ppm / B adsorbed-ppm/g
ppm	ppm	ppm/g	
1	.751	.623	1.205
2	1.523	1.193	1.277
4	3.223	1.943	1.659
6	4.980	2.550	1.953
8	6.506	3.738	1.741
10	8.187	4.533	1.806
15	12.858	3.355	2.401
20	17.030	7.425	2.294
25	21.910	7.725	2.836
30	26.350	9.125	2.888
35	30.940	10.150	3.048
40	35.620	10.950	3.253
45	41.690	8.275	5.038
50	46.330	9.175	5.040

Table 4a. Equilibrium solution and adsorbed boron concentration in Aiken soil with solutions containing fixed concentration of boron with the presence of various concentrations of phosphorous at 11° C. Soil-water ratio = 1:2.5

Initial conc. of B + P	B in solution	B adsorbed	B in solution-ppm / B adsorbed-ppm/g
ppm	ppm	ppm/g	
50 B + 0P	34.730	38.175	.910
+ 25 P	35.580	36.050	.987
+ 50 P	36.430	33.925	1.074
+ 100 P	37.850	30.375	1.246
+ 200 P	39.990	25.025	1.598
+ 300 P	39.990	25.025	1.598
+ 400 P	39.990	25.025	1.598

Table 4b. Equilibrium solution and adsorbed boron concentration in Aiken soil with solution containing fixed concentration of boron with the presence of various concentrations of phosphorous at 30° C. Soil-water ratio = 1:2.5

Initial conc. of B + P	B in solution	B adsorbed	B in solution-ppm / B adsorbed-ppm/g
ppm	ppm	ppm/g	
50 B + 0 P	36.780	33.050	1.113
+ 25 P	37.100	32.250	1.150
+ 50P	37.830	30.425	1.240
+ 100 P	38.360	29.100	1.318
+ 200 P	38.780	28.050	1.382
+ 300 P	39.210	26.975	1.454
+ 400 P	40.050	24.857	1.610

Table 5a. Equilibrium solution and adsorbed phosphorous concentration in Aiken soil with solution containing various concentrations of phosphorous with the presence of fixed concentration of boron at 12° C. Soil-water ratio = 1:2.5

Initial conc. of B + P	P in solution	P adsorbed	P in solution-ppm / P adsorbed-ppm/g
ppm	ppm	ppm/g	
50 B + 25 P	0	62.500	0
+ 50 P	.0134	124.967	.0001
+ 100 P	.2700	249.325	.0010
+ 200 P	11.8750	470.313	.0252
+ 300 P	40.9250	647.688	.0631
+ 400 P	86.5500	783.625	.1104

Table 5b. Equilibrium solution and adsorbed phosphorous concentration in Aiken soil with solution containing various concentrations of phosphorous with the presence of fixed concentration of boron at 20° C. Soil-water ratio = 1:2.5

Initial conc. of B + P	P in solution	P adsorbed	P in solution-ppm / P adsorbed-ppm/g
ppm	ppm	ppm/g	
50 B + 25 P	.0046	62.489	.000073
+ 50 P	.0420	124.895	.000340
+ 100 P	.5050	248.740	.002000
+ 200 P	16.6500	458.375	.036000
+ 300 P	37.4500	656.375	.057000
+ 400 P	77.7200	805.700	.097000

Table 5c. Equilibrium solution and adsorbed phosphorous concentration in Aiken soil with solution containing various concentrations of phosphorous with the presence of fixed concentration of boron at 30° C. Soil-water ratio = 1:2.5

Initial conc. of B + P	P in solution	P adsorbed	P in solution-ppm / P adsorbed-ppm/g
ppm	ppm	ppm/g	
50 B + 25 P	.002	62.495	--
+ 50 P	.164	124.590	.0011
+ 100 P	1.205	246.988	.0048
+ 200 P	20.775	448.063	.0463
+ 300 P	54.525	613.688	.0890
+ 400 P	102.450	743.875	.1377

Table 6a. Equilibrium solution and adsorbed boron concentration in Vernal soil with solutions containing fixed concentration of boron with the presence of various concentrations of phosphorous at 12° C. Soil-water ratio = 1:2.5

Initial conc. of B + P	B in solution	B adsorbed	B in solution-ppm / B adsorbed-ppm/g
ppm	ppm	ppm/g	
50 B + 0 P	36.430	33.925	1.074
+ 5 P	37.570	31.075	1.210
+ 10 P	37.850	30.375	1.246
+ 20 P	38.130	29.675	1.285
+ 30 P	38.700	28.250	1.370
+ 40 P	38.70	28.250	1.370
+ 50 P	38.70	28.250	1.370

Table 6b. Equilibrium solution and adsorbed boron concentration in Vernal soil with solution containing fixed concentrations of boron with the presence of various concentrations of phosphorous at 30° C. Soil-water ratio = 1:2.5

