

BORON CHEMISTRY IN SELECTED VIRGINIA SOILS
AND HYDROXY ALUMINUM AND IRON SYSTEMS

by

Ji-yun Jin

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APPROVED:

D. C. Martens, Co-chairman

L. W. Zelazny, Co-chairman

G. W. Hawkins

D. E. Brann

J. P. Wightman

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Blacksburg, Virginia

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Committee Co-chairmen: David C. Martens

Lucian W. Zelazny

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(ABSTRACT)

Greenhouse and laboratory experiments were conducted to investigate the distribution of native B, the availability of native and applied B in 14 Virginia soils and the specific reactions of B in soil and hydroxy Al and Fe systems.

Total B in the 14 soils ranged from 21.5 to 96.3 mg kg⁻¹. Only a small portion of the total B was in soil solution, non-specifically and specifically adsorbed forms and Mn minerals. These fractions of B are readily available to plants. A large part of the total B was associated with non-crystalline and crystalline Al and Fe minerals and soil silicates. These forms of B contribute little to B absorption by plants. Hot water soluble B, NH₄-acetate extractable B, mannitol exchangeable B and Mehlich III extractable B from the soils closely correlated with the concentrations in

corn plants from native B in the greenhouse experiment. A yield response of corn plants to B application did not occur on the soils.

Both tissue B concentration from applied B and maximum B adsorption by the soils closely correlated with soil clay, hydroxylamine hydrochloride extractable Mn and NH_4 -oxalate (pH 3.25) extractable Al and Fe (under UV light). These data indicated that soil clay and Al-, Fe- and Mn-oxides and hydroxides have high affinities to adsorb B in plant unavailable forms.

Boron adsorption on both gibbsite and goethite was pH and temperature dependent. At pH 6.5, boric acid was major species in the system and B was adsorbed by the negatively charged surface of gibbsite and the positively charged surface of goethite. At pH 10, borate was primarily species in the system and B was adsorbed on negatively charged surfaces of both minerals. Boron adsorption was greater at pH 10 than at pH 6.5. An increase in temperature increased B adsorption on both minerals at both pH levels. This indicated that the B adsorption was an exothermic process. Boron adsorption on gibbsite and goethite shifted the ZPC of the minerals downward. This verified that specific B adsorption occurred on the surfaces. Aluminum substitution in goethite increased the affinity of the surface for B adsorption.

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Chapter I

INTRODUCTION

As a essential micronutrient for normal growth of plants, boron (B) has received much attention since the beginning of this century. In Virginia, B application as a fertilizer was started in 1940's. Boron fertilization on alfalfa has been a common practice in Virginia. Recently, application of B for corn, wheat and other crops has been recommended by some laboratories. However, very few detailed studies have been conducted on the forms of native B in Virginia soils, the reactions of B with soil components after B application and the availabilities of native and applied B to plants as affected by soil properties. This information is essential for fertilization recommendations.

Adsorption of B by soil components affects the availability of B to plants. Boron is a unique micronutrient. In normal soil pH, it exists as an uncharged species, the boric acid molecule, $B(OH)_3$. It hydrolyzes to the borate anion, $B(OH)_4^-$, in alkaline conditions. Consequently, the adsorption of B in soils is a complex phenomenon. Although research has been completed on B adsorption in soils and pure systems, the mechanism of B adsorption in soils is still in question.

It generally has been accepted that Al- and Fe-oxides and hydroxides have high affinities for B. Gibbsite and goethite are common Al and Fe minerals in soils. Detailed research on B reactions with gibbsite and goethite surfaces undoubtedly will add insight to the knowledge of soil B chemistry.

Pure Al or Fe minerals do not exist in the heterogeneous soil system. Aluminum substitution for Fe in goethite is a common phenomenon in soils. The substitution of Al for Fe affects unit cell dimension, particle size, surface area and other mineralogical and morphological properties of the goethite, which, in turn, may influence the adsorption of B on the surface.

Based on the updated knowledge of soil B chemistry, three research projects were conducted to investigate the reactions of B in soil and hydroxy Al and Fe systems. The specific objectives of this investigation were as follows:

1. To study the distribution of native soil B in different forms and their contribution to plant uptake in selected 14 Virginia soils.
2. To estimate the B fixation power and the availability of applied B to the 14 soils as affected by soil properties.

3. To investigate the influences of pH and temperature on B adsorption by gibbsite and goethite and the effects of B adsorption on surface charge characteristics of these minerals, and thereby to explore the specific reaction of B with surfaces of gibbsite and goethite.
4. To ascertain the effect of Al substitution for Fe in goethite on B adsorption, and thereby to estimate the relative affinity of hydroxy Al and Fe to B adsorption.

Chapter II

LITERATURE REVIEW

2.1 INTRODUCTION

Boron (B) is one of the essential micronutrients required for normal growth of plants. The presence of B in plant ashes was discovered by Wittstein and Apoiger (cited by Fleming, 1980). The plant essentiality of B was first mentioned by Maze in 1914 (cited by Fleming, 1980). However, it was the work of Warington (1923) that provided firm knowledge of the B requirement for plant growth. The proof of essentiality of B for higher plants in general is accredited to Sommer and Lipman (1926). Since then, the importance of B as an agricultural chemical has grown very rapidly. In the last 50 years, there have been hundreds of reports dealing with the essentiality of B to plants and its reactions in soils. A complete review on B nutrition of crops has been provided by Gupta (1979), while Sims (1966), Evans and Sparks (1983), and Keren and Bingham (1985) prepared extensive reviews on the physical-chemical reactions of B in soils.

2.2 GENERAL CHEMISTRY AND GEOCHEMISTRY OF BORON

Boron is the first member of the third periodic group. Unlike the other members, it is a nonmetal element with $2S^22P^1$ electronic structure. Because the ionization potential of B is rather high (the first ionization potential of B is 8.296 eV, and the next two are even much higher), simple electron loss to form a cation plays no part in B chemistry. Instead, covalent bond formation is of major importance. Despite the $2S^22P^1$ electronic structure, B is always trivalent, because the hybridization of the $2S^22P^1$ orbitals to form trivalent compound with three hybridized SP^2 orbitals provides lower potential energy for the system (Runquist et al., 1974).

Boron occurs in nature as boric acid and as salts of various condensed boric acid, such as borax, $Na_2B_4O_7 \cdot 10H_2O$. It constitutes only about 0.001% of the earth's crust (Garrett et al. 1968). Boric acid forms white needle-like crystals in which there are $B(OH)_3$ units linked together by hydrogen bonds to form layers of nearly hexagonal symmetry. Boric acid is a very weak and exclusively monobasic acid which acts not as a proton donor but as a Lewis acid, accepting OH^- . It hydrolyzes to form the borate ion as shown below (Cotton and Wilkinson, 1966):



The pK value for this reaction is 9, indicating that in acid and neutral soils B is predominantly in the boric acid form while in alkaline soils the borate ion become important. Raman and infrared spectroscopic analysis has shown boric acid molecules to be trigonal and borate ion to be tetrahedral in aqueous solution (Baes and Mesmer, 1976).

When B occurs in solution at concentrations above 0.1 M, polyborate species are formed by the addition of one OH^- per $\text{B}(\text{OH})_3$ molecule. Generally a lower concentration occurs in normal soil condition and, consequently, $\text{B}(\text{OH})_3$ exists essentially as a monomer in soils.

The distribution of B among the common rock types is shown in Table 1 Sedimentary rocks, especially shales, contain more B than igneous rocks. The abundance of B in shales indicates that dissolved borates have been predominant in sea water throughout the earth's history (Krauskopf, 1973).

At present, there are about 150 known B minerals (Erd, 1980). Some common B containing minerals in soils are shown in Table 2 The anhydrous borates and complex borosilicates are high temperature minerals, whereas hydrous borates are low temperature minerals. The primary mineral tourmaline, which is highly resistant to weathering, is the most common of the high temperature B minerals (Krauskopf, 1973).

TABLE 1
Distribution of Boron in Common Rock Types¹.

Rock Class	Rock type	Content (g kg ⁻¹)
Igneous	Granite	15
	Basalt	5
Sedimentary	Limestone	20
	Sandstone	35
	Shale	100

¹ From Krauskopf, 1973.

TABLE 2
Boron Containing Minerals¹.

Class	Mineral	Chemical Formula
Hydrous Borates	Borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
	Kernite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$
	Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$
	Ulexite	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$
Anhydrous Borates	Ludwigite	Mg_2FeBO_5
	Kotoite	$\text{Mg}_3(\text{BO}_3)_2$
Complex Borosilicates	Tourmaline	$\text{Na}(\text{Mg}, \text{Fe}, \text{Mn}, \text{Li}, \text{Al})_3\text{Al}_6\text{Si}_6\text{O}_{18}$ $(\text{BO}_3)_3(\text{OH}, \text{F})_4$
	Axinite	$(\text{Ca}, \text{Mn}, \text{Fe})_3\text{Al}_2\text{BO}_3\text{Si}_4\text{O}_{12}(\text{OH})$

¹ From Krauskopf, 1973.

2.3 BORON IN SOILS

2.3.1 Content and Forms of Boron in Soils

Total B content of normal soils ranges from 2 to 100 mg kg⁻¹ (Fleming, 1980). Lowest values are found in soils derived from acid igneous rocks from fresh water sedimentary deposits and in soils low in organic matter. Higher values are found in soils formed from shales, loess, and alluvium.

Total B in soils has been divided into the following four forms (Fleming, 1980):

- 1) water soluble B
- 2) B in organic matter
- 3) B adsorbed on soil complex and
- 4) B in silicates.

Water soluble B in soils is readily available to plants. Its composition may be quite variable depending on soil type and pH. Schaller (1948) recorded values ranging from 0.28 to 2.0 mg kg⁻¹ of water soluble B in shale and sandstone soils and from 0.32 to 0.88 mg kg⁻¹ in limestone soils. Strongly leached soils of acid gray shale and sandstone origin were lowest in water soluble B. Walsh and Golden (1952) reported that water soluble B in quartzite soils ranged from

0.1 to 0.4 mg kg⁻¹, in sandstone soils from 0.2 to 0.47 mg kg⁻¹, and in shale soils from 0.3 to 0.7 mg kg⁻¹. In arid soils where B salts accumulated, water soluble B may be very high indeed. Values of up to 1000 mg kg⁻¹ have been recorded from Peru (Fox, 1968).

Boron, like any other agronomically important trace elements, is associated with organic matter and soils high in organic matter are frequently high in B. Berger and Truog (1945) reported that organic matter had the greatest influence on B availability in soils of pH less than 7.0 with increased organic matter content causing an increase in available B. Berger (1962) also found that a large part of the total B in soils is held in organic matter and postulated that it becomes available through microbial release. Gupta (1968) showed that the relationship between hot water soluble B and organic matter was closer than that with total B, suggesting that clays hold only a small part of this replaceable B. However, the exact reactions of B with organic matter are not yet clear. In pure systems, B exhibits an affinity for alpha-hydroxy aliphatic acids and for ortho-dihydroxy derivatives of aromatic compounds (Parks and White, 1952). It is thought that B may combine as B-diol complexes with compounds such as xylose, mannose, glucose and galactose, which form organic matter decomposition.

The adsorbed B refers to a fraction of B which is held on adsorption sites of many surface active components. Since the soil is a complex heterogeneous system, many soil components are responsible for B adsorption. The proposed soil components which adsorb B in soils are:

- 1) layer silicates (Metwally, 1966; Keren and Mezuman, 1981),
- 2) Fe- and Al-oxides and hydroxides (Sims and Bingham, 1968a),
- 3) Mg hydroxides (Rhoades, et al., 1970a), and
- 4) organic matter (Parks and White, 1952).

These fractions of B are in equilibrium with the water soluble fraction in soils and, therefore, plays an important role in controlling the amount of plant available B in soils.

It has been reported that B can be specifically adsorbed by clay minerals (Hingston, 1964; Keren and Mezuman, 1981; Sims and Bingham, 1967). On a weight basis, illite is the most reactive among the clay minerals, whereas kaolinite is characterized by the lowest level of B adsorption (Hingston, 1964; Keren and Mezuman, 1981). Experimental findings and theoretical calculations have indicated that B is adsorbed on clay edges rather than on planar surfaces.

The existence of B in the lattice of layer silicates is still in question. Norrish (1975) suggested that B could substitute for tetrahedrally coordinated Si in some minerals and that much of the B in rocks and soils was dispersed in the silicate minerals by such substitution and would be available only after long periods of weathering. Couch and Grim (1968) studied B fixation by illite. They found that following an initial rapid adsorption B uptake proceeded very slowly with no evidence of reaching equilibrium after several months of treatment. They indicated that B atoms adsorbed on the positively charged edges of illite could migrate from surface sites into tetrahedral sites by intracrystalline diffusion. Further study and more direct evidence is needed to support this interpretation.

Though layer silicate clays undoubtedly exhibit an affinity for B retention, much adsorption has been attributed to hydroxy Al and Fe compounds present as coatings on surfaces of clays (Sims and Bingham, 1968b; Ellis and Knezek, 1972). Sims and Bingham (1968b) found that hydroxy Al coated on montmorillonite was less retentive on a weight basis than that coated on kaolinite. Keren and Gast (1983) found that B adsorption by hydroxy Al at pH 9.5 was about 7.5 times greater than by Ca-montmorillonite under the same conditions.

In a study of B adsorption by arid-zone soils, Rhoades et al. (1970a) proposed that these soils could have appreciable B adsorption capacities in their silt, sand and clay fractions. The site of this adsorption appeared to be hydroxy-Mg clusters or coatings that existed on the weathering surfaces of ferromagnesium minerals such as olivine, enstatite, diopside, augite, tremolite, and hornblende, as well as on hydroxy Al, hydroxy Fe and the micaceous layer silicates.

It appears from the literature that soil organic matter plays an important role in either B adsorption or soil B availability. However, very few detailed studies have been completed to verify the role of soil organic matter on B chemistry in soils. The research by Parks and White (1952) showed that humus had a chemical affinity for B and that hydrogen-saturated humus adsorbed approximately twice as much B as the calcium-saturated humus. Formation of a diol type complex between B and the soil organic matter compound was proposed to explain the B retention by soil organic matter (Parks and White, 1952).

2.3.2 Availability of Boron in Soils

The availability of a nutrient in soils is affected by many soil, plant and climatic factors and their interactions. It is very difficult, if not impossible, to relate the availability of a nutrient to one factor. The recognized soil factors which affect B availability in soils are pH and clay and organic matter contents.

Olson and Berger (1946) noted that B sorption was independent of pH below neutrality but increased rapidly under alkaline conditions, while Okazaki and Chao (1968) found that B sorption and soil pH were highly correlated ($r=0.90$) between pH 4.0 and pH 6.2. Wear and Patterson (1962) recorded a decrease in plant B content with increasing pH; whereas, Lehr and Henkens (1959) found no relation between the plant B content and soil pH. Peterson and Newman (1976) studied the effect of pH on the availability of added B at pH levels of 4.7, 5.3, 5.8, 6.3, and 7.4. Boron uptake by tall fescue (Festuca elatior) was relatively uniform for the first four pH levels but a 2.5 fold drop in uptake occurred at pH 7.4, indicating substantial B fixation. Plant uptake of B at the five pH levels was unrelated to the amount of water soluble B, but plant concentration of B was higher per unit of water soluble B at a lower pH level than at a higher pH level.

Total B contents usually are higher in clay and loam soils than in sandy soils (Gupta, 1968). However, the availability of B in soils is greatly affected by B adsorption on clays. Olson and Berger (1946) suggested that B fixation in humid region soils was caused by a group of minerals whose activity predominates in the clay fraction. Kubota et al. (1948) found that B was most mobile in surface horizons of sandy soils and that mobility decreased in subsoil horizons due to increased clay content and to reduced water movement. Wilson et al. (1951) showed that B movement was rapid in sandy soil with accumulations of applied B being greatest in the 30-90 cm zone for sandy loam soils, but restricted to the upper 15 cm in clay soils.

The greater availability of B in surface soils compared with subsurface soils is undoubtedly related to relative organic matter levels in humid regions, because soluble salts are leached and available B is largely held in the organic fraction. Organic matter, therefore, minimizes B loss from soils and maintains this element in a reasonably available form. Organic matter may also determine the degree to which water soluble B is affected by pH change (Fleming, 1980). Miljkovic et al. (1966) obtained a high correlation coefficient ($r=0.80$) between water soluble B and organic matter \times pH, indicating that increases in water soluble B associated

with pH are greater in soils with higher organic matter contents.

In acid soils organic matter exercises a powerful influence on B availability, while in alkaline soils its effects are generally subordinate to those of pH and available Ca (Berger and Truog, 1945). Page and Paden (1954) noted that in acid soils, organic matter exerted a greater influence on B availability than either pH or soil texture.

2.3.3 Determination of Available Boron in soils

In 1939, Berger and Truog published the hot water soluble B procedure, whereby B is extracted from soil by boiling in water for 5 minutes with a 1:2 soil to water ratio. In the last 40 years, the procedure has been the only accepted method to estimate B availability in soils. The hot water soluble B levels in soils correlate well with plant response to fertilization (Berger and Truog, 1939; Bedrosian and Hanna, 1966) and with B uptake by plants (Katalymov and Ryabova, 1958). Correlation coefficients ranging from 0.69 to 0.94 were obtained for the B content of some plants versus hot water soluble B in different soils (Baird and Dawson, 1955; Wear and Patterson, 1962; Werkhoven, 1964). In order to minimize the influence of color in the extraction solu-

tion on the B determination with azomethine-H method, Parker and Gardner (1981) modified the hot water soluble B procedure by boiling the soil sample in 0.02 M CaCl_2 instead in water. Extractable B level was not affected by the presence of CaCl_2 . The use of acid extractants for solubilizing B has also been investigated but the levels obtained do not correlate well with B concentrations in crops grown on calcareous soils (Cox and Kamprath, 1972). Baker (1971) extracted soils with 85% (v:v) H_3PO_4 and found that the B extracted by this reagent provided a less reliable indication of the B status than hot water soluble B. Gupta and Stewart (1975) extracted soil samples with 1 M NH_4 acetate (pH 4.8) and concluded that it was a more reliable extractant for the determination of soil available B as compared with the hot water extraction. It was less time consuming and more suitable for either calcareous or noncalcareous soils. The results from greenhouse research indicated that the 1 M NH_4 acetate extraction procedure gave similar assessment of plant available B with the hot water extraction, and a tentative concentration of $0.35 \mu\text{g/g}$ soil was suggested as a critical level for alfalfa (Medicago sativa). However, more field work is needed to substantiate the finding. Soltanpour and Schwab (1977) developed the NH_4HCO_3 -DTPA (AB-DTPA) soil test for the simultaneous extraction of P, K, Zn, Fe,

Cu, and Mn in alkaline soils. It has been used to estimate soil available B. However, the correlation coefficient with plant uptake was low as compared with the hot water soluble B (Gestring and Soltanpour, 1984). Mannitol exchangeable B method was developed to estimate the leachable B of soils (Rhoades et al., 1970b) and has been used to estimate available B (Bingham, 1982).

Reisenauer et al. (1973) categorized the water soluble B values in soil into the following three groups: 1) soils with less than 1 mg kg^{-1} water soluble B may not supply sufficient B to support normal growth of plants, 2) soils with 1 to 5 mg kg^{-1} water soluble B usually allow normal growth of plants, and 3) soils with greater than 5 mg kg^{-1} water soluble B may supply toxic level of B. However, it is necessary to realize that many other factors affect the B supplying power of soils. For instance, more B is required on heavy textured soils than on light textured soils. Stinson (1953) noted that B deficiency in lucerne (Medicago sativa) on heavy textured soils with a water soluble B content of 0.5 mg kg^{-1} , while on sandy soils the critical value was estimated to be 0.3 mg kg^{-1} . Organic matter levels must also be taken into consideration. As organic matter levels increase, critical values for water soluble B become greater. Thus in peats, Prasad and Byrne (1975) noted that, with wa-

ter soluble B values of up to 10 mg kg^{-1} , B toxicity was not apparent even in such a semi-tolerant crop as sweet corn (Zea mays). Climate factor can also affect the critical values. Lehr and Henkens (1959) reported that the levels of water soluble B associated with heart-rot of beets (Chenopodiaceae) were higher in warm, dry years (0.35 mg kg^{-1}) than in cool, wet years (0.30 mg kg^{-1}).

It is clear from the above discussion that a comparison of hot water soluble B from different soils must be used with caution and especially in correlation with field data. The use of more than one parameter may be necessary. Martens (1968) evaluated the effects of hot water soluble B, pH, organic matter and clay content on plant uptake of B and found that uptake was best predicted by the two independent variables, hot water soluble B and pH. A multiple correlation coefficient ($r=0.637$) was obtained between these two variables and B uptake by plants.

2.4 MECHANISM OF BORON ADSORPTION

A number of studies have been conducted to determine the mechanisms of B adsorption in clay and soil systems. The most definitive finding is that B adsorption increases with an increase in pH (Hingston, 1964; Metwally, 1966; Keren and Mezuman, 1981). Metwally studied the B adsorption with five clay minerals, montmorillonite, illite, vermiculite and kaolinite, at a pH range of 4 to 10. In all the clay systems, B adsorption increased with an increase in pH and reached a maximum at pH 7.5 to 8.2. The amount of B adsorbed decreased sharply with a further pH increase. He interpreted these results as both boric acid and borate could be adsorbed. Below pH 7, almost all B in solution should be in the boric acid form, and the main form adsorbed was boric acid. In this range, as the pH increases, more adsorption sites would be available for B adsorption. When the pH increased beyond pH 7, the borate ion becomes the dominant species, then borate ion adsorption became significant. When the pH was higher than 8 or 9, B adsorption decreased because of competition from hydroxyl ions with the borate ions for the adsorption sites.

Keren et al. (1981) introduced the following phenomenological equation to study B adsorption:

$$Q = T [K_1 (HB) + K_2 (B)] / 1 + K_1 (HB) + K_2 (B) + K_3 (OH)$$

where Q is the total amount of B adsorbed; T is the maximum B adsorption; (HB) , (B) and (OH) are activities of boric acid, borate ion and hydroxyl ion in the system, respectively, and K_1 , K_2 , and K_3 are affinity coefficients related to the adsorption energy of boric acid, borate ion and hydroxyl ion, respectively. Using this equation they calculated the adsorption coefficients for several clays and soils. They found that with any clays and soils, the k_2 value was always greater than K_1 , but smaller than K_3 , indicating that the affinity of the borate ion to the adsorption sites was higher than boric acid, but lower than for the hydroxyl ion. In another experiment, Keren and O'Connor (1982) compared B adsorption by montmorillonite and illite. They found that B adsorption by Na-illite surface was much greater than that by Na-montmorillonite, although the total surface area of montmorillonite was much greater than that of illite. They indicated that B was adsorbed mainly on the clay edges rather than on the planar surfaces.