Initial conc. of B + P	B in solution	B adsorbed	B in solution-ppm / B adsorbed ppm/g
ppm	ppm	ppm/g	
50 B + 0 P	38.57	28.575	1.350
+ 5 P	38.78	28.050	1.383
+ 10 P	38.99	27.525	1.417
+ 20 P	39.21	26.975	1.454
+ 30 P	40.16	24.600	1.633
+ 40 P	40.68	23.300	1.746
+ 50 P	40.11	22.225	1.850

Table 7a. Equilibrium solution and adsorbed phosphorous concentration in Vernal soil with solution containing various concentrations of phosphorous with the presence of fixed concentration of boron at 11° C. Soil-water ratio = 1:2.5

Initial conc. of B + P	P in solution	P adsorbed	P in solution-ppm / P adsorbed-ppm/g
ppm	ppm	ppm/g	
50 B + 5 P	0.0000	12.500	0.0000
+ 10 P	.1004	24.749	.0040
+ 20 P	.7720	48.070	.0160
+ 30 P	2.4950	68.763	.0362
+ 40 P	4.8150	87.963	.0547
+ 50 P	9.3100	101.725	.0915

Table 7b. Equilibrium solution and adsorbed phosphorous concentration in Vernal soil with solution containing various concentrations of phosphorous with the presence of fixed concentration of boron at 20° C. Soil-water ratio = 1:2.5

Initial conc. of B + P	P in solution	P adsorbed	$\frac{\text{P in solution-ppm}}{\text{P adsorbed ppm/g}}$
ppm	ppm	ppm/g	
50 B + 5 P	.033	12.418	.0027
+ 10 P	.165	24.588	.0067
+ 20 P	1.129	47.178	.0240
+ 30 P	3.000	missing	missing
+ 40 P	5.410	86.475	.0630
+ 50 P	9.380	101.550	.0920

Table 7c. Equilibrium solution and adsorbed phosphorous concentration in Vernal soil with solution containing various concentrations of phosphorous with the presence of fixed concentration of boron at 30° C. Soil-water ratio = 1:2.5

Initial conc. of B + P	P in solution	P adsorbed	$\frac{\text{P in solution-ppm}}{\text{P adsorbed-ppm/g}}$
ppm	ppm	ppm/g	
50 B + 5 P	.026	12.435	.0020
+ 10 P	.232	24.420	.0095
+ 20 P	1.222	46.945	.0260
+ 30 P	2.445	68.888	.0350
+ 40 P	5.655	85.863	.0660
+ 50 P	10.250	99.400	.1003

Table 8a. Equilibrium solution and adsorbed boron concentration in Aiken soil with solution containing fixed concentration of boron with the presence of various concentrations of chloride at 20° C. Soil-water ratio = 1:2.5

Initial conc. of B + Cl	B in solution	B adsorbed
ppm	ppm	ppm/g
50 B + 0 Cl	39.03	27.30
+ 25 Cl	38.63	27.30
+ 50 Cl	39.53	27.30
+ 100 Cl	38.86	27.30
+ 200 Cl	41.78	20.55
+ 400 Cl	42.23	19.43
+ 600 Cl	42.23	19.43

Table 8b. Equilibrium solution and adsorbed chloride concentration in Aiken soil with solution containing various concentrations of chloride with the presence of fixed concentration of boron at 20° C. Soil-water ratio = 1:2.5

Initial Cl conc.	Cl in solution	Cl adsorbed
ppm	ppm	ppm/g
50 B + 0 Cl	3.6	9.00
+ 25 Cl	21.3	9.25
+ 50 Cl	42.6	18.50
+ 100 Cl	84.3	39.25
+ 200 Cl	174.8	63.00
+ 400 Cl	352.8	118.00
+ 600 Cl	543.6	141.00

Table 9a. Equilibrium solution and adsorbed boron concentration in Vernal soil with solution containing fixed concentration of boron with the presence of various concentrations of chloride at 20° C. Soil-water ratio = 1:2.5

Initial conc. of B + Cl	B in solution	B adsorbed
ppm	ppm	ppm/g
50 B + 0 Cl	42.68	18.30
+ 25 Cl	42.68	18.30
+ 50 Cl	42.68	18.30
+ 100 Cl	42.68	18.30
+ 200 Cl	42.68	18.30
+ 400 Cl	42.68	18.30
+ 600 Cl	44.03	14.93

Table 9b. Equilibrium solution and desorbed chloride concentration in Vernal soil with solution containing various concentrations of boron at 20° C. Soil-water ratio = 1:2.5

Initial Cl conc.	Cl in solution	Cl desorbed
ppm	ppm	ppm/g
50 B + 0 Cl	13.49	33.63
+ 25 Cl	39.90	37.35
+ 50 Cl	64.80	37.00
+ 100 Cl	115.70	39.25
+ 200 Cl	224.10	60.25
+ 400 Cl	428.20	70.50
+ 600 Cl	636.80	92.00

VITA

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