Structural cations are not always fully coordinated into the ideal ionic lattice and this may result in a residual charge. These surfaces are known as constant potential surfaces on edge surfaces of clay minerals and Al- and Fe-oxides and hydroxides. The net charge on the surface depends upon the zero point of charge (ZPC) of the mineral and

the pH of the embedding solution (Gast, 1977). If the pH of the embedding solution is less than the ZPC of the mineral, the surface will be positively charged and will adsorb anions by electrostatic attraction. However, under acid and neutral condition, B is in the boric acid form which is an undissociated molecule and, under alkaline conditions, B is in the borate anion form. Since most soil clays and Al- and Fe-oxide and hydroxide systems are negatively charged, electrostatic attraction fails to explain the B adsorption in either boric acid or borate anion forms. Evidently, some coordinate binding is involved in the specific adsorption of B on these surfaces.

In a study of adsorption of some incompletely dissociated acids on goethite and gibbsite, Hingston et al. (1972) proposed a ligand exchange hypothesis in which they suggested that even on negatively charged surfaces, undissociated acid molecules could be adsorbed as long as they could dissociate at the surface to provide protons to react with surface hydroxyls. The ligand exchange may be used to explain the boric acid molecule adsorption phenomenon. As a Lewis acid, boric acid may form a complex with surface hydroxyls or with a surface cation through replacement of surface hydroxyl and water, as long as the free energy of the system decreased, regardless of the sign of the net surface charge.

Borate adsorption on negatively charged surfaces may be explained by formation of a surface complex. Sims and Bingham (1968a) proposed three possible mechanisms, exchange of borate for surface hydroxyl, reaction of borate to become an end member of a hydroxy Al and Fe polymer, and formation of a borate-diol complex. Based on a mole ratio method, they suggested several possible formulas of Al- or Fe-B complex, such as $\text{Al}[\text{B}(\text{OH})_4]_x$, and $\text{Fe}_4[\text{B}(\text{OH})_4]_3(\text{OH},\text{O})_x$. In a study on B adsorption, Metwally (1966) found an increase in pH with B adsorption, which indicated that an exchange reaction occurred between borate and hydroxyl ions.

Although much effort has been spent in many studies on B adsorption phenomenon, the actual B adsorption mechanism still remains in question. Further research is needed to verify any aforementioned hypotheses.

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Chapter III

PLANT AVAILABILITY OF NATIVE AND APPLIED BORON IN SELECTED VIRGINIA SOILS

3.1 ABSTRACT

A laboratory and greenhouse experiment was conducted to study the distribution of native B and availability of native and applied B in 14 Virginia soils. Total B in these 14 soils ranged from 21.5 to 96.3 mg kg⁻¹. From trace up to 0.34% of the total B was in water soluble form, <0.23% was 0.02 M CaCl₂ extractable (non-specifically adsorbed B), from 0.05 to 0.30% was mannitol exchangeable (specifically adsorbed B) and from 0.23 to 1.52% was hydroxylamine hydrochloride extractable (Mn mineral occluded B). Ammonium oxalate in the dark adjusted to pH 3.25 extracted 2.8-34.4% of the total B, while under UV light, from 17.5 to 73.9% of the total B was extractable. These two fractions are probably associated with non-crystalline and crystalline Al and Fe in soils. Residue B accounted for 2.4-79.2% of the total B, which was considered to be in association with soil silicates.

Boron concentration in corn tissue from native B correlated with water soluble B and CaCl₂ soluble B at the 0.01

probability level. A curvilinear relation was found between B concentration in corn tissue from native soil B and mannitol exchangeable B or hydroxylamine hydrochloride extractable B. The sum of these four fractions accounted for only 0.4-2.0% of the total soil B. No significant correlation existed between the B concentration in corn tissue from native B and NH_4 -oxalate extractable B either in the dark or under UV light and the residue fraction of B. These relationships indicated that B in non-crystalline and crystalline Al- and Fe-oxides and hydroxides and in silicates was relatively unavailable for plant uptake in the greenhouse.

A curvilinear correlation occurred between B in corn tissue from native B and soil B extracted by hot water extraction, NH_4 -acetate extraction, mannitol exchange and Mehlich III extraction. After logarithmic transformation, B extracted by these four methods was significantly correlated with B in corn tissue from the native B at 0.01 probability level. Within these four procedures, mannitol exchangeable B correlated most closely with B in corn tissue from native B and could be a convenient method for the estimation of available B in Virginia soils.

Boron in corn tissue from native B correlated with soil organic matter content at the 0.01 level and with soil clay content at the 0.10 level, with soil pH providing no signi-

ficant correlation. Maximum B adsorption estimated with the Langmuir equation ranged from 2.4 to 26.5 mg kg⁻¹ of soil, and significantly correlated with soil clay content, surface area, NH₄-oxalate extractable Al and Fe and hydroxylamine hydrochloride extractable Mn content at 0.01 probability level.

From 0.4 to 13.5% of the applied B was absorbed by corn plants. Curvilinear relationships were found between B in corn tissue from applied B and soil clay content, surface area, NH₄-oxlate extractable Al and Fe and hydroxylamine hydrochloride extractable Mn. It is evident from these relationships that soil clay, Al-, Fe- and Mn-oxides and hydroxides have high affinity to adsorb B in relatively unavailable forms.

Key words: boron fractionation, boron adsorption isotherm, total soil B, hot water soluble B, mannitol extractable B, NH₄-acetate extractable B, Mehlich III extractable B, NH₄-oxalate soluble B.

3.2 INTRODUCTION

Knowledge of elemental distributions in different fractions and their contributions to plant uptake is fundamental to an understanding of the soil chemistry of the nutrient. Although the distribution between forms is not always experimentally clear cut, fractionation research has provided insight on nature and availability of some nutrients in soils, such as P (Chang and Jackson, 1957; Martens et al., 1969), Zn (Iyengar et al., 1981) and Cu (McLaren and Crawford, 1973). Boron (B) in soils exists in various forms and has been divided into several categories (Fleming, 1980; Keren and Bingham, 1985). However, the fractionation of soil B and the availability of each fraction has not been extensively examined.

Based on the assumption that certain reagents can specifically attack discrete soil components and release the nutrients associated with them, many reagents have been used in nutrient fractionation studies. Calcium chloride extractable nutrients have been referred to as the portion non-specifically adsorbed on soil surfaces (McLaren and Crawford, 1973; Iyengar, et al., 1981). Mannitol has been used to estimate leachable B (Rhoades et al., 1970) which probably included B in soil solution, non-specifically and spe-

cifically adsorbed forms. Acidified hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) was recommended for separation of Mn minerals from Fe minerals in sediments and soils (Chao, 1972) and has been used for nutrient fractionation studies (McLaren and Crawford, 1973; Iyenger et al., 1981). Acidic NH_4 -oxalate (AMOX) extraction in the dark has been commonly used to extract non-crystalline materials (Hodges and Zelazny, 1980; Schwertmann, 1964, 1973; Fey and Roux, 1977; Mckeague and Day, 1966). With ultraviolet (UV) light, on the other hand, the AMOX could remove both crystalline and non-crystalline oxides from soils (DeEndredy, 1963; Schwertmann, 1964). AMOX extraction method has been used for other soil nutrient fractionation studies (McLaren and Crawford, 1973; Iyenger et al., 1981).

The recognized soil factors which affect availability of B are soil pH (Olson and Berger, 1946; Okazaki and Chao, 1968; Wear and Patterson, 1962; Lehr and Henkens, 1959; Peterson and Newman, 1976), clay content (Olson and Berger, 1946; Kubota et al., 1948; Gupta, 1968; Wilson et al., 1951), and organic matter content (Page and Paden, 1954; Miljkovic et al., 1966; Fleming, 1980).

Several methods have been used to estimate availability of B in soils. The most common one has been the hot water soluble B procedure (Berger and Truog, 1939). In order to

minimize the influence of color in the extraction solution on B determination with azomethine-H method, Parker and Gardner (1981) modified the hot water soluble B procedure by boiling the soil sample in 0.02 M CaCl_2 instead of water. The extractable B level was not affected by the presence of CaCl_2 . The other available B estimation methods are NH_4 -acetate extraction at pH 4.8 (Gupta and Stewart, 1975) and mannitol exchange method (Rhoades et al., 1970; Bingham, 1982).

Boron in the soil environment exists in a dynamic equilibrium between solid and liquid phases. Availability of B added to a soil depends upon, at least partially, the B adsorption power of the soil. Many soil components are responsible for B adsorption. Those proposed are layer silicates (Metwally, 1966; Keren and Mezuman, 1981), Al- and Fe-oxides and hydroxides (Sims and Bingham, 1968), and soil organic matter (Parks and White, 1952).

The objectives of this study were to investigate the distribution of native B, characterize the adsorption of added B, and determine the availability of native and applied B in selected Virginia soils.

3.3 MATERIALS AND METHODS

3.3.1 Soil Characterization

Fourteen Virginia soils with diverse properties (Table 3) were selected for this investigation. Soil pH was determined from a 2:1 water-to-soil mixture with a Fisher pH meter, model 825 MP. Clay content was determined by the pipette method and organic matter content was determined by the Walkley-Black procedure. Surface area (SA) was determined using the ethylene glycol monoethyl ether adsorption procedure (Carter et al., 1965). Ammonium oxalate extractable Al (AMOX-Al) and Fe (AMOX-Fe) were estimated by NH₄-oxalate extraction adjusted to pH 3.25 under UV light at 85 °C (Miller, 1981). The hydrous Mn content (HYHCL-Mn) was determined by hydroxylamine hydrochloride extraction (Chao, 1972). The Al, Fe and Mn contents in these extracts were determined by atomic absorption spectrophotometry.

3.3.2 Native B Fractionations

The fractionation of native B was conducted following the scheme shown in Figure 1. It was assumed that each ex-

TABLE 3
Selected properties of the 14 Virginia soils examined.

Soil Series	Taxonomic Class	pH	OM	Clay	SA	AMOX-Al	AMOX-Fe	HYI(Cl-Hh)	V _{max}
			-----mg kg ⁻¹ -----	-----mg kg ⁻¹ -----	-----m ² g ⁻¹ -----	-----g kg ⁻¹ -----	-----g kg ⁻¹ -----	-----mg kg ⁻¹ -----	-----
Craven	Aquic Hapludults, clayey, mixed, thermic	5.5	38	121	35	2.4	3.3	73.6	9.9
Rumford	Typic Hapludults, coarse-loamy, siliceous, thermic	6.6	10	54	12	2.8	4.3	51.0	3.5
Slagle	Aquic Hapludults, fine-loamy, siliceous, thermic	6.6	35	88	33	4.6	4.1	179.2	9.8
Emporia	Typic Hapludults, fine-loamy, siliceous, thermic	6.5	20	97	20	3.6	6.7	12.5	4.9
Kempsville	Typic Hapludults, fine-loamy, siliceous, thermic	6.0	10	71	11	2.3	4.1	56.7	---
Rains	Typic Hapludults, fine-loamy, siliceous, thermic	6.0	24	156	28	3.2	4.5	4.5	11.0
Nyall	Typic Ochraqults, fine-loamy, siliceous, thermic	6.8	11	79	12	1.7	2.4	2.5	---
Dragstown	Typic Ochraqults, fine-loamy, siliceous, thermic	6.9	11	96	15	4.4	5.2	3.2	9.6
Starr	Fluventic Dystrachrepts, fine-loamy, mixed, thermic	6.1	22	489	108	17.0	77.1	2984.8	24.1
Dyke	Typic Rhodudults, clayey, mixed, mesic	6.9	16	454	92	16.9	66.2	3699.1	26.5
Lodi	Typic Hapludults, clayey, kaolinitic, mesic	7.4	26	168	37	5.4	12.6	314.1	13.5
Christian	Typic Hapludults, clayey, kaolinitic, mesic	5.7	19	164	35	4.5	27.8	499.7	4.7
Farboro	Typic Udipsamments, mixed, thermic	5.4	4	64	18	4.6	8.0	48.2	3.3
Lauqueter	Udic Hapludalf, fine, mixed, mesic	7.3	30	255	95	17.3	87.6	1880.1	22.6

traction would remove all B in previous fractions and would not attack B in subsequent fractions. A separate sample was taken for each extraction. The B in each fraction was calculated by subtracting the B in previous fractions from the B content in the extraction solution. The extraction procedures are outlined below.

Water soluble B (WS-B) was extracted by shaking 10 g of soil with 20 ml of deionized water at 25 °C for 24 hours. The CaCl₂ extractable B (CACL-B) was obtained by shaking 10 g of soil with 20 ml of 0.02 M CaCl₂ solution at 25 °C for 24 hours. Mannitol exchangeable B (EXCH-B) was extracted by shaking 6 g of soil with 30 ml of 0.01 M mannitol in 0.02 M CaCl₂ solution at 25 °C for 24 hours. Hydroxylamine hydrochloride extractable B (HYHCL-B) was solubilized by shaking 4 g of soil with 40 ml of 0.1 M hydroxylamine hydrochloride in 0.01 N HNO₃ solution at 25 °C for 30 minutes. Oxalate extractable B in the dark (AMOXD-B) was obtained by shaking 1 g of soil with 40 ml of 0.175 M NH₄-oxalate solution adjusted to pH 3.25 in the dark at 25 °C for 4 hours. Oxalate extractable B under UV light (AMOXL-B) was solubilized by shaking 0.5 g of soil with 25 ml of the NH₄-oxalate solution adjusted to pH 3.25 under UV light at 85 °C for 3 hours. The B in the residue (RESIDUE-B) was determined by Na₂CO₃ fusion. The B concentration in the extraction solutions

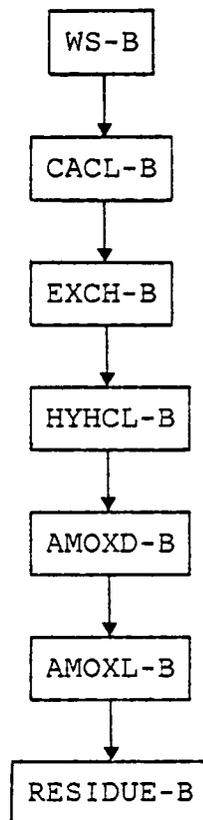


Figure 1: Fractionation scheme of native B in soils.

were determined colorimetrically by the azomethine-H procedure or by ICP method.

3.3.3 Available Boron Determinations

Four procedures were used to estimate available B in the soils. Hot water soluble B (HWS-B) was determined following the procedure modified by Parker and Gardner (1981). A 15 g soil sample was refluxed with 30 ml of 0.02 M CaCl_2 solution in a B-free flask for 5 minutes. Ammonium acetate extractable B ($\text{NH}_4\text{OAc-B}$) was displaced from soil according to the method of Gupta and Stewart (1975). Ten g of soil sample was shaken with 50 ml of 1 N NH_4 -acetate (pH 4.8) at 25 °C for 30 minutes. The Mehlich III extractable B (MIII-B) was extracted by shaking 5 g of soil sample with 40 ml of Mehlich III solution at 25 °C for 5 minutes. The Mehlich III solution contained 0.2 N CH_3COOH , 0.25 N NH_4NO_3 , 0.015 N NH_4F , 0.013 N HNO_3 and 0.001 M EDTA (Mehlich, 1984). The mannitol exchange procedure used for available B estimation (Mannitol-B) was the same as the extraction of EXCH-B outlined in the fractionation section except that B in the previous fractions were not subtracted. For all the extractions, the suspension was centrifuged at 2000 rpm for 5 min and passed through Whatman No. 42 filter paper. Boron cen-

tent in the solution was determined by the azomethine-H procedure.

3.3.4 Boron Adsorption Study

A ten-g soil sample of ≤ 10 mesh was shaken with 20 ml of 0.02M CaCl_2 at 30 °C for 24 hours in a water bath shaker. The initial B concentration in the solutions ranged from 0.23 to 1.39 mmol L^{-1} . After equilibrium, the suspension was centrifuged at 2000 rpm for 5 min and filtered through Whatman No. 42 filter paper, and then the B concentration in the supernatant was determined by the azomethine-H procedure. The amount of B adsorbed by the soil was calculated by the difference between B concentrations in initial and equilibrium solutions. The amount of B originally adsorbed in the soil was estimated by the mannitol exchange as outlined in the previous section and was taken into account in calculation of the amount of B adsorbed.

3.3.5 Greenhouse Experiment

A 2.4 kg portion of soil, passed through a 2-mm sieve, was used for the greenhouse experiment. There were two treatments, B application at a rate of 1 mg kg^{-1} of soil as

boric acid and a control. Other amendments were 75 mg N kg^{-1} as NH_4NO_3 , 75 mg P kg^{-1} as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, 75 mg K kg^{-1} as KCl, 15 mg Mg kg^{-1} as MgSO_4 , 15 mg Mn kg^{-1} as $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 15 mg Zn kg^{-1} as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and 5 mg Cu kg^{-1} as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The amended soils were mixed, placed in plastic-lined pots, arranged in a randomized complete block design with three replications, and equilibrated at approximately field capacity for 8 days. After the equilibration, eight corn seeds 'Pioneer 3396A' were planted in each pot and, 10 days later, plants were thinned to 4 seedlings per pot. The soil moisture was brought to approximately field capacity daily. Widelight was supplied from 6:00 a.m. to 8:00 p.m. Supplemental N was added at a total level of 150 mg kg^{-1} of soil during a 23-day plant growth period. Thereafter, plants were harvested by clipping at the first node, rinsed with deionized water, dried at 70 °C, weighed, and ground to pass through a 20-mesh stainless steel screen. Boron content in plant tissue was determined following the method of Gaines and Mitchell (1979). A one-gram subsample was ashed in a ceramic crucible at 550 °C for 5 hours, the ash was dissolved in 0.36 N H_2SO_4 solution, and B was determined by azomethine-H procedure. Boron concentration in plant tissue in control treatment was considered plant absorption of native B. Boron concentration in plant tissue absorbed from

applied B was estimated by subtracting tissue B concentration in control from tissue B concentration in the B application treatment.

3.3.6 Data Analyses

Simple and multiple correlation and regression analyses were performed to evaluate the relationships between the dependent variables (B concentration in plant tissue from native or applied B and maximum B adsorption) and the independent variables (B fractions, available B estimations and soil properties). Logarithmic transformation of some variables were performed where a corresponding curvilinear relationship was observed (Little and Hills, 1978).

The B adsorption by soils was described by linear form of the Langmuir equation and maximum B adsorption (V_{max}) by the soils was estimated from this equation.

3.4 RESULTS AND DISCUSSION

3.4.1 Native Boron Fractionation

Total B in the 14 soils ranged from 21.54 to 96.27 mg kg⁻¹, which was within the range of 2 to 100 mg kg⁻¹ normally found in soils (Fleming, 1980). Distribution of the total B in different fractions varied widely in the soils (Table 4). The first four fractions (WS-B, CaCl₂-B, EXCH-B and HYHCL-B) only account for a small portion of the total B. From trace up to 0.34 percent of the total native soil B was in the water soluble form which may be considered the B in soil solution. Less than 0.23% was in the CaCl₂ extractable form which probably was non-specifically adsorbed on the soil colloid surface. The EXCH-B fraction accounted for 0.05-0.30% of the total B, which could be considered the fraction of B specifically adsorbed by soil colloid materials. From 0.23 to 1.52% of the total B was hydroxylamine hydrochloride extractable. Since this extraction has been recommended for separation of soil Mn-oxides from Fe-oxides (Chao, 1972), it is reasonable to assume that this fraction was mainly associated with Mn oxides in the soils. The last three fractions, AMOXD-B, AMOXL-B and RESIDUE-B, accounted

for 2.8-34.4, 17.5-73.9 and 2.4-79.2% of the total B, respectively. Because the acidified NH_4 -oxalate has been commonly used to extract non-crystalline (in the dark) (Hodges and Zelazny, 1980; Schwertmann, 1964, 1973; Fey and Roux, 1977; Mckeague and Day, 1966) and crystalline Al and Fe (with UV light) (DeEndredy, 1963; Schwertmann, 1964), these fractions could be considered in association with non-crystalline Al and Fe, crystalline Al and Fe, and soil silicates, respectively.

3.4.2 Plant Availability of B in Different Forms

Boron application did not increase dry weights of corn plants on the 14 soils in the greenhouse experiment. Boron concentration in plant tissue from native B in the 14 soils ranged from 7.7 to 21.9 mg kg^{-1} (Table 5). Boron concentration in corn tissue from native B was significantly correlated with WS-B and CACL-B at the 0.01 probability level (Table 6). The WS-B and CACL-B are either in soil solution or weakly adsorbed by soil components. They are easily available for plant uptake and may be considered as intensity factors of B supplying power of these soils.

The relationship of B concentration in corn tissue from native B with EXCH-B and HYHCL-B tends to be curvilinear

TABLE 4
Fractionation data of native B in the 14 soils.

Soil	WS-B		CACL-B		EXCII-B		HYHCl-B		ANOXD-B		AMOXL-B		RESIDUE-B		TOTAL B	
	mg kg ⁻¹	%	mg kg ⁻¹	%												
Craven	0.07	0.17	0.02	0.05	0.02	0.06	0.17	0.40	2.9	6.7	15.3	35.2	25.0	57.5	43.5	
Rumford	<0.01*	----	0.04	0.18	0.03	0.15	0.10	0.46	2.8	12.9	10.1	46.9	8.5	39.4	21.5	
Slagle	0.12	0.26	0.02	0.06	0.09	0.20	0.48	1.07	3.8	8.5	11.4	25.5	28.7	64.4	44.5	
Emporia	0.18	0.34	0.10	0.19	0.06	0.10	0.27	0.51	2.4	4.4	19.0	35.6	31.4	58.9	53.3	
Kempsville	<0.01	----	0.03	0.10	0.07	0.21	0.14	0.40	2.6	7.5	6.1	17.7	25.7	74.1	34.6	
Rains	<0.01	----	0.09	0.23	0.06	0.16	0.17	0.46	1.8	4.8	9.2	24.0	26.9	70.4	38.3	
Myatt	0.04	0.15	<0.01	----	0.03	0.10	0.14	0.54	2.2	8.6	6.8	26.1	16.8	64.6	26.1	
Dragstown	0.03	0.09	<0.01	----	0.03	0.11	0.12	0.40	2.7	9.3	12.3	42.1	14.0	48.0	29.2	
Starr	0.13	0.16	0.17	0.20	0.14	0.17	1.13	1.36	11.9	14.4	61.5	73.9	8.2	9.8	83.1	
Dyke	0.13	0.15	0.12	0.14	0.17	0.20	1.31	1.52	18.6	21.6	39.1	45.3	26.8	31.1	86.3	
Lodi	0.20	0.32	0.15	0.23	0.19	0.30	0.72	1.12	3.4	5.3	15.3	23.8	44.3	68.9	64.3	
Christian	0.02	0.02	0.07	0.07	0.05	0.05	0.37	0.38	2.6	2.8	16.9	17.5	76.3	79.2	96.3	
Barboro	0.05	0.19	<0.01	----	0.02	0.08	0.06	0.23	3.5	14.3	8.0	32.4	13.0	52.8	24.7	
Fauquier	0.22	0.32	0.12	0.18	0.20	0.29	0.74	1.06	23.8	34.4	42.5	61.3	1.7	2.4	69.3	

* The value was considered undetectable when less than 0.01, and 0.00 was used for the correlation analysis.

TABLE 5

Boron concentrations in corn tissues from the greenhouse experiment.

Soil Series	Tissue B Concentration -----mg kg ⁻¹ -----			% of Applied B Absorbed by Corn Plant
	Control	B Treatment	Difference	
Craven	14.8	49.2	34.4	5.4
Rumford	8.1	61.9	53.8	10.7
Slagle	17.6	43.8	26.2	5.1
Emporia	18.4	60.1	41.7	11.4
Kempsville	12.0	57.6	45.6	9.7
Rains	15.5	56.0	40.5	5.7
Myatt	9.5	60.3	50.8	13.5
Dragstown	9.4	47.2	37.8	6.4
Starr	16.3	20.8	4.5	1.4
Dyke	17.6	22.3	4.7	0.4
Lodi	21.9	38.4	16.5	3.5
Christian	13.1	25.0	11.9	2.6
Tarboro	7.7	69.3	61.5	9.5
Fauquier	17.1	24.6	7.5	1.2

TABLE 6

Correlation coefficients between corn tissue B concentration from native B and the fractions of native B.

B Fraction	Simple r
WS-B	0.782**
CACL-B	0.770**
EXCH-B	0.758**
Log(EXCH-B)	0.776**
HYHCL-B	0.638**
Log(HYHCL-B)	0.806**
AMOXD-B	0.349ns
AMOXL-B	0.431ns
RESIDUE-B	0.289ns
Total B	0.615†

**--Significant at 0.01 probability level.

†--Significant at 0.10 probability level.

ns--Not Significant at 0.10 probability level.

(Figure 2, 3). Logarithm transformations of these data increased the correlation coefficients between B in plant tissue from native B and EXCH-B or HYHCL-B (Table 6). The correlation was significant at 0.01 probability level with both fractions (Table 6). The EXCH-B has been referred to as leachable B in soils (Rhoades et al., 1970). It may be specifically adsorbed on clay surface or associated with organic matter. The HYHCL-B may be mainly associated with Mn oxides which is more easily decomposed, releasing the occluded B, compared with Fe-oxides in soils (Chao, 1972). These two fractions of B seem slowly available during the growing period of the corn plants. It is reasonable to consider EXCH-B and HYHCL-B fractions as a quantitative factor of B supplying power of the soils. The first four fractions together accounted for only 0.4-2.0% of the total B in the soils.

Boron concentration in corn tissue from native B is not significantly correlated with AMOXD-B, AMOXL-B and RESIDUE-B (Table 6), indicating that these fractions of B mainly associated with non-crystalline, crystalline Al and Fe, and in silicate supplied very little B to corn plants during the growing period in the greenhouse experiment. Boron concentration in corn tissue from native B is significantly correlated with the total B content of the soils, probably through the influence of total B content on B levels of the more available forms, i.e. WS-B, CACL-B, EXCH-B and HYHCL-B.

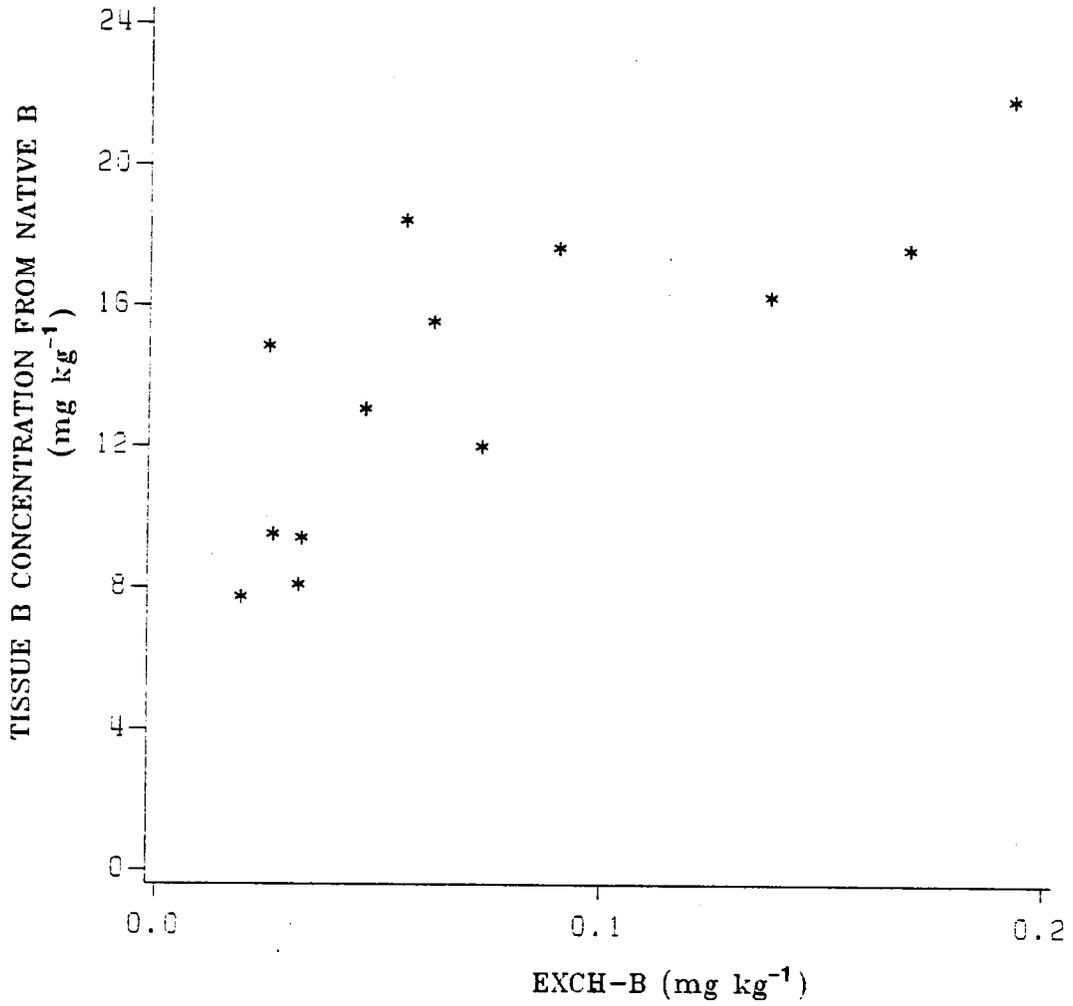


Figure 2: Plot of tissue B concentration from native B versus EXCH-B.

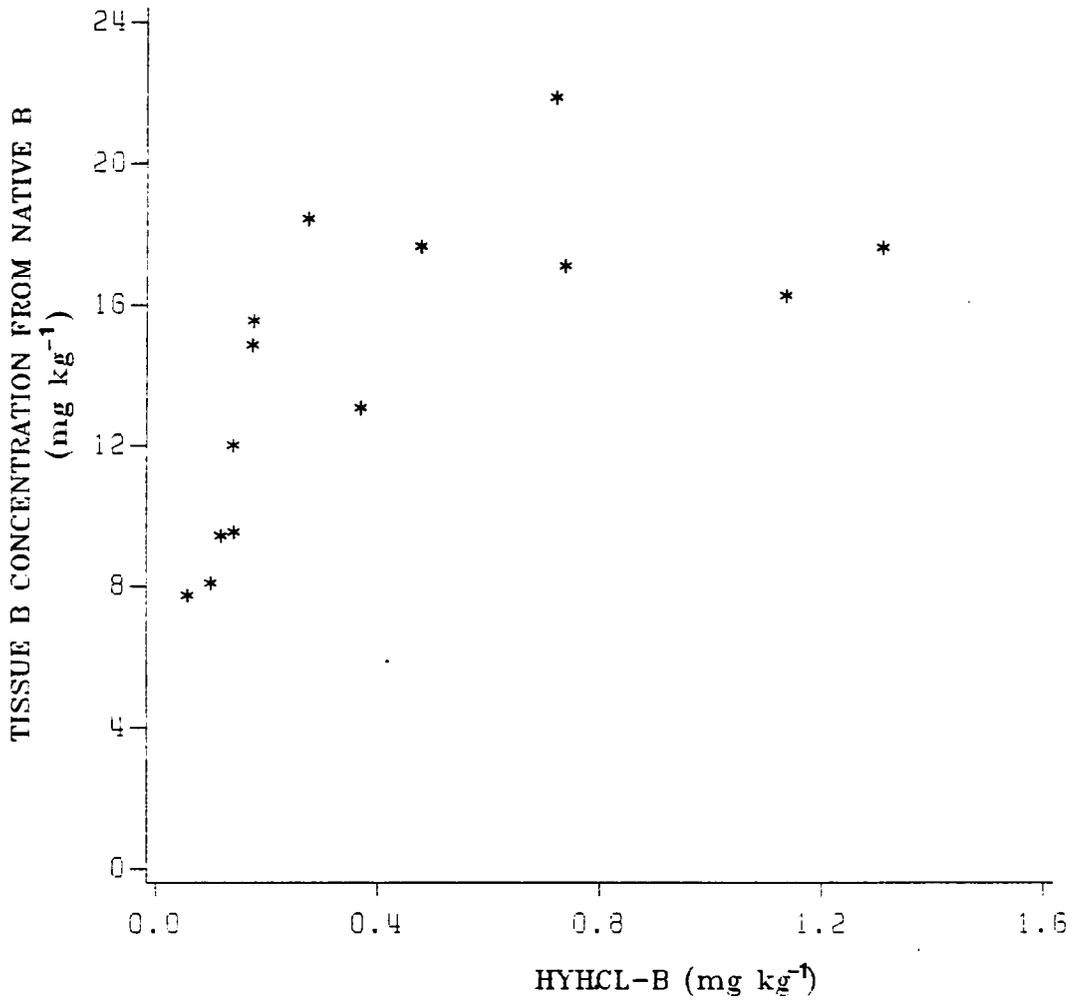


Figure 3: Plot of tissue B concentration from native B versus HYHCL-B.

3.4.3 Available B Estimation

Ranges of HWS-B, $\text{NH}_4\text{OAc-B}$, Mannitol-B and MIII-B were 0.03-1.05, 0.15-0.88, 0.05-0.55 and 0.13-1.41, respectively (Table 7). The HWS-B, $\text{NH}_4\text{OAc-B}$ and Mannitol-B were significantly correlated with each other at the 0.01 probability level, but correlation coefficients with MIII-B were significant only at the 0.05 probability level (Table 8).

A curvilinear relationship occurred between tissue B concentration from native B and available B estimations by the four procedures, HWS-B (Figure 4), $\text{NH}_4\text{OAc-B}$ (Figure 5), Mannitol-B (Figure 6) and MIII-B (Figure 7). After transformation of these data to a logarithm form, the correlation coefficient was improved compared with the original data (Table 9). The correlation coefficients with HWS-B, $\text{NH}_4\text{OAc-B}$ and Mannitol-B were greater than with MIII-B. The close correlation between B concentration in plant tissue from native B and HWS-B, $\text{NH}_4\text{OAc-B}$ and Mannitol-B indicated that the hot water soluble B extraction, the NH_4 -acetate extraction B and the mannitol exchangeable B could be used for available B estimation in these soils. Within the four procedures examined, mannitol exchangeable B showed the highest correlation coefficient with tissue B concentration from native B (Table 9). This procedure may be a reliable and easy method for available B estimation in these soils.

TABLE 7

Available B levels estimated by the four procedures tested.

Soil Series	HWS-B	NH ₄ OAc-B	Mannitol-B	MIII-B
	-----mg kg ⁻¹ -----			
Craven	0.30	0.29	0.12	1.27
Rumford	0.10	0.16	0.07	0.28
Slagle	0.43	0.43	0.23	1.30
Emporia	0.57	0.42	0.34	1.15
Kempsville	0.14	0.21	0.11	0.28
Rains	0.30	0.30	0.15	0.38
Myatt	0.13	0.26	0.07	0.30
Dragstown	0.07	0.17	0.05	0.72
Starr	0.82	0.48	0.44	0.62
Dyke	0.78	0.50	0.42	0.48
Lodi	0.84	0.87	0.55	1.41
Christian	0.31	0.25	0.13	0.68
Tarboro	0.03	0.15	0.05	0.11
Fauquier	1.05	0.88	0.55	1.11

TABLE 8

Correlation coefficients among the four available B estimations.

	NH ₄ OAc-B	Mannitol-B	MIII-B
HWS-B	0.927**	0.983**	0.560*
NH ₄ OAc-B		0.947**	0.643*
Mannitol-B			0.555*

**---Significant at 0.01 probability level.

*---Significant at 0.05 probability level.

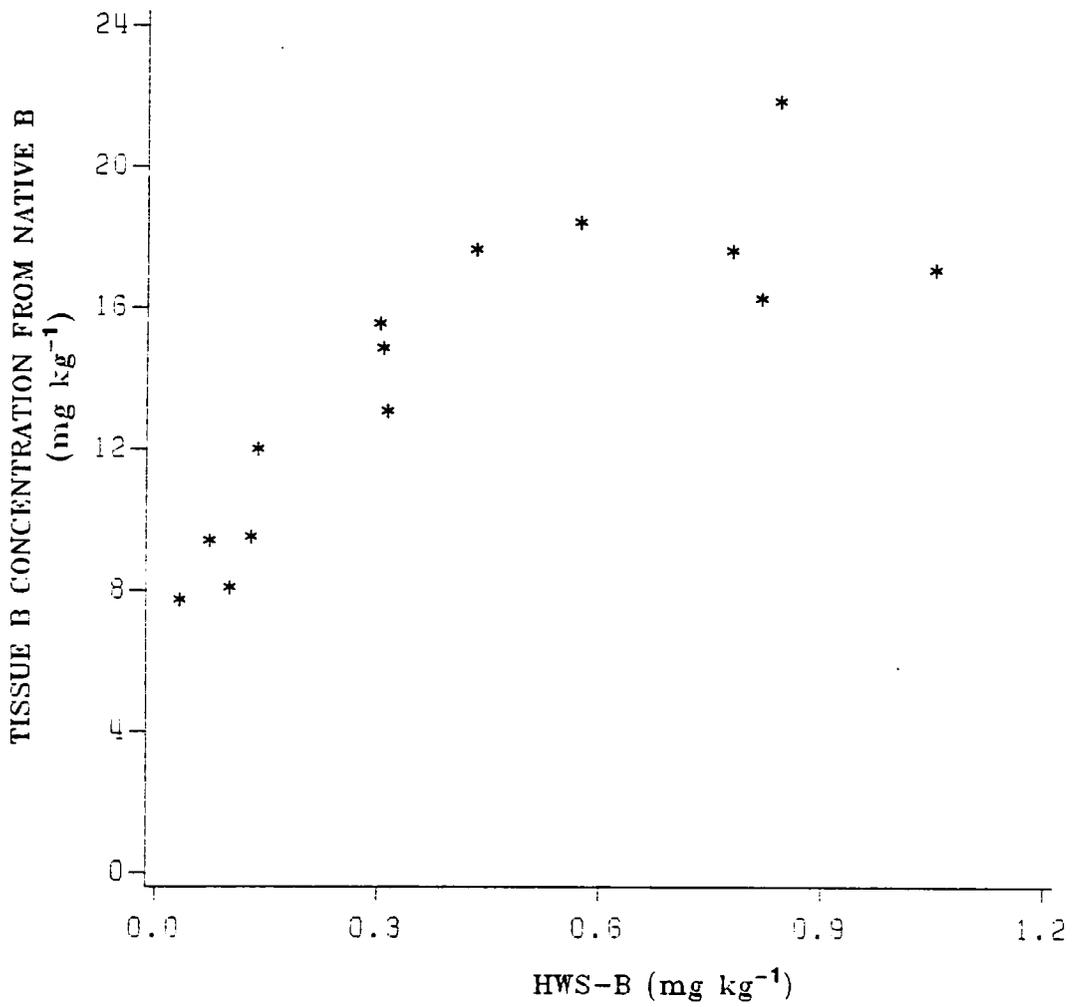


Figure 4: Plot of tissue B concentration from native B versus HWS-B.

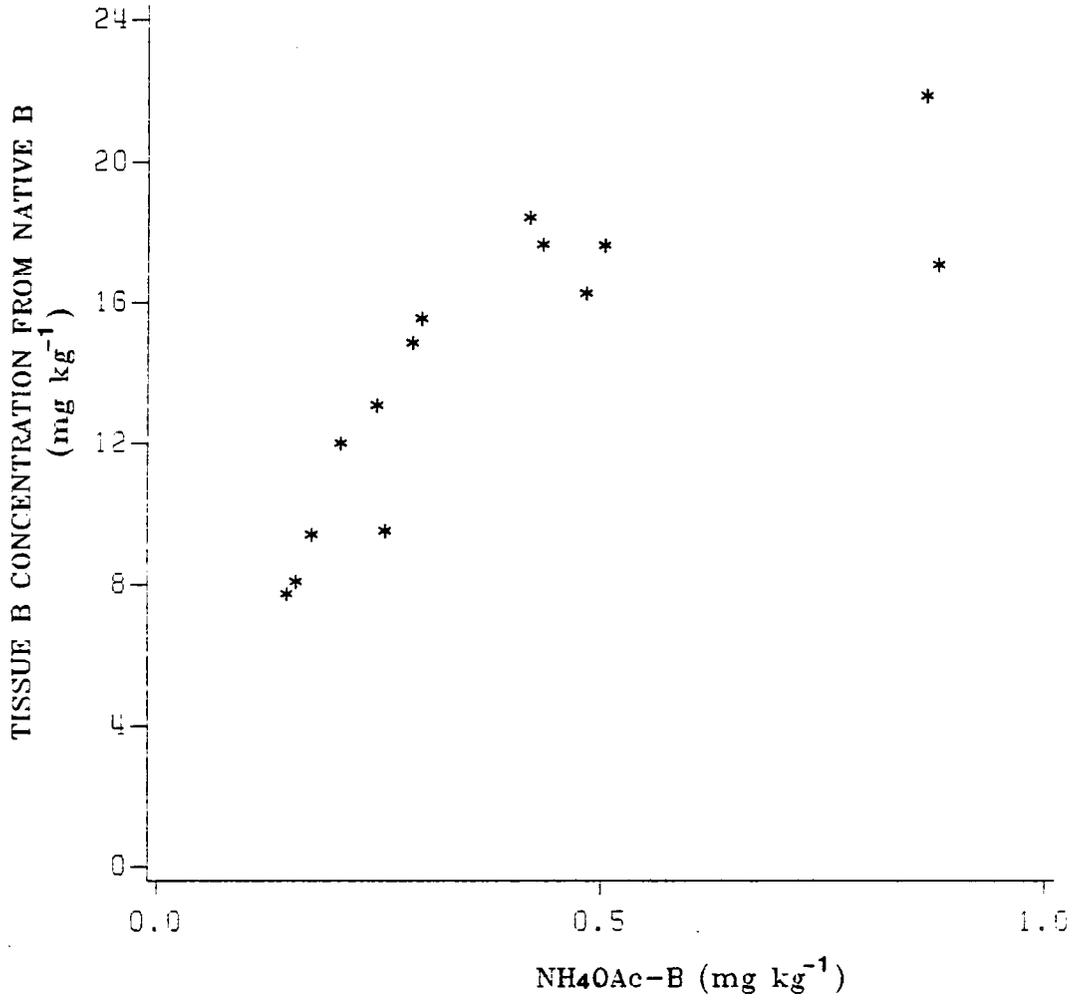


Figure 5: Plot of tissue B concentration from native B versus $\text{NH}_4\text{OAc-B}$.

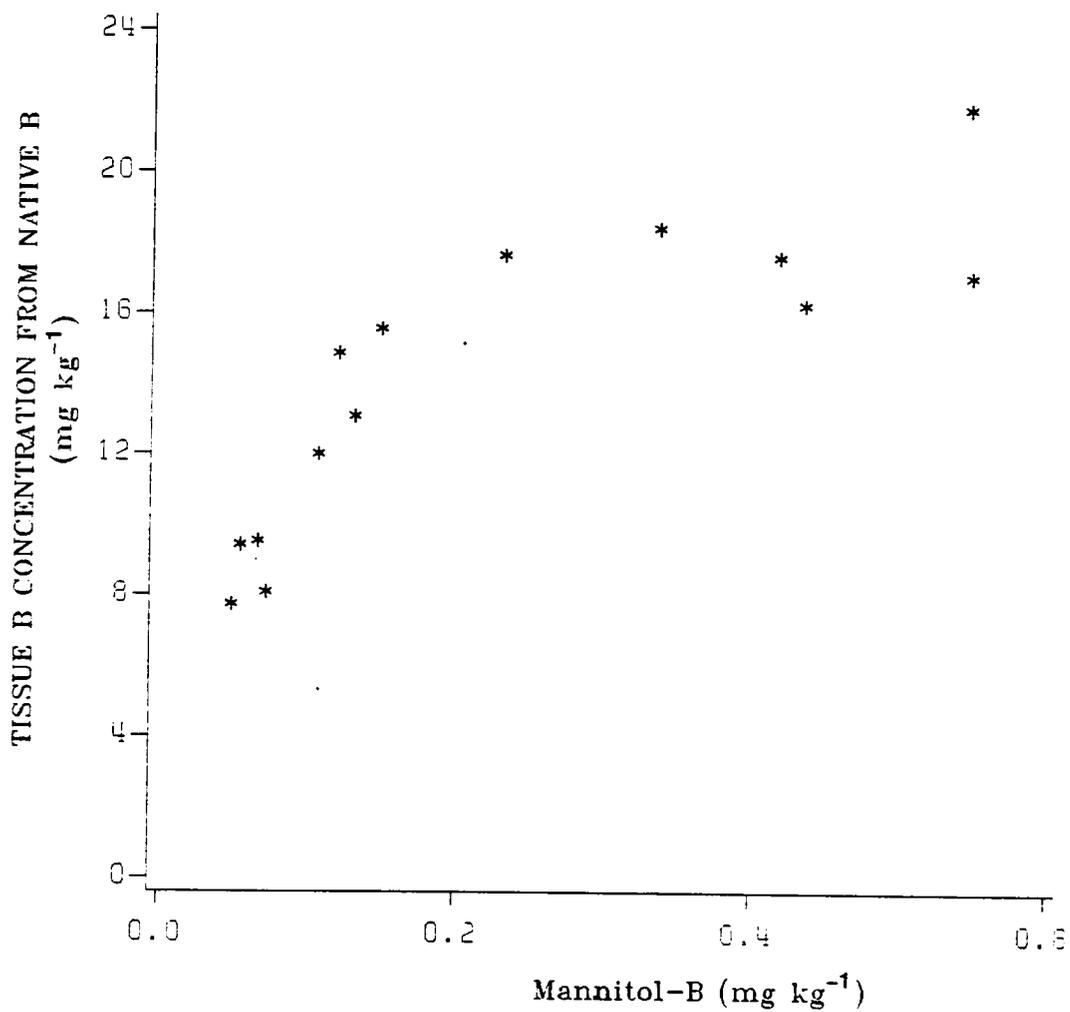


Figure 6: Plot of tissue B concentration from native B versus Mannitol-B.

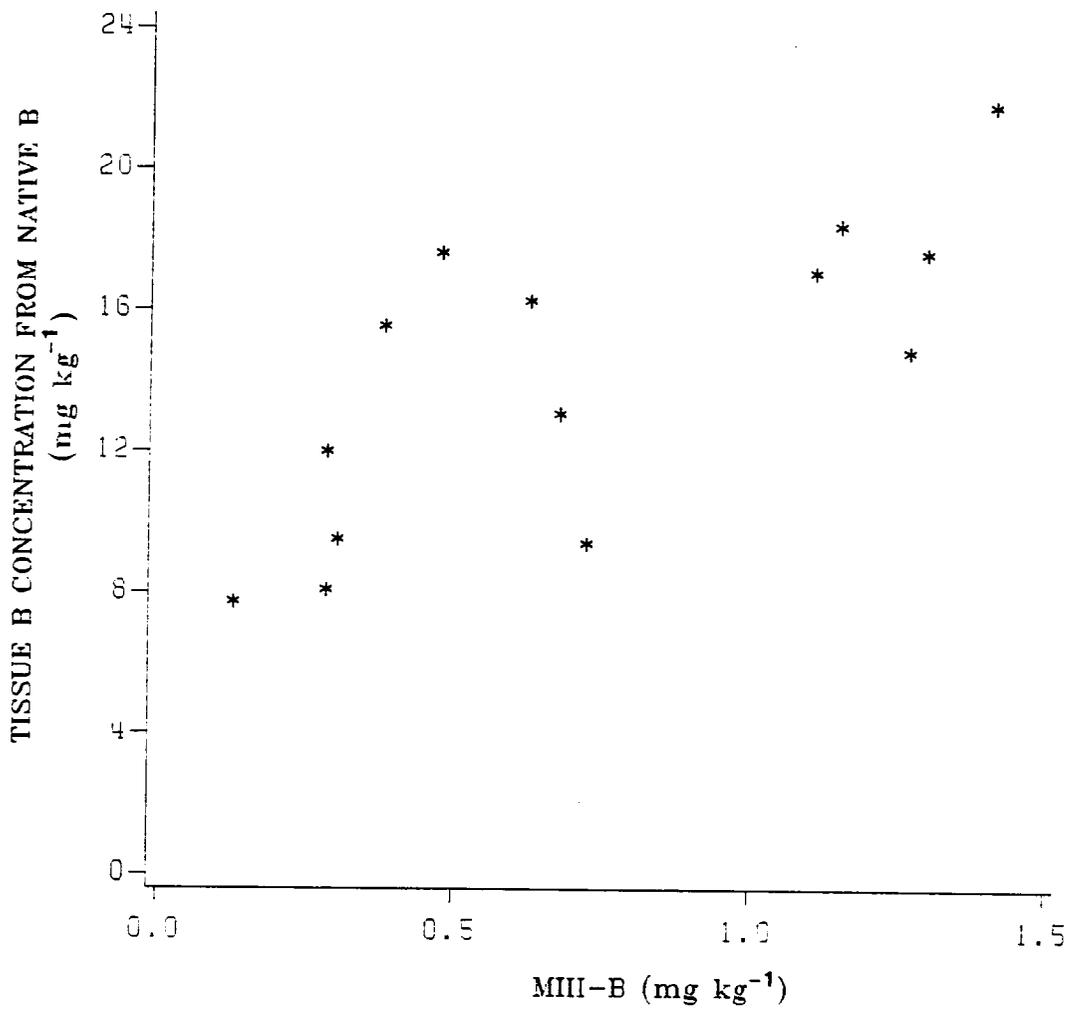


Figure 7: Plot of tissue B concentration from native B versus MIII-B.

TABLE 9

Correlation analysis of relationships between dependent variable, tissue B concentration from native B, and independent variables, available B estimations and soil properties.

Independent Variable	Simple r
pH	0.400ns
OM	0.711**
Clay	0.460+
HWS-B	0.834**
Log(HWS-B)	0.913**
NH ₄ OAc-B	0.813**
Log(NH ₄ OAc-B)	0.905**
Mannitol-B	0.841**
Log(Mannitol-B)	0.923**
MIII-B	0.742**
Log(MIII-B)	0.756**

**---Significant at 0.01 probability level.

+---Significant at 0.10 probability level.

ns---Not Significant at 0.10 probability level.

No significant correlation was found between tissue B concentration from native B and soil pH (Table 9). In the literature, contradictory results have been reported regarding the effect of pH on B availability. Wear and Patterson (1962) recorded a decrease in plant B content with increase of soil pH, while Lehr and Henkens (1959) found no relation between the plant tissue B content and soil pH. A weak correlation was found between B concentration in corn tissue from native B and soil clay content (Table 9), probably due to the relatively higher total B level in high clay soils. The relationship of soil clay content and B supplying power is complicated by the fact that soil clay can minimize B leaching from the soil profile and, thereby, maintain a relatively high B level in the soil. However, the B availability is low because of the B adsorption on the clay surface. Tissue B concentration from native B was significantly correlated with soil organic matter content (Table 9). It has been noticed that soil organic matter plays an important role on B availability, it can minimize B loss from soil while at the same time maintain the B in relatively available forms (Berger and Truog, 1945; Page and Paden, 1954).

3.4.4 Boron Adsorption by the Soils

In 12 of the 14 soils, B adsorption could be described by the Langmuir equation, and maximum B adsorption in the 12 soils ranged from 2.4 to 26.5 mg kg⁻¹ of soil (Table 3). Simple correlation analyses showed that maximum B adsorption correlated with clay content, surface area, AMOX-Al, AMOX-Fe and HYHCL-Mn at the 0.01 probability level, but did not significantly correlate with soil pH or organic matter content (Table 10).

However, in a multiple correlation analysis of maximum B adsorption versus soil pH and clay content, the partial correlation coefficient with pH was significant at 0.05 level, and the partial correlation coefficient with clay content was significant at 0.01 level (Table 10). A multiple regression equation:

$$V_{\max} = -19.3 + 3.51\text{pH} + 0.048\text{clay}$$

accounted for 89.6% of the variation in maximum B adsorption by the soils (V_{\max}) estimated with the Langmuir equation.

3.4.5 Availability of Applied B

Boron concentration in corn tissue from applied B ranged from 4.6 to 61.5 mg kg⁻¹ of plant tissue, which accounted for 0.4 to 13.5% of the total B applied (Table 5).

TABLE 10

Correlation analysis of the relationship between maximum B adsorption and soil properties.

Soil Property	Simple r	Partial r	Multiple R
pH	0.455ns	0.674*	0.947**
Clay	0.903**	0.934**	
OM	0.292ns		
SA	0.933**		
AMOX-Al	0.917**		
AMOX-Fe	0.855**		
HYHCL-Mn	0.900**		

**---Significant at 0.01 probability level.

*---Significant at 0.05 probability level.

ns---Not Significant at 0.10 probability level.

Although the B was added to the soils in a water soluble form, only a small portion of the total added B was adsorbed by the corn plants, partially due to B adsorption by soil components.

No significant correlation was found between tissue B concentration from applied B and soil pH. A weak negative correlation was observed between tissue B concentration from applied B and soil organic matter content. As previously discussed, soil organic matter tends to adsorb B and keep it in relatively available forms.

Curvilinear relationships were found between tissue B concentration from applied B and soil clay content (Figure 8), surface area (Figure 9), AMOX-Al (Figure 10), AMOX-Fe (Figure 11) and HYHCL-Mn content (Figure 12). Logarithmic transformation were applied to both dependent and independent variables to evaluate the correlations (Little and Hills, 1978). After the transformation, tissue B concentration from applied B negatively correlated with soil clay content, surface area, AMOX-Al, AMOX-Fe and HYHCL-Mn at the 0.01 probability level (Table 11). A simple correlation analysis showed a high negative correlation between the plant uptake of applied B and the maximum B adsorption estimated in the B adsorption study. Evidently, soil clay and Al-, Fe- and Mn-oxides and hydroxides have high affinity to adsorb B in relatively unavailable forms.

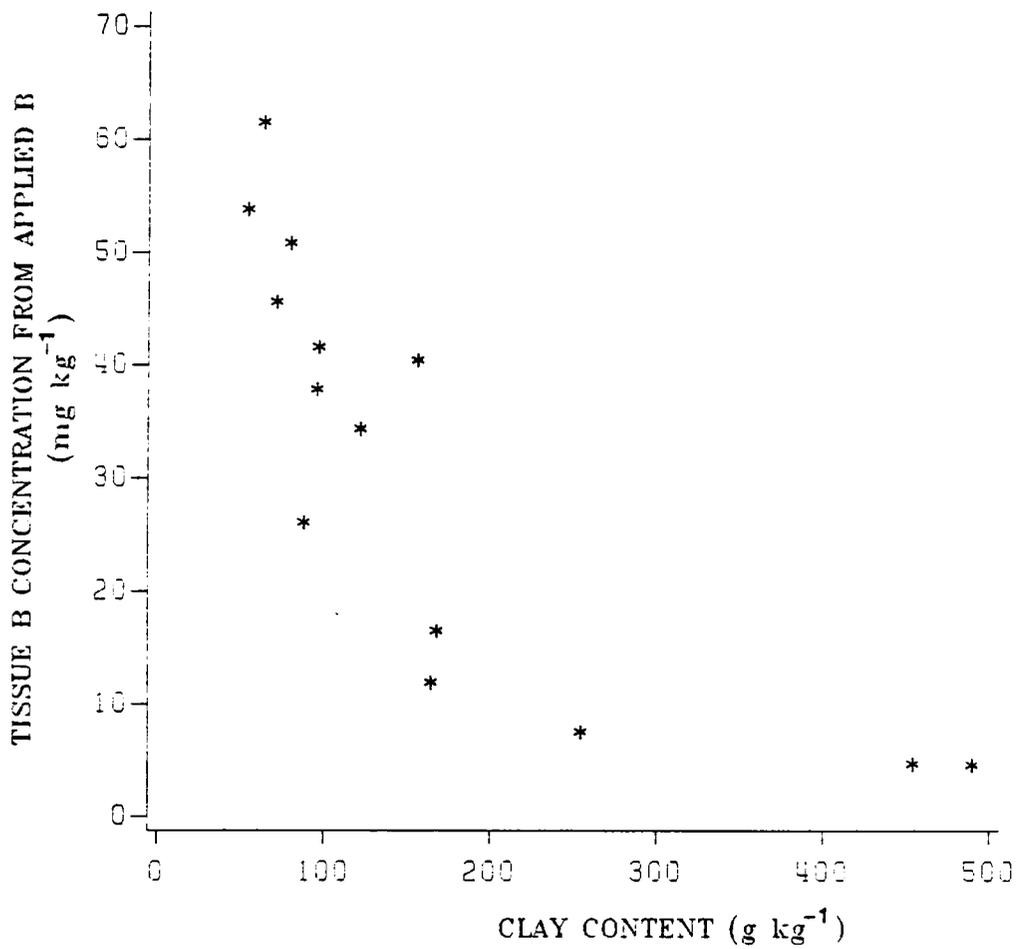


Figure 8: Plot of tissue B concentration from applied B versus clay content.

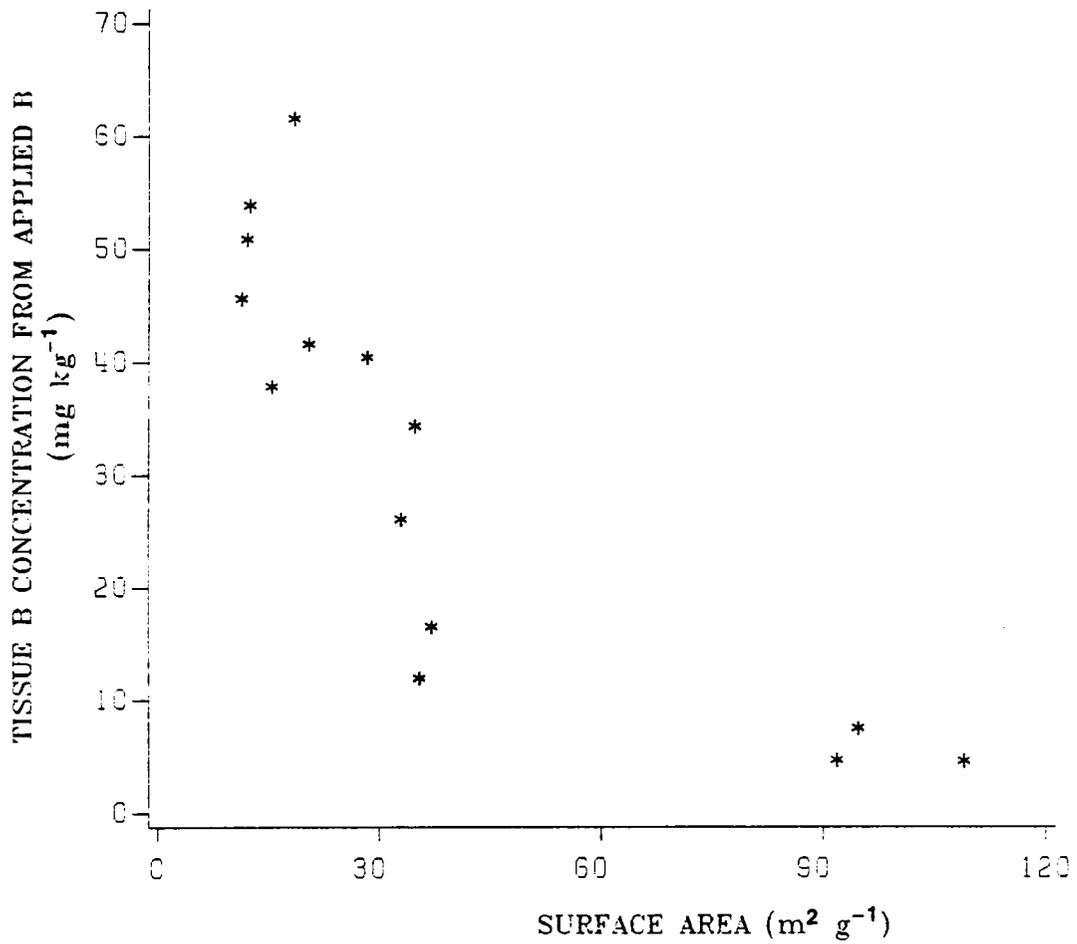


Figure 9: Plot of tissue B concentration from applied B versus surface area.

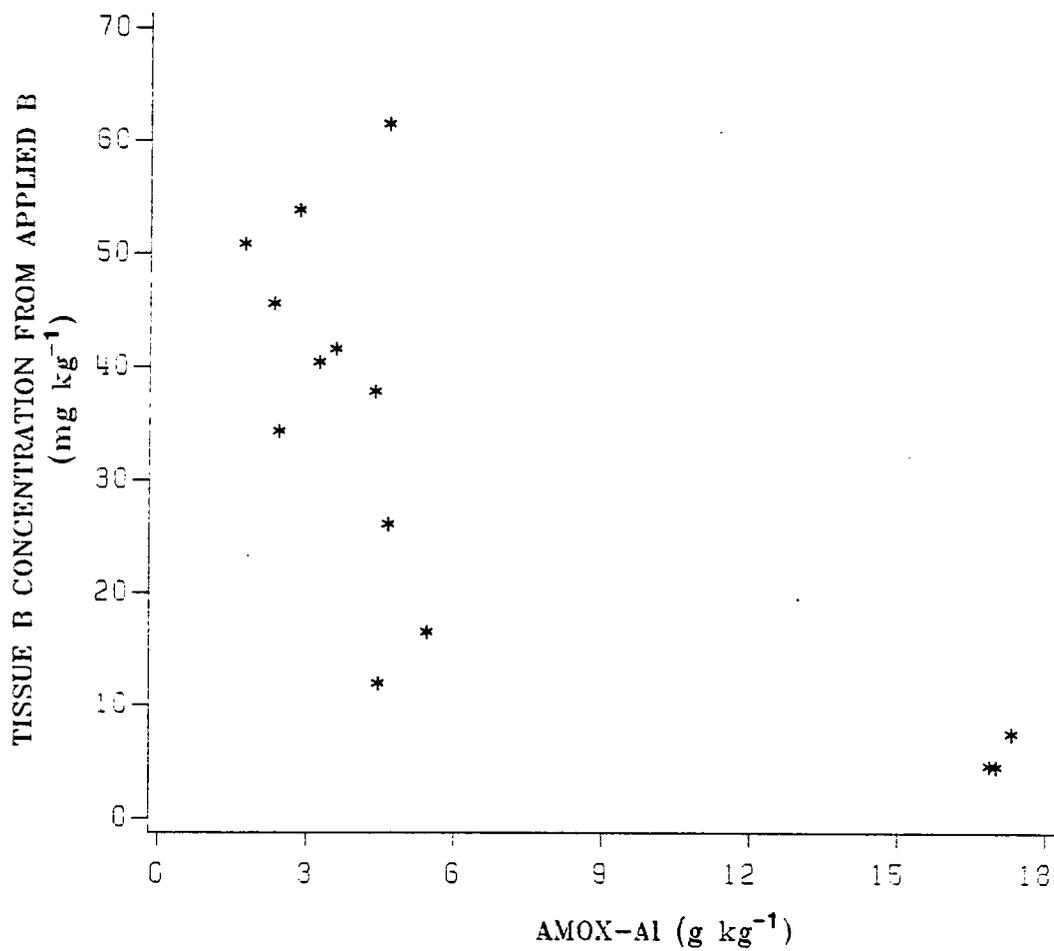


Figure 10: Plot of tissue B concentration from applied B versus AMOX-Al.

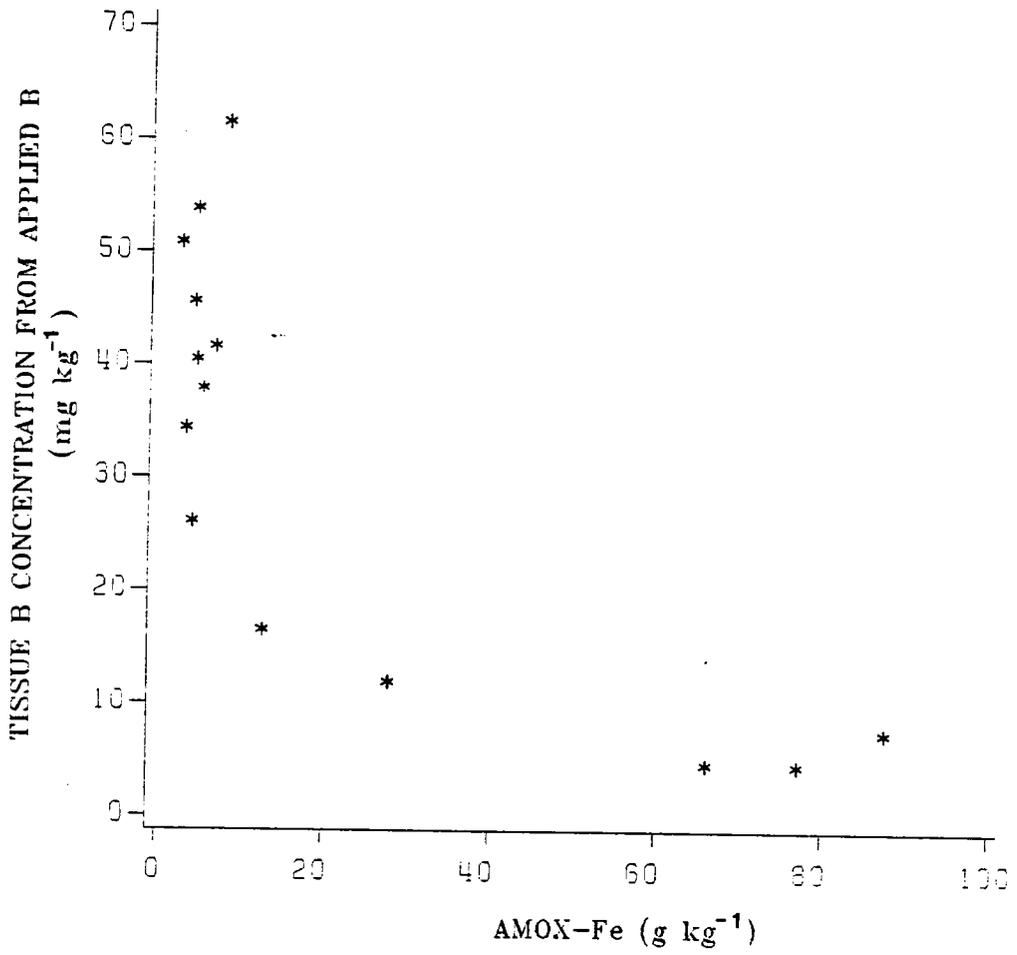


Figure 11: Plot of tissue B concentration from applied B versus AMOX-Fe.

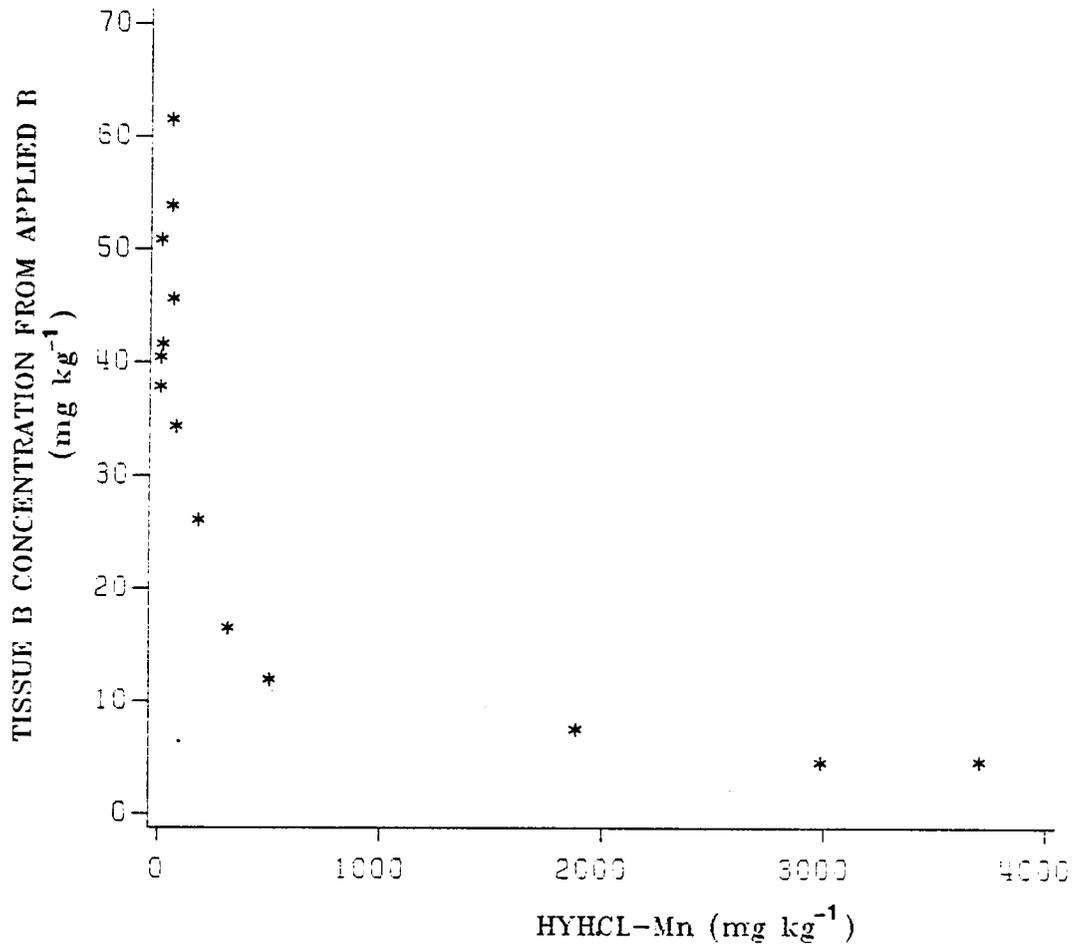


Figure 12: Plot of tissue B concentration from applied B versus AMOX-Mn.

TABLE 11

Correlation data for relationships between tissue B concentration from applied B (Y) and soil properties.

Dependent Variable	Independent Variable	Simple r
Y	pH	-0.357ns
	OM	-0.523†
	Vmax	-0.794**
log(Y)	log(clay)	-0.942**
	log(SA)	-0.926**
	log(AMOX-Al)	-0.891**
	log(AMOX-Fe)	-0.925**
	log(HYHCL-Mn)	-0.869**

**---Significant at 0.01 probability level.

†---Significant at 0.10 probability level.

ns---Not Significant at 0.10 probability level.

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Chapter IV

BORON ADSORPTION ON GIBBSITE AND GOETHITE

4.1 ABSTRACT

Boron (B) adsorption on gibbsite and goethite was investigated at a pH of 6.5 and 10 and at a temperature of 10 and 30 °C. Both boric acid and borate in the systems were adsorbed by both minerals. At pH 6.5, boric acid molecule was the major species in the system and B was adsorbed on the negatively charged surface of gibbsite and on the positively charged surface of goethite, while at pH 10, the borate anion was the major species in the system and B was adsorbed on the negatively charged surfaces of both gibbsite and goethite. More B was adsorbed at pH 10, than at pH 6.5, by both minerals at both temperatures. At pH 10, more B adsorption occurred on gibbsite than on goethite at 10 °C, while at 30 °C, B adsorption was greater on goethite than on gibbsite. These data indicated a greater temperature effect for B adsorption on goethite than on gibbsite.

Increasing temperature decreased B adsorption on both gibbsite and goethite at either pH 6.5 or 10, which indicated that B adsorption was an exothermic process. Using the Clausius-Clapeyron equation, the estimated isosteric heat of

adsorption of B on goethite was more negative than on gibbsite at both pH 6.5 and 10, further indicating the greater effect of temperature for B adsorption on goethite than on gibbsite. The temperature effect for B adsorption was greater at pH 10 than at pH 6.5.

Titration in NaCl solution showed that the specific adsorption of B shifted the ZPC of the minerals downward, from pH 5.8 to 5.3 for gibbsite and from pH 8.0 to 7.8 for goethite. However, by titrating the minerals in Na borate solutions, the crossover points shifted upward which further confirmed the occurrence of specific adsorption of B on both surfaces.

Key words: exothermic adsorption, isosteric heat of adsorption, boric acid, borate ion, molecule adsorption, anion exchange, zero point of charge.

4.2 INTRODUCTION

Boron (B) occurs in nature as boric acid and as salts of various condensed boric acid (Garrett et al., 1968). Boric acid is a very weak and exclusively monobasic acid and does not act as a proton donor but as a Lewis acid, accepting OH^- . It hydrolyzes to form the borate ion (Cotton and Wilkinson, 1966) as follows:



The pK value for the reaction is 9.00, indicating that in acid and neutral conditions B is in boric acid form, and in alkaline condition the borate ion become the main species in solution.

Both boric acid and borate ion can be adsorbed by soils and various soil components (Evans and Sparks, 1983). It has been proposed that hydroxy Fe and Al materials have a marked, though pH dependent, affinity for B (Sims and Bingham, 1968; Keren and Gast, 1983). Unlike fluoride and sulfate, for which Hingston et al. (1972) found that there was no adsorption at pH levels higher than the ZPC, B can be specifically adsorbed by hydroxy Al regardless of the sign of the net surface charge (Keren and Gast, 1983).

Gibbsite and goethite are common Al and Fe hydroxides in soils. Their structures and surface characteristics have

been studied extensively. They are constant surface potential minerals and their net surface charge depends upon the ZPC of the mineral and pH of the embedding solution.

Adsorption equations have been commonly used to characterize adsorption phenomena in soil and clay systems. Although adsorption isotherms by themselves do not indicate the mechanism involved, they do illustrate the equilibrium relationship between amounts of adsorbed and dissolved species at a given temperature. If adsorption is carried out at two or more temperatures, the heat of adsorption may be estimated. The Clausius-Clapeyron equation was originally developed to estimate the isosteric heat of vaporization and sublimation (Chang, 1981):

$$\ln(P_2/P_1) = (\Delta H/R)(1/T_1 - 1/T_2)$$

where P_1 and P_2 are the vapor pressures at temperature T_1 and T_2 , respectively, ΔH is the isosteric heat of vaporization or sublimation and R is the molar gas constant. Despite differences between the liquid-solid interface and the vapor-liquid or vapor-solid interface, the Clausius-Clapeyron equation has been used to estimate the heat of adsorption of phosphate on a resin and calcite (Griffin and Jurinak, 1973; Taylor and Ellis, 1978).

Specific adsorption of some anions, such as phosphate and sulfate, changes the surface charge characteristics of a

constant surface potential mineral (Keng and Uehara, 1974; Wann and Uehara, 1978; Pyman et al., 1979). It has been experimentally and theoretically indicated that, if the titration was carried out in an indifferent electrolyte, the occurrence of specific adsorption of an anion shifted the ZPC of the mineral downward and that, if the specifically adsorbed anion was the only anion in the electrolyte, the crossover point of the titration curves shifted upward relative to the ZPC (Pyman et al., 1979; Sposito, 1981, 1983).

The objective of this study was to investigate the influence of pH and temperature on B adsorption by gibbsite and goethite and the effect of B adsorption on surface charge characteristics of both minerals.

4.3 MATERIALS AND METHODS

A clay size (<2 μm) synthetic gibbsite sample was Ca-saturated, washed 5 times with 0.02 M CaCl_2 solution and freeze-dried. The goethite used for this experiment was synthesized according to the procedure of Atkinson et al. (1968) by slow addition of 0.1 N NaOH to 0.4 N FeCl_3 up to pH 12 with vigorous stirring. This solution was aged at 60 $^\circ\text{C}$ for 6 hours and then Ca-saturated, washed with 0.02 M CaCl_2 solution and freeze-dried. X-ray diffraction analysis showed that there was no other mineral in the product. Some properties of the minerals were shown in Table 12. Surface area was determined by N_2 -BET method using a Micrometrics surface-area analyzer, Model 2100D. ZPC of the minerals was measured by titrations in selected NaCl solutions with a Radiometer autotitration system. Noncrystalline material was extracted with 0.2 M NH_4 -oxalate (pH 3) in the dark (Hodges and Zelazny, 1980).

For the B adsorption study, 20 g of freeze-dried gibbsite or 2 g of freeze-dried goethite was dispersed in 0.02 M CaCl_2 solution in a centrifuge bottle and pH adjusted to 6.5 or 10 by addition of either HCl or $\text{Ca}(\text{OH})_2$ solution. Samples were subsequently washed 4 times with 0.02 M CaCl_2 solution adjusted to pH 6.5 or 10, and the final volume made

TABLE 12

Specific properties of the gibbsite and goethite studied.

	Surface Area ($\text{m}^2 \text{g}^{-1}$)	ZPC	Non-crystalline Material (%)
Gibbsite	4.05	5.8	0.40
Goethite	70.05	8.0	2.70

up to 200 ml. An aliquot of suspension containing 2 g of gibbsite or 0.1 g of goethite was pipetted into a 100 ml polypropylene centrifuge tube, centrifuged and the supernatant discarded. The amount of solution left in the tube was measured by weighing and used to calculate the initial B concentration. Tubes with samples and bottles containing B solutions were put in either a cold room at 10 °C or in a water-bath-shaker at 30 °C. After reaching the surrounding temperature, 10 ml of B solution in 0.02 M CaCl₂ adjusted to pH 6.5 or 10 was added to the centrifuge tubes containing the samples. The initial concentrations of B in the solutions ranged from 0.18 to 18.5 mmol L⁻¹. A previous study showed that equilibrium was reached within 15 minutes. However, 4 hours shaking was selected for all samples for convenience. After equilibration, suspensions were filtered through a Gelman membrane and B concentration in solution determined by the azomethine-H procedure (Wolf, 1974). Difference between contents of B in initial and equilibrium solutions was considered the amount of B adsorbed and was calculated on an oven dried basis (110 °C).

The linear form of the Langmuir equation was used to describe B adsorption. A modified form of the Clausius-Clapeyron equation was employed to estimate the isosteric heat of adsorption of B on the minerals:

$$\ln(C_2/C_1)_\theta = (-\Delta H/R)/(1/T_1 - 1/T_2)$$

where C_1 and C_2 are the equilibrium concentrations of B in the solutions at temperature T_1 and T_2 , respectively, ΔH is the isosteric heat of adsorption, R is the gas constant and θ indicates the same amount of B adsorption on the surface at both temperatures.

A Radiometer autotitration system was used for all titrations in which sample size was 1 g for gibbsite and 0.2 g for goethite. Three type of titrations were conducted:

1. Titration in NaCl solution before B adsorption.

Samples were dispersed and washed 5 times with appropriate NaCl solutions (1.0, 0.1 and 0.01 N for gibbsite and 0.25, 0.025 and 0.0025 N for goethite) with centrifugation and decantation. Duplicate samples were then equilibrated with the appropriate NaCl solutions over night and one titrated with 0.04 N NaOH and the other with 0.04 N HCl solution.

2. Titration in NaCl solution after B adsorption.

Samples were washed 4 times with 0.5 M Na borate solution which had a pH pre-adjusted to that of the corresponding NaCl electrolyte used for the titration. As above, the sample was washed 5 times, equilibrated over night with the appropriate NaCl solution and titrated.

3. Titration in sodium borate solution.

Samples were washed 5 times with 0.005, 0.05 or 0.25 mM Na borate solution. The suspensions were equalibrated over night and than titrated in the sodium borate solution as above.

Surface charge was calculated according to the amount of H^+ or OH^- adsorbed on each mineral surface at a given pH.

4.4 RESULTS AND DISCUSSION

More B was adsorbed at pH 10 than at pH 6.5 by both gibbsite (Figure 13) and goethite (Fig. 14) at either 10 or 30 °C. Boron adsorption was greater at 10 °C compared with 30 °C by both gibbsite and goethite at either pH 6.5 or 10 (Figure 13, 14, Table 13).

Boron adsorption could be described by the linear form of the Langmuir equation, except for B adsorption on gibbsite at pH 6.5. At pH 10 and 30 °C, maximum B adsorption on gibbsite was greater than on goethite. Decreasing temperature from 30 to 10 °C increased B adsorption on both minerals. However, the increase of B adsorption with decreasing temperature was greater on goethite than on gibbsite. At 10 °C, more B was adsorbed on goethite than on gibbsite (Table 13).

Since increasing temperature decreased B adsorption, it was evident that B adsorption on gibbsite and goethite at either pH 6.5 or pH 10 was an exothermic process, releasing heat to the surrounding. The effects of temperature on B adsorption at pH 10 was greater than that at pH 6.5 (Figure 13, 14, and Table 13), and more significant for goethite than gibbsite. Using the Clausius-Clapeyron equation, the isosteric heat of B adsorption was calculated and plotted as

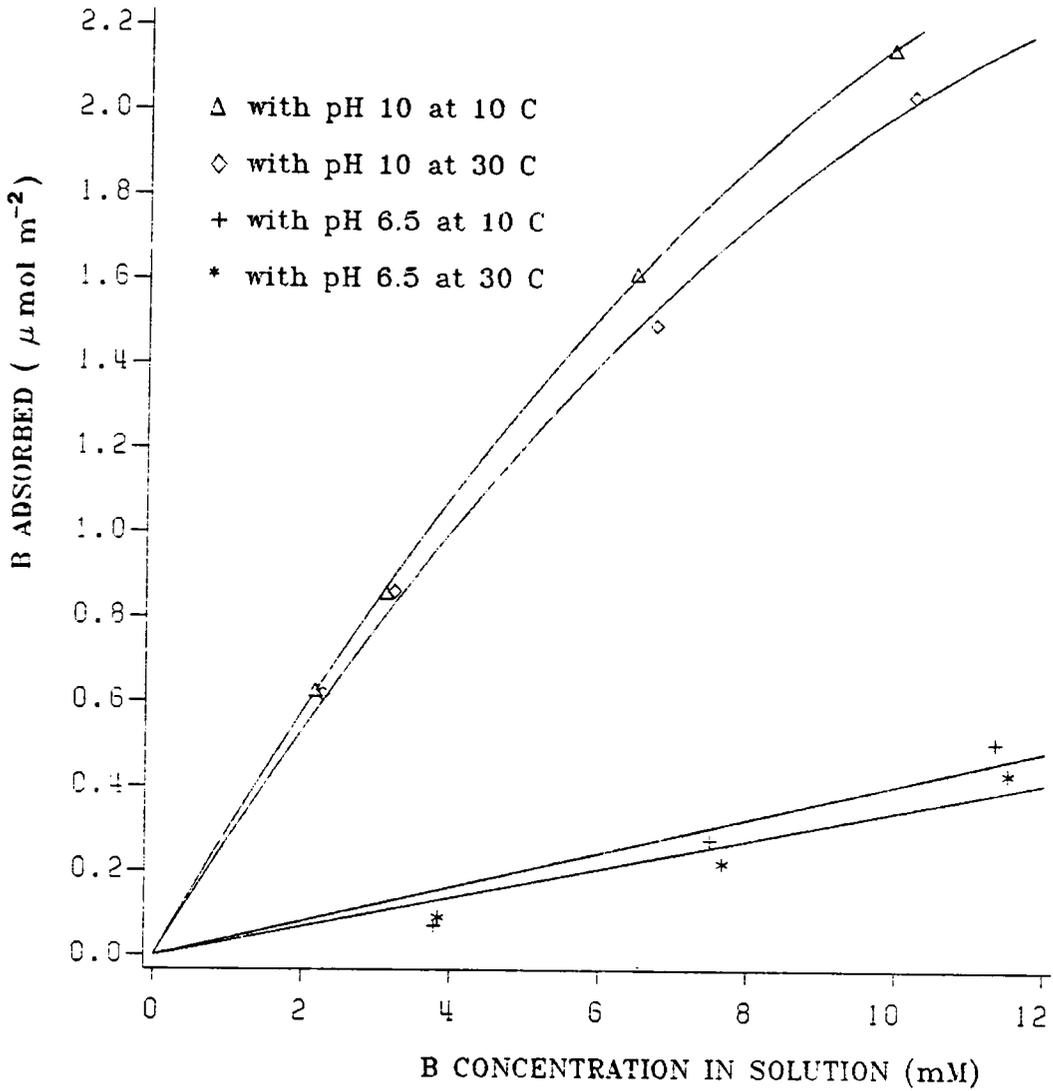


Figure 13: Boron adsorption by gibbsite at pH 6.5 and 10 and at 10 and 30 °C.

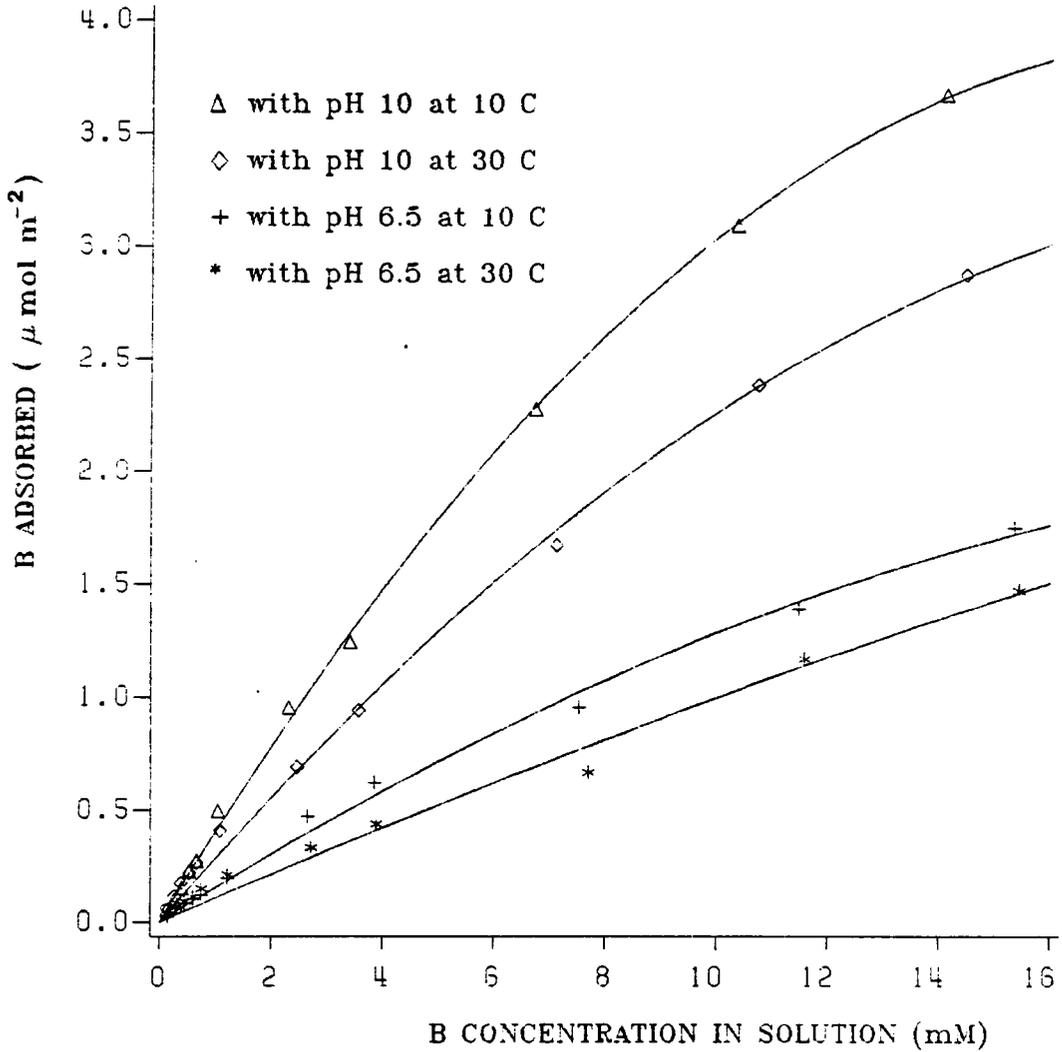


Figure 14: Boron adsorption by goethite at pH 6.5 and 10 and at 10 and 30 °C.

TABLE 13

Effects of pH and temperature on maximum B adsorption on gibbsite and goethite estimated by using the Langmuir equation.

	pH 6.5		pH 10	
	10 °C	30 °C	10 °C	30 °C
	----- $\mu\text{mol m}^{-2}$ -----			
Gibbsite	--	--	6.93	5.72
Goethite	4.01	2.28	10.29	4.96

a function of the amount of B adsorbed on each mineral surface (Figure 15). The isosteric heats of adsorption became less negative with an increase in amount of B adsorbed, except for gibbsite at pH 10 which became more negative. The isosteric heat of adsorption was more negative for goethite at pH 10 than at pH 6.5 and more negative for goethite than for gibbsite. These data also imply that the temperature effect on B adsorption at pH 10 was greater than that at pH 6.5 and that the influence was more significant for B adsorption on goethite than on gibbsite.

The ZPC of gibbsite and goethite used for this experiment were 5.8 and 8.0, respectively (Table 12). At pH 6.5, net surface charge was negative on gibbsite and positive on goethite. The B in the system was primarily in the boric acid form. It seems evident that boric acid molecule could adsorb on either positively or negatively charged surfaces and that this adsorption was an exothermic process.

It has been proposed that undissociated acid molecules can be adsorbed as long as they dissociate at the surface to provide protons which react with surface OH^- (Hingston et al., 1972). As a Lewis acid, the unhydrated boric acid may be adsorbed on surfaces as long as it can accept an electron pair from the surface and decrease the free energy of the system regardless of net surface charge sign. Based on this

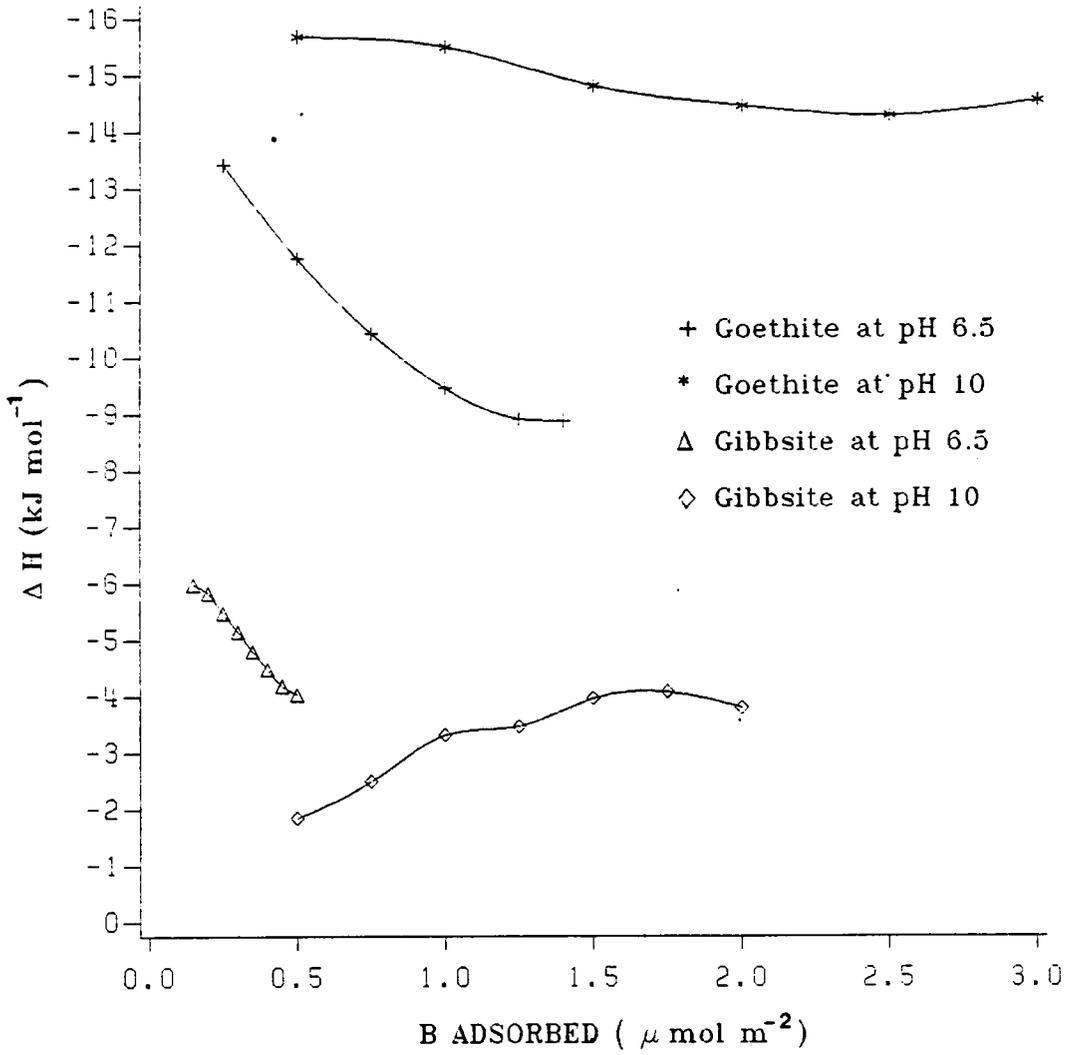


Figure 15: Isosteric heat of adsorption of B on gibbsite and goethite.

hypothesis, Parfitt (1978) proposed a possible complex, $\text{FeOH}\cdot\text{B}(\text{OH})_3$, for boric acid on goethite surfaces.

At pH 10, surfaces of both gibbsite and goethite were negatively charged and B in the system was mainly in the borate form. However, B was adsorbed on these negatively charged surfaces and adsorption was even significantly greater than at pH 6.5 (Figure 13, 14). Apparently, electrostatic attraction forces cannot explain the B adsorption on negatively charged surfaces. Ion exchange between borate and hydroxyls on the surface might be responsible for B adsorption. An increase in pH in the suspension as a result of B adsorption by hydroxy Al at alkaline condition was reported by Metwally (1966), indicating that this exchange between the borate ion and the hydroxyl on the surface did occur.

Specific adsorption of B did change the surface charge characteristics of both gibbsite and goethite. By titration in appropriate NaCl solutions without B adsorption, the crossover points indicative of the ZPC of the minerals occurred at pH 5.8 and 8.0 for gibbsite and goethite, respectively (Figure 16, 17). However, after B adsorption, these crossover points shifted downward to pH 5.3 and 7.8 for gibbsite and goethite, respectively (Figure 16, 17). Similar effects of anion adsorption on ZPC determinations have

been reported by Wann and Uehara (1978) and Pyman et al. (1979). According to the operational definition of ZPC by Sposito (1981), the crossover points still coincide with the ZPC of the B adsorbing minerals, which shifted downward due to B adsorption.

By titrations in appropriate Na borate solutions, the crossover points shifted upward to pH 9.8 for goethite (Figure 18). The crossover point for gibbsite was undetectable. However, the titration curves did not cross with each other below pH 7, which was above the ZPC of these mineral (pH 5.8) (Figure 19). These results agreed with the findings of Keng and Uehara (1974) and Pyman et al. (1979) and confirmed the occurrence of specific adsorption of B on both gibbsite and goethite.

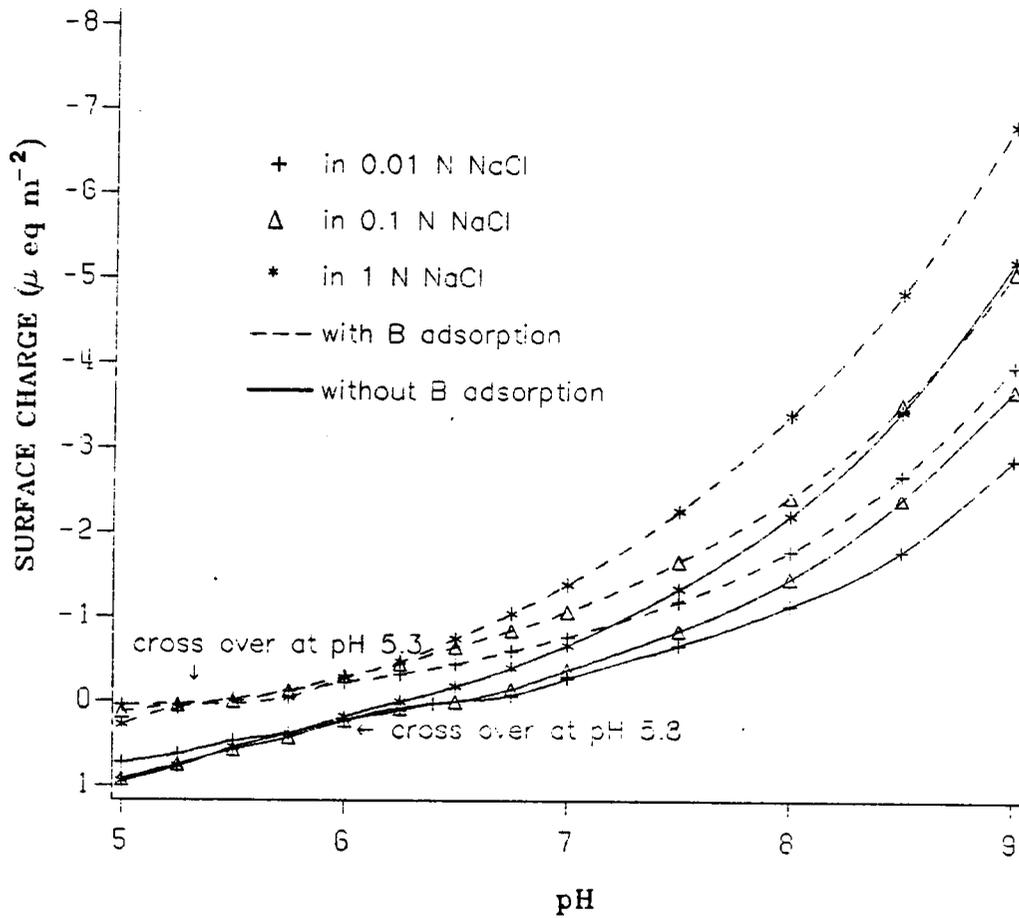


Figure 16: Titration curves of gibbsite in selected NaCl solutions.

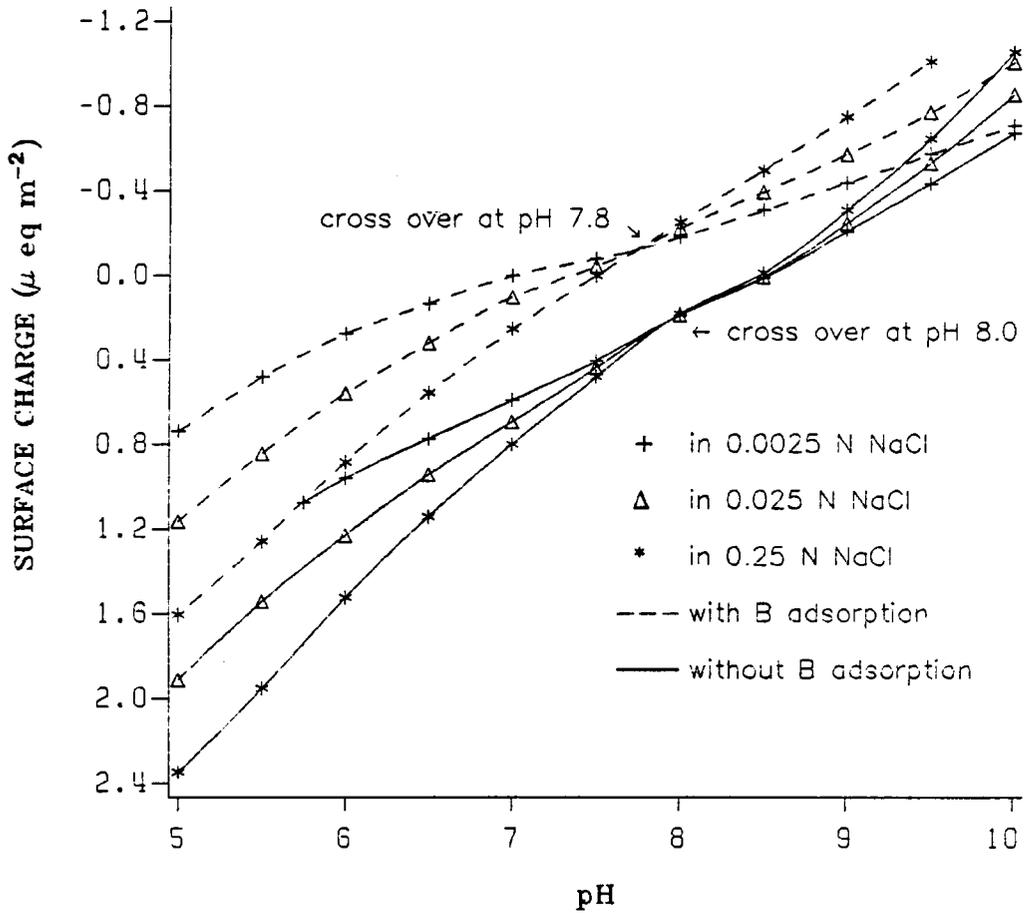


Figure 17: Titration curves of goethite in selected NaCl solutions.

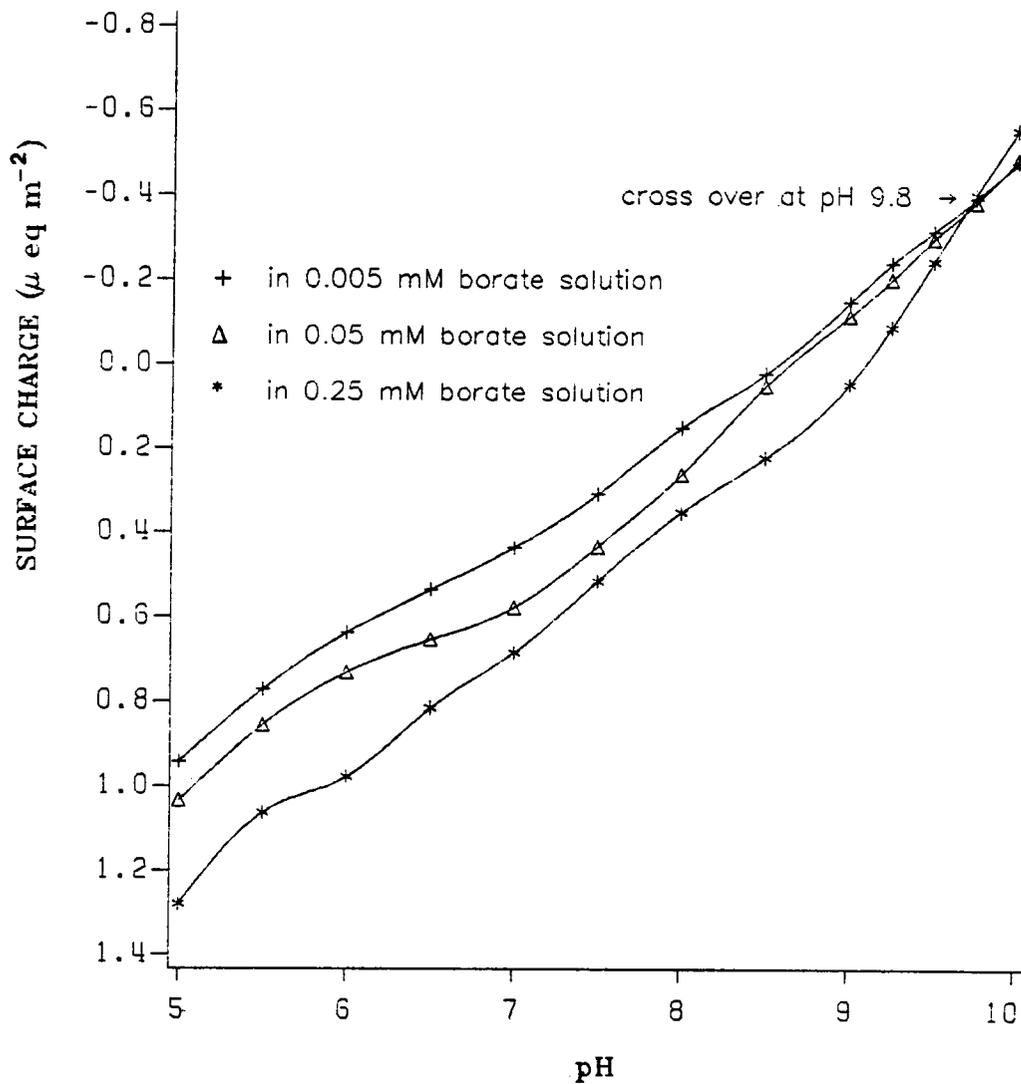


Figure 18: Titration curves of goethite in selected Na borate solutions.

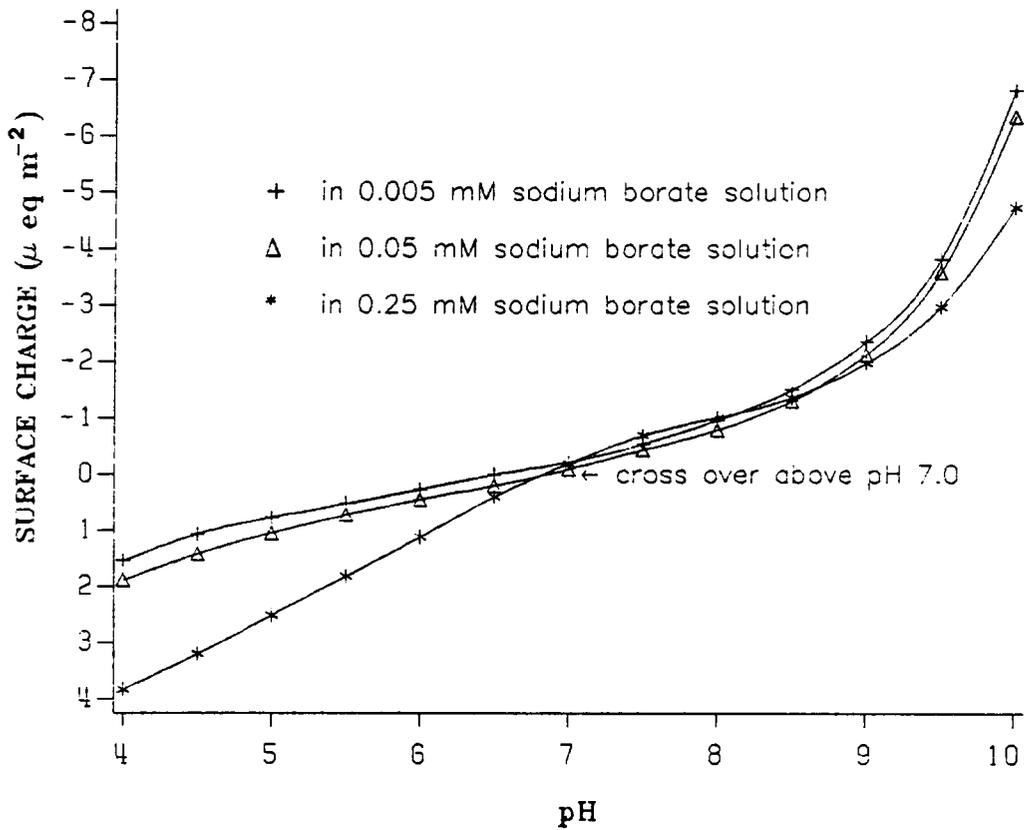


Figure 19: Titration curves of gibbsite in selected Na borate solutions.

4.5 CONCLUSIONS

Both boric acid and borate ion may be specifically adsorbed by gibbsite and goethite, regardless of the sign of net charge on the surface. At pH 6.5, a complex of boric acid and surface hydroxyl may be formed, while at pH 10, exchange of borate ion and hydroxyl on the surface may be responsible for B adsorption. The B adsorption, either in boric acid or borate anion form, was an exothermic process. The isosteric heat of B adsorption at pH 10 was more negative than that at pH 6.5 and more on goethite than on gibbsite. The titrations of the minerals in either NaCl or Na borate solutions verified the occurrence of specific B adsorption, which changed the surface charge characteristics of the minerals.

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Chapter V

BORON ADSORPTION ON AL-SUBSTITUTED GOETHITES

5.1 ABSTRACT

Aluminum substituted goethites (Al-goethites) were synthesized by oxidation of the Fe^{2+} -Al chloride system (Al mole %=0, 10, 20, 30 and 100) at fast and slow oxidation rates. Almost all of the Al in the system was incorporated into the products. No other crystalline Al and Fe mineral was found by X-ray diffraction analysis. Only X-ray amorphous material was produced from the pure Al system.

A large portion of the Al and Fe in the Al-goethites was oxalate soluble (pH 3, in the dark). However, after oxalate extraction, the X-ray diffraction pattern was the same with the nontreated sample. This indicated that the oxalate soluble material was very fine Al-goethite crystal instead of X-ray amorphous material.

Oxidation rate affected the mineralogical properties of the Al-goethites. Slow oxidation produced Al-goethites with larger particle size, better crystallinity, and thereby, smaller surface area, compared with the fast oxidation treatment.

A small amount of Al substitution (Al mole %=10) increased the crystallinity and decreased the surface area of the Al-goethites, probably due to the relief of lattice strain by substituting a smaller Al cation for Fe. A further increase in Al substitution (Al mole %=20, 30) decreased crystallinity and increased surface area of the Al-goethites.

Nonsubstituted goethite showed a reddish yellow color (7.5 YR 6/8). With an increase of Al substitution, the color of the samples changed from reddish yellow to red, and became darker and darker. The mole fraction of Al in the Al-goethites negatively correlated with the Munsell hue, value and chroma at the 0.01 probability level.

Boron adsorption by the Al-goethite was described by the Langmuir equation. Aluminum substitution increased the B adsorption power of the goethite surface. After the oxalate extraction, maximum adsorption of B by the residues of the slow oxidation Al-goethites correlated with the Al mole fraction in the samples at the 0.01 probability level.

Key words: oxidation rate, surface area, crystallinity, oxalate extraction, X-ray diffraction, X-ray amorphous material, Langmuir equation, Munsell color charts.

5.2 INTRODUCTION

Aluminum substitution for Fe in goethite is a common phenomenon in soils (Norrish and Taylor, 1961; Davey et al., 1975; Nahon et al., 1977; Bingham et al., 1978; Mendelovic, et al., 1979; Torrent et al., 1980; Fitzpatrick and Schwertmann, 1981). The Al-substituted goethite has been synthesized in laboratories either by aging Fe³⁺-Al precipitation in base (Lewis and Schwertmann, 1979; Schulze, 1982) or by oxidation of the Fe²⁺-Al system (Schwertmann, 1959; Goodman and Lewis, 1981; Fey and Dixon, 1981).

The goethite can tolerate Al substitution up to 33 mole % (Schwertmann and Taylor, 1977). The Al³⁺ ion is slightly smaller than the Fe³⁺ ion, 0.53 Å vs. 0.66 Å (Shannon and Prewitt, 1969). It has been found that the Al substitution for Fe in goethite reduced the unit cell size (Thiel, 1963; Jonas and Solymar, 1970) and influenced the crystal growth and thereby the surface area (Schulze and Schwertmann, 1984).

Since hydroxy Al and Fe materials have a marked affinity for B retention (Sims and Bingham, 1968; Keren and Gast, 1983) and hydroxy Al shows greater B adsorption power than hydroxy Fe material (Sims and Bingham, 1968), it is more likely that Al substitution for Fe will affect the B adsorption on the goethite.

The objectives of this study were to investigate the effect of oxidation rate of Fe^{2+} -Al chloride solution on properties of the synthesized Al-goethites and to determine the influence of Al substitution of goethite on B adsorption.

5.3 MATERIALS AND METHODS

5.3.1 Synthesis of Al Substituted Goethites

Al-goethites were synthesized according to the method of Schwertmann (1959) and Fey and Dixon (1981) which involves oxidation of FeCl_2 in the presence of CO_2 to inhibit lepidocrocite formation. Given quantities of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were mixed to obtain $\text{Al}/(\text{Al}+\text{Fe})$ molar ratios of 0, 10, 20, 30, and 100% and diluted to 9 liters with deionized water. The final concentration of $(\text{Al}+\text{Fe})$ was 0.02 M in all the solutions.

The solution was rapidly brought to and then maintained at pH 6.8 with vigorous stirring using a Radiometer automatic titration system and 5 M KOH as titrant until the suspension was fully oxidized by an $\text{O}_2:\text{CO}_2$ gas mixture with 10% O_2 . The gas mixture was introduced to the system through four glass fritted millipore filters. Two oxidation rates were employed for each Al-Fe combination in order to produce Al-goethites with different crystallinity and different particle size. In the fast oxidation treatment, the mixture gas was introduced to the system at a rate of approximately 1000 ml per min for pure Fe solution and reduced for the

aluminous solutions so that the period required for complete oxidation was approximately 3 hours in each case. For the slow oxidation, the gas flow rate was 40 ml per min for pure Fe solution and reduced for the aluminous solution. The period for complete oxidation was approximately 15 hours.

After the oxidation, the suspension was left overnight and the supernatant was discarded. The Al-goethite product was washed 5 times with 0.02 N KCl solution by centrifugation. Half of the product was freeze-dried for mineralogical analyses, and the other half was stored in suspension for B adsorption.

A portion of the freeze-dried sample of the slow oxidation Al-goethites was treated by the ammonium oxalate (pH 3) extraction in the dark following the method of Schwertmann (1964). After the oxalate extraction, the Al-goethite sample was washed 5 times with 0.02 N KCl solution, then a part of the sample was freeze-dried for mineralogical study, and the rest was stored in suspension for B adsorption.

5.3.2 Chemical Dissolution

The oxalate soluble Al and Fe in the products were determined following the procedure of Schwertmann (1964). A 100-mg Al-goethite sample was shaken with 100 ml of the am-

monium oxalate solution (pH 3) in the dark for 2 hours. The suspension was centrifuged and the Al and Fe content in the supernatant were determined by the atomic absorption spectrophotometry.

The Al-goethites were prepared for total Al and Fe analyses by HCl digestion (Schwertmann, 1984). Fifty mg of sample were digested with 10 ml of concentrated HCl in a teflon bomb at 150 °C for 4 hours. The sample was transferred to a 100 ml volumetric flask and the volume was made up with deionized water. The Al and Fe contents in the solution were determined by atomic absorption spectrophotometry.

5.3.3 Mineralogical Analyses

Surface area of the Al-goethite samples was determined by N₂-BET adsorption method with a Micromeritics surface analyzer, Model 2100. X-ray powder diffraction data were obtained with a GE-Diano 8300 XRD controlled by DEC-LSI-11 using CuK α radiation.

The color of the dry powder of the Al-goethite was estimated by comparing the sample with the Munsell soil color charts (Munsell Color, 1975).

5.3.4 Boron adsorption by Al-goethite

For B adsorption on the Al-goethites, an aliquot of the Al-goethite suspension containing 0.1 g dry sample was taken into a 100 ml centrifuge tube, centrifuged, and the supernatant was discarded. The solution left in the tube was estimated by weighing and taken into account in calculation of B concentration of the initial solution. Ten ml of B solution ranging from 2.3 to 18.5 mmol L⁻¹ in 0.02 N KCl solution were added to the tube. The sample was shaken at 30 °C in a water bath shaker for 4 hours. The suspension was centrifuged and the B concentration in the supernatant was determined by the azomethine-H procedure. The amount of B adsorbed was calculated by the difference between B contents in the initial and the equilibrium solutions and expressed in $\mu\text{mol m}^{-2}$ surface in order to compare the B adsorption power of the Al-goethites with different surface areas.

5.4 RESULTS AND DISCUSSION

5.4.1 Effects of Oxidation Rates and Al Substitution on Al-goethites.

Almost all of the Al in the solution was incorporated into the products by either fast or slow oxidation procedures (Table 14). A large portion of the Al in the products was oxalate soluble. The percentage of total Al dissolved in oxalate solution was greater in the fast oxidation sample than in the slow oxidation sample. Similar results were found for Fe. A larger portion of Fe was oxalate soluble in the fast oxidation Al-goethites, compared with the slow oxidation sample. A higher proportion of total incorporated Al was oxalate soluble, compared with the incorporated Fe. After oxalate extraction, the mole fraction of Al in the residue was smaller than in the original sample. This indicated that the Al in the Al-goethite products is not uniformly distributed, more Al is either in noncrystalline material or in very fine crystals which are oxalate soluble (Table 14). The products from pure Al solution from both fast and slow oxidation were totally oxalate soluble.

X-ray diffraction analysis showed that the Al-goethites did not contain other crystalline Fe and Al minerals (Figure

TABLE 14

Chemical Compositions of the Al-goethites.

<u>Sample</u>	<u>Al mole % in Solution</u>	<u>Al mole % in Product</u>	<u>% of Total Al Soluble in oxalate</u>	<u>% of Total Fe Soluble in Oxalate</u>	<u>Al mole % in Residue after Oxalate Extr.</u>
GAOF*	0	0.0	--	36	0.0
GA10F	10	10.7	30	21	9.6
GA20F	20	20.1	35	21	17.2
GA30F	30	28.4	61	44	21.7
A100F	100	100.0	100	--	--
GAOS**	0	0.0	--	25	0.0
GA10S	10	10.3	22	14	9.4
GA20S	20	20.4	23	13	18.7
GA30S	30	29.4	36	19	24.7
A100S	100	100.0	100	--	--

* Fast oxidation Al-goethite,
the number is Al mole % in solution.

** Slow oxidation Al-goethite,
the number is Al mole % in solution.

20, 21, 22). A small amount of Al substitution increased crystallinity of the Al-goethite, compared with the nonsubstituted goethites. Further increase of the Al substitution decreased the crystallinity. The slow oxidation products showed better crystallinity than the fast oxidation Al-goethite (Figure 20, 21, 22). Only X-ray amorphous material was found in the products from pure Al solution (Figure 20, 21).

After oxalate extraction, the X-ray diffraction patterns of the residues of the slow oxidation Al-goethites (Figure 22) were almost identical to the original samples (Figure 21). The crystallinity of the slow oxidation Al-goethite was not improved by the oxalate extraction. In other words, the oxalate-removed material had similar crystallinity, but a larger surface area as compared with the residue. The oxalate extraction was originally developed (Schwertmann, 1964) and has been commonly used to extract noncrystalline materials from soils (Mckeague and Day, 1966; Fey and LeRoux, 1977; Hodges and Zelazny, 1980). However, from this experiment, it seems likely that the oxalate removed material from the Al-goethite is very fine crystal instead of noncrystalline material.

The surface area of the slow oxidation Al-goethites was smaller than that of fast oxidation Al-goethites (Table 15,

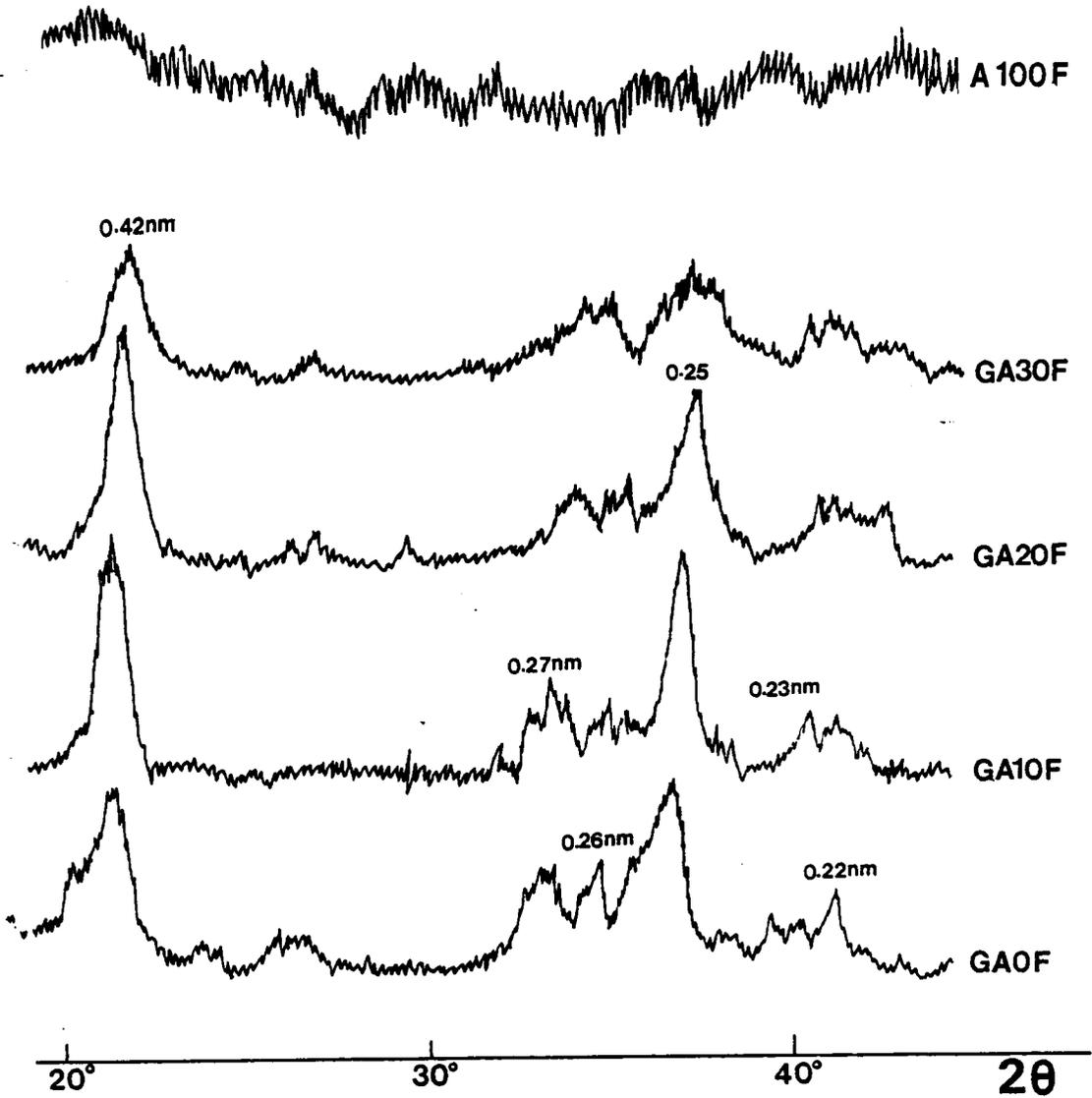


Figure 20: X-ray diffraction patterns of fast oxidation Al-goethites.

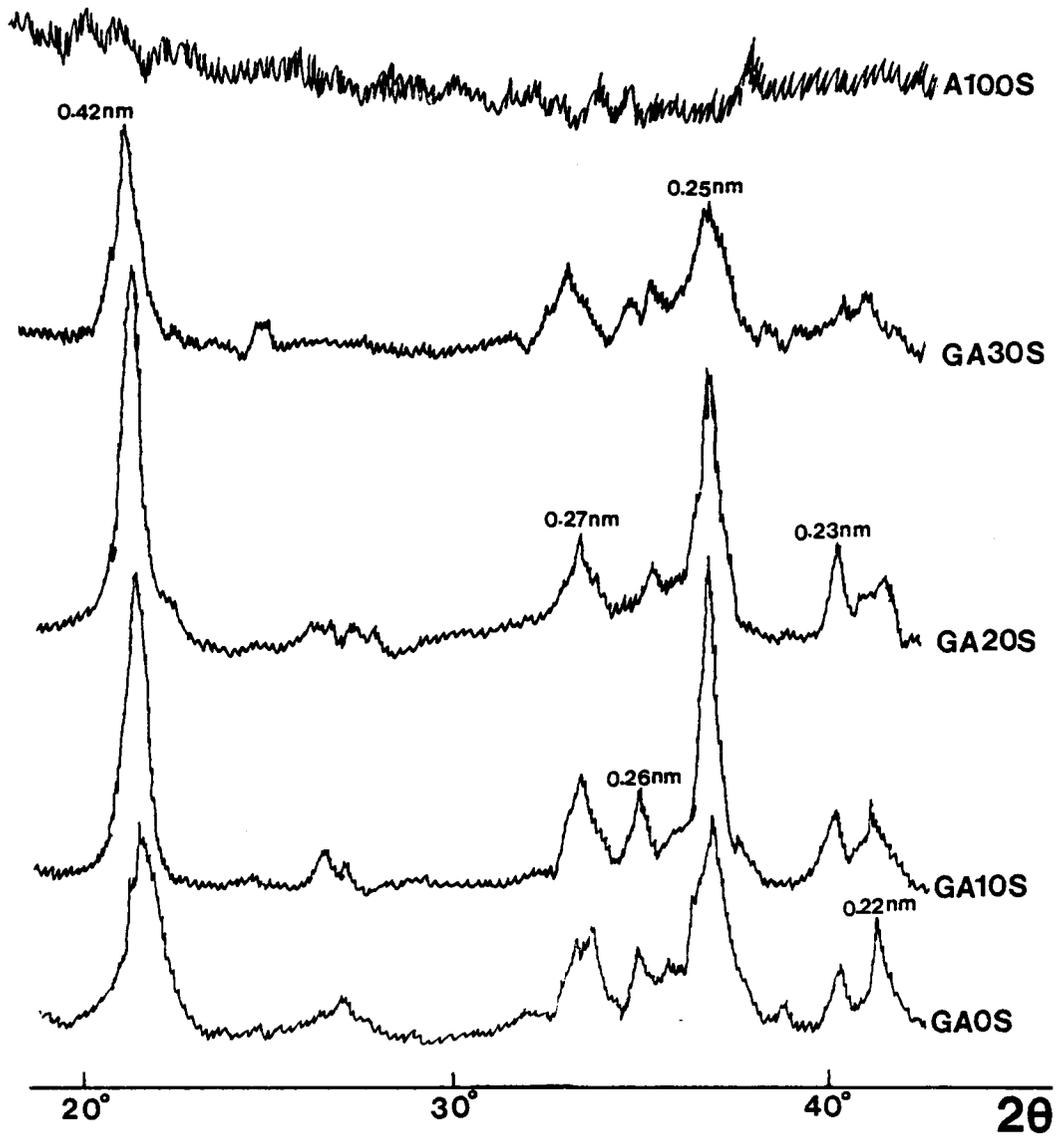


Figure 21: X-ray diffraction patterns of slow oxidation Al-goethites.

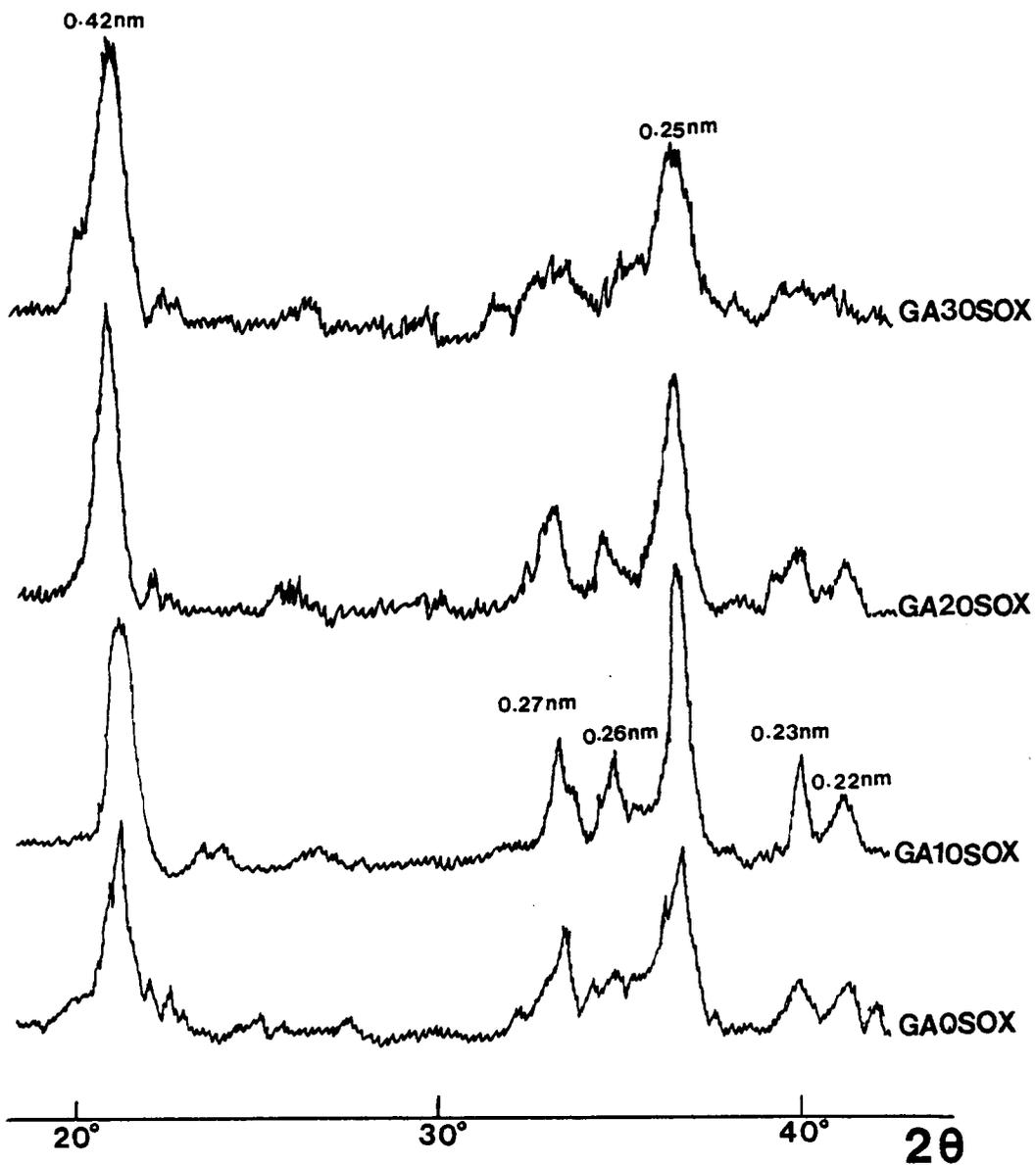


Figure 22: X-ray diffraction patterns of residues of slow oxidation Al-goethites after oxalate extraction.

TABLE 15

Surface Area and Maximum B Adsorption of the Al-goethites.

Sample	Surface Area ($\text{m}^2 \text{g}^{-1}$)	Maximum B Adsorption ($\mu\text{mol m}^{-2}$)
GAOF	274	1.64
GA1OF	199	3.83
GA2OF	230	3.66
GA3OF	280	3.81
A100F	222	10.65
GAOS	217	1.46
GA1OS	163	2.61
GA2OS	199	2.13
GA3OS	246	1.80
A100S	290	3.74
GAOSOX*	152	0.18
GA1OSOX	139	0.22
GA2OSOX	178	0.24
GA3OSOX	225	0.26

* The residue of slow oxidation Al-goethite after oxalate extraction.

Figure 23). After the oxalate extraction, the surface area of the residue from the slow oxidation Al-goethite was smaller than the original sample, due to the removal of the very fine crystalline material which had a large surface area (Table 15, Figure 23).

A small amount of Al substitution (Al mole %=10) decreased the surface area of the Al-goethite. However, with further increase of the Al substitution (Al mol %=20, 30), the surface area increased. This observation was found in the fast and slow oxidation Al-goethites as well as the residue after oxalate extraction (Table 15, Figure 23).

From all the mineralogical analyses discussed above, it is evident that the slow oxidation produced Al-goethites with a larger crystal size, and therefore, a smaller surface area than the fast oxidation treatment. A small amount of Al substitution (mole Al %=10) increased the crystallinity, and thereby, decreased the surface area, compared with the nonsubstituted Al-goethite. Similar results have been reported by Fey and Dixon (1981) for Al substituted goethite and by Schwertmann et al. (1979) for Al substituted hematite. Schwertmann et al. (1979) indicated that a small amount of Al substitution for Fe improved the crystallinity due to the relief of lattice strain, because of the slightly smaller cation size of Al than Fe. Further increase of Al

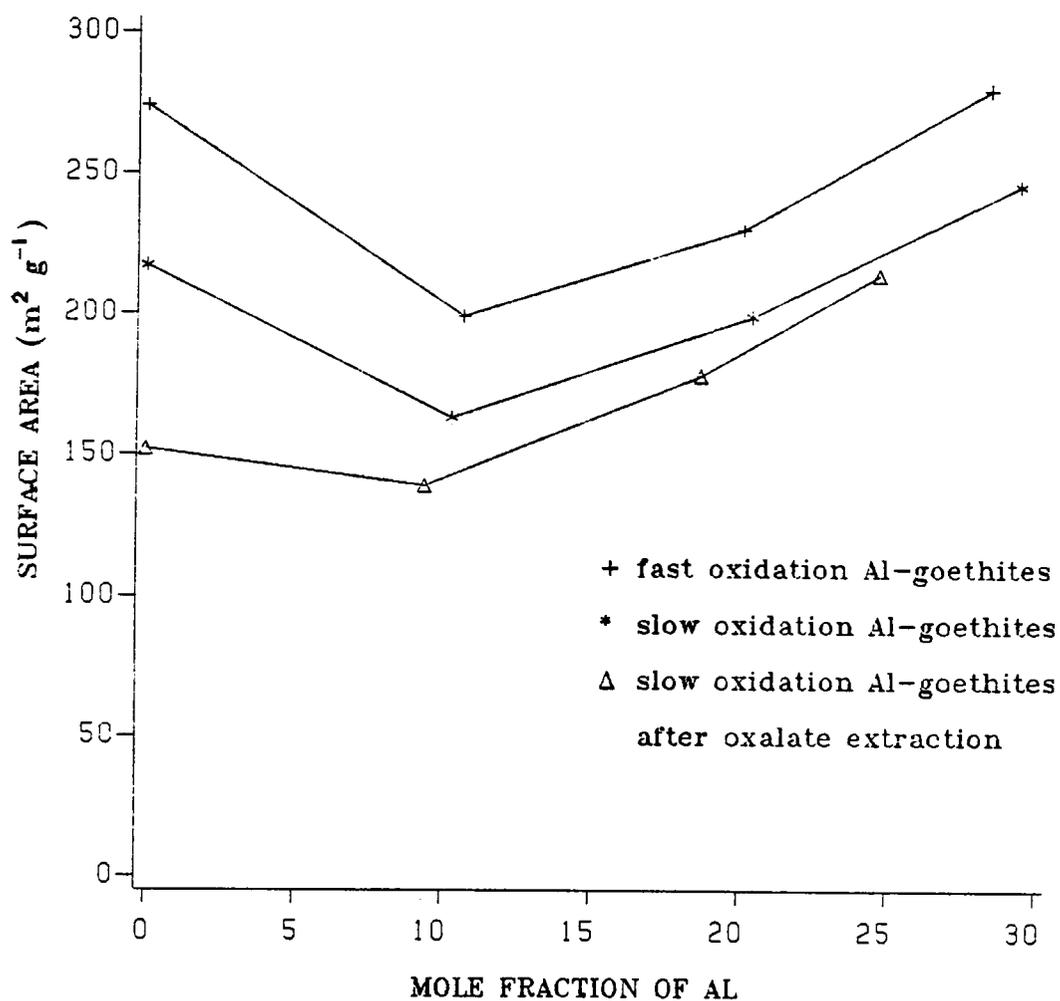


Figure 23: Plot of surface area versus Al mole fractions in Al-goethites.

substitution in the goethites (Al mole%=20 or 30) increased the surface area of the Al-goethites, probably due to decreased unit cell and particle size (Thielk, 1963; Jonas and Solymar, 1970; Schulze, 1982; Schulze and Schwertmann, 1984).

The nonsubstituted goethite showed a reddish yellow color (7.5YR 6/8). With increase of Al substitution, the color of the sample changed from yellow to red, and became darker and darker. The Munsell hue changed from 7.5YR for nonsubstituted goethite to 2.5YR for Al-goethite with 30% Al substitution, value from 6 to 3, and chroma from 8 to 6 (Table 16). The mole fraction of Al in the Al-goethites negatively correlated with the Munsell hue, value and chroma at the 0.01 probability level (Figure 24, 25, 26). A color change of synthetic hematite due to Al substitution has been reported by Barron and Torrent (1984). They found that the color of Al-substituted hematite was lighter than the non-substituted sample.

It is evident from the above discussion that soils containing similar amounts of goethite can show differences in color due, among other factors, to the degree of Al substitution in this mineral. A reddish soil may have goethite with Al substitution instead of hematite.

TABLE 16
Colors of the Al-goethites.

Sample	Color	Munsell Notations
GAOF	Reddish Yellow	7.50YR 6.0/8
GA10F	Yellowish Red	5.00YR 5.0/8
GA20F	Red	2.50YR 4.0/6
GA30F	Dark Red	2.50YR 3.0/6
GAOS	Reddish Yellow	7.50YR 6.0/8
GA10S	Yellowish Red	5.00YR 4.5/7
GA20S	Red	3.75YR 4.0/7
GA30S	Red	2.50YR 4.0/6

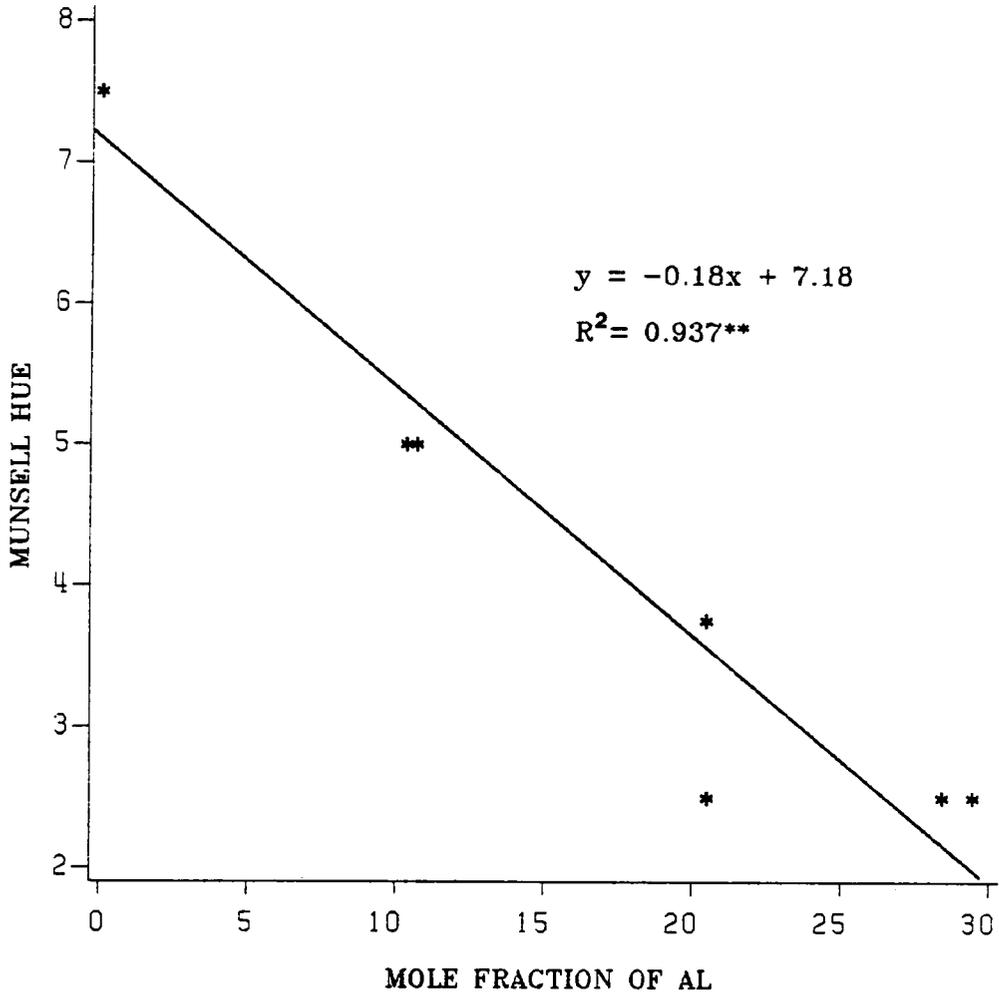


Figure 24: Plot of Munsell hue versus Al mole fractions of Al-goethites.

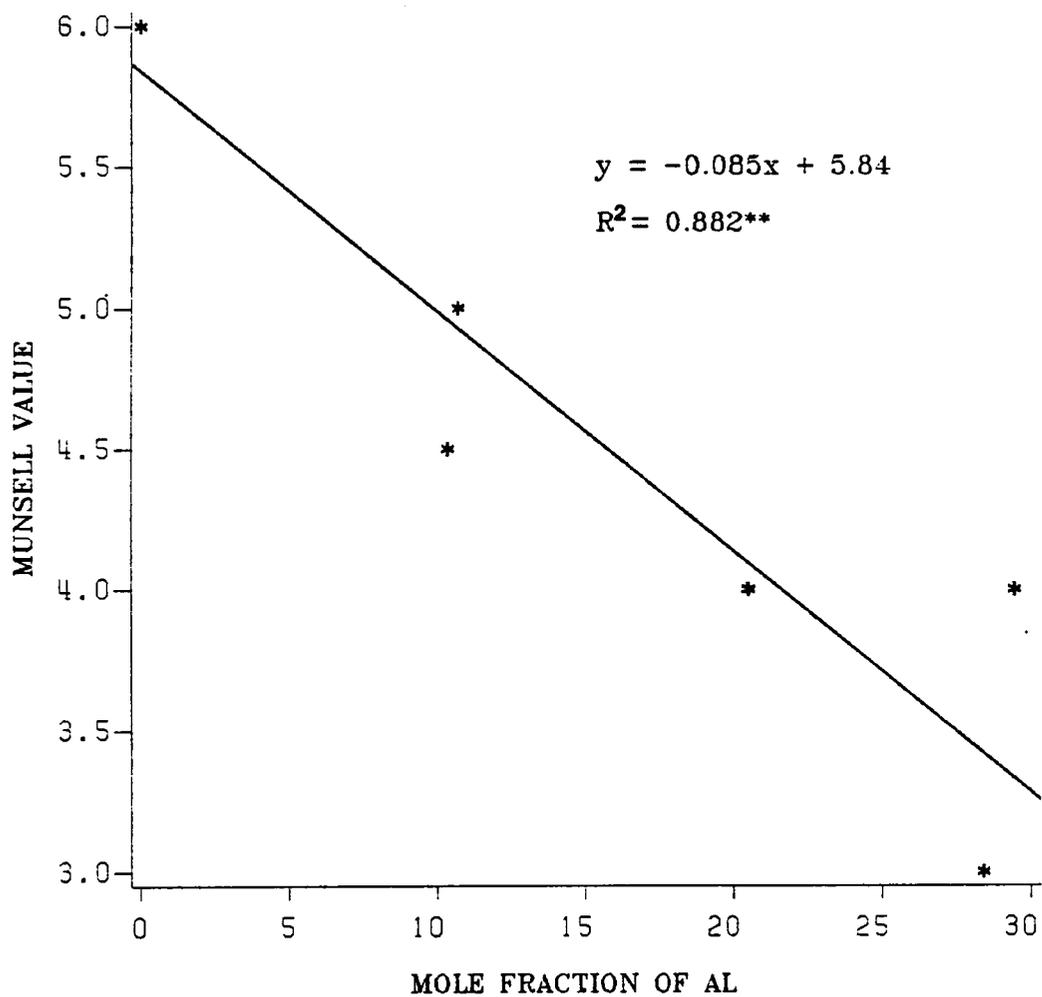


Figure 25: Plot of Munsell value versus Al mole fractions of Al-goethites.

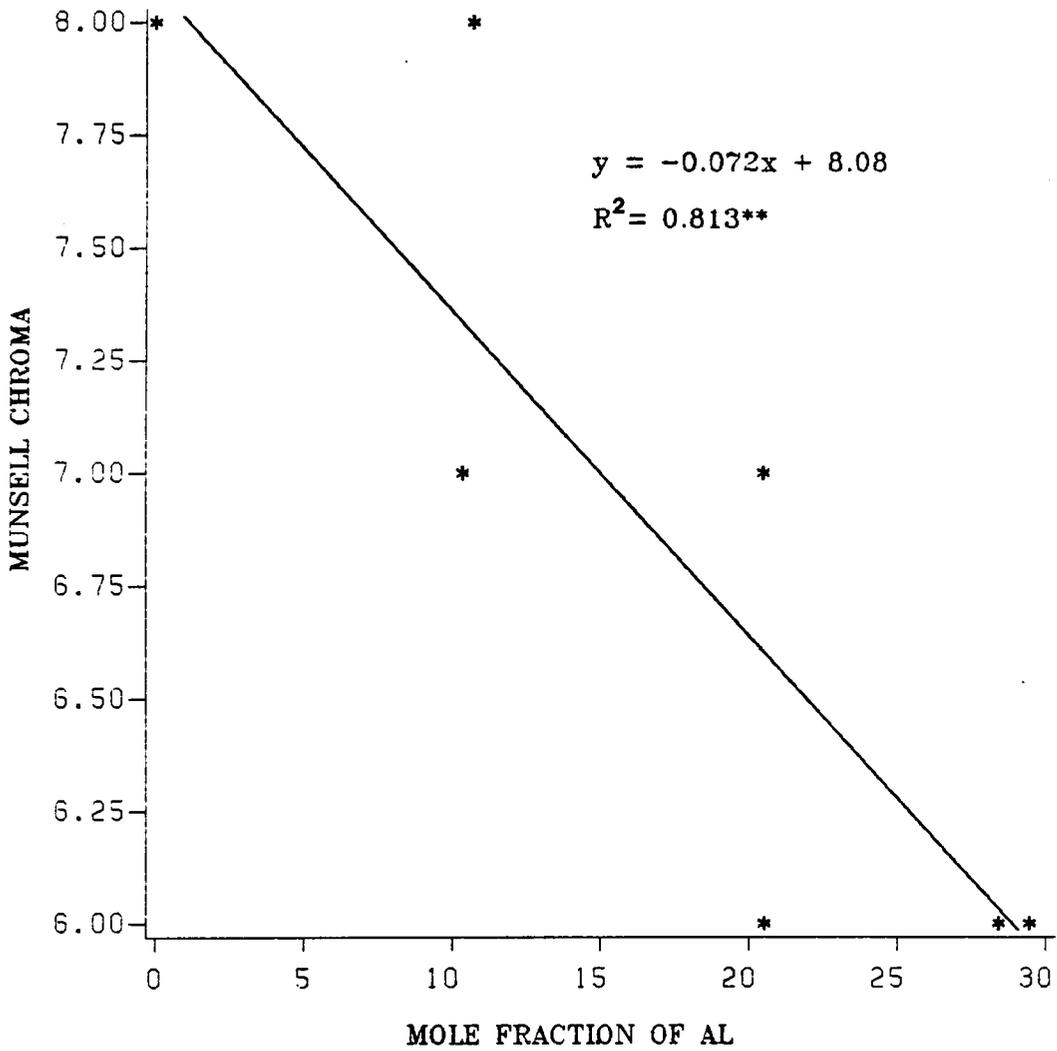


Figure 26: Plot of Munsell chroma versus Al mole fractions of Al-goethites.

5.4.2 Boron Adsorption on the Al-goethites

Maximum B adsorption on the Al-goethites was estimated by using the Langmuir equation (Table 15). Boron adsorption increased with an increase of the Al mole fraction in the products (Fig. 27,28, 29, Table 15). Because the B adsorption was calculated on unit surface area basis, it is apparent that Al substitution in goethite increased the B adsorption power of the surface. The noncrystalline Al hydroxide showed higher B adsorption power than the Al-goethites (Fig. 27, 28, Table 15). These were in agreement with the findings of Sims and Bingham (1968) who showed a higher affinity of hydroxy Al for B than hydroxy Fe material.

After oxalate extraction, the B adsorption on the residues of the slow oxidation samples decreased approximately 10 times as compared with B adsorption on the untreated samples (Table 15). There are two possible reasons for the tremendous decrease of B adsorption power of the Al-goethite after oxalate extraction. One is competition of the oxalate left in the system. After the oxalate extraction, the samples were washed with 0.02 M KCl solution 5 times. However, all of the oxalate may not have been washed free from the system and this oxalate could compete with the B on the surface.

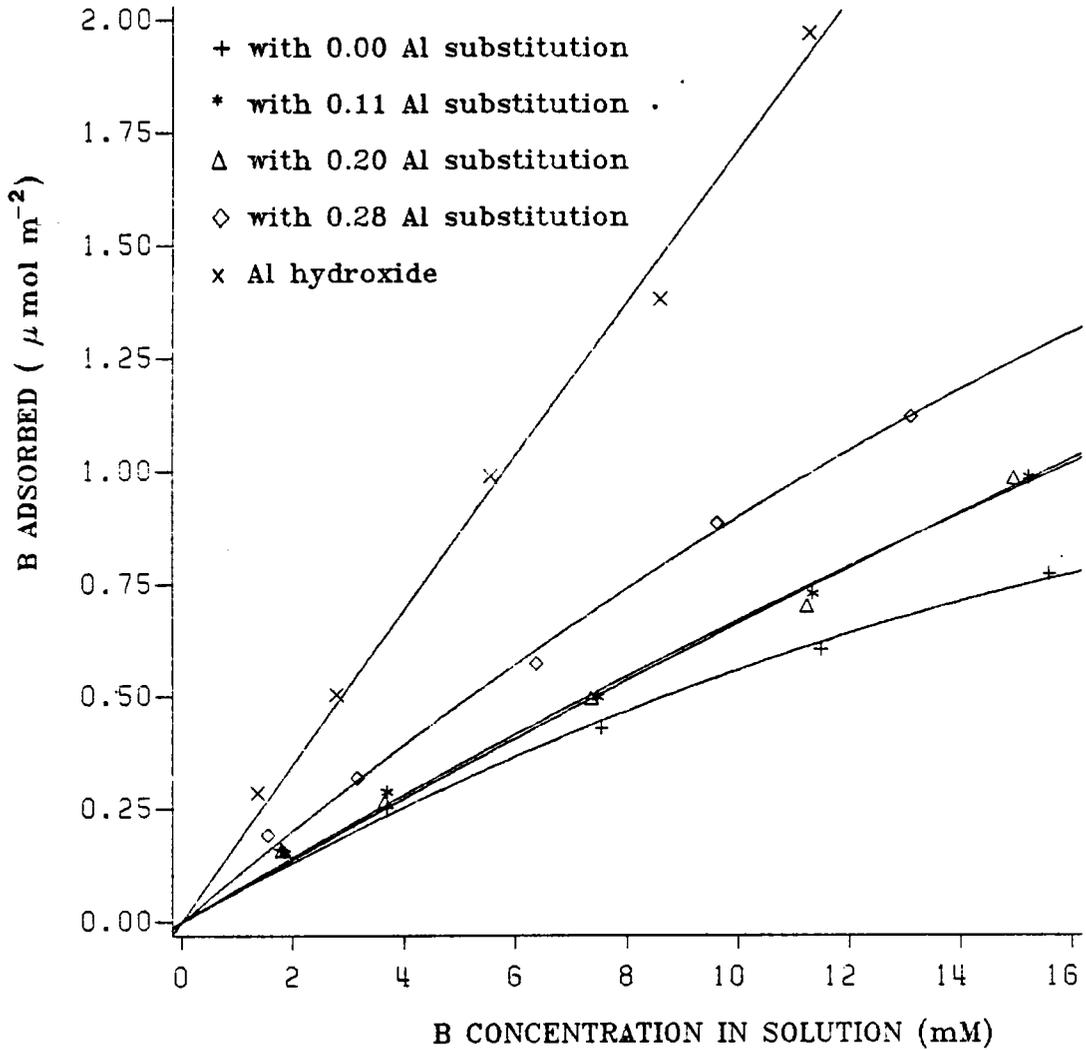


Figure 27: Boron adsorption by fast oxidation Al-goethites.

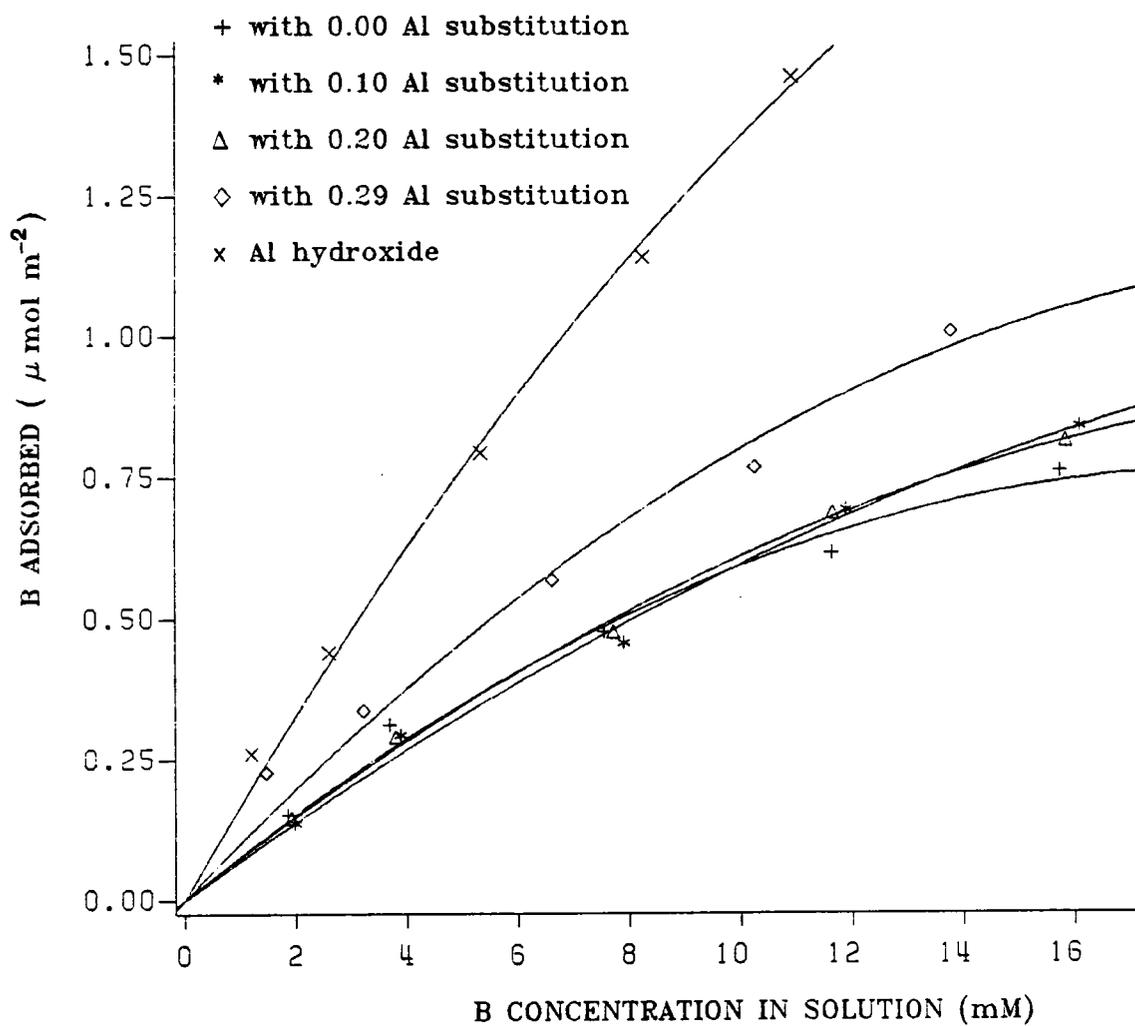


Figure 28: Boron adsorption by slow oxidation Al-goethites.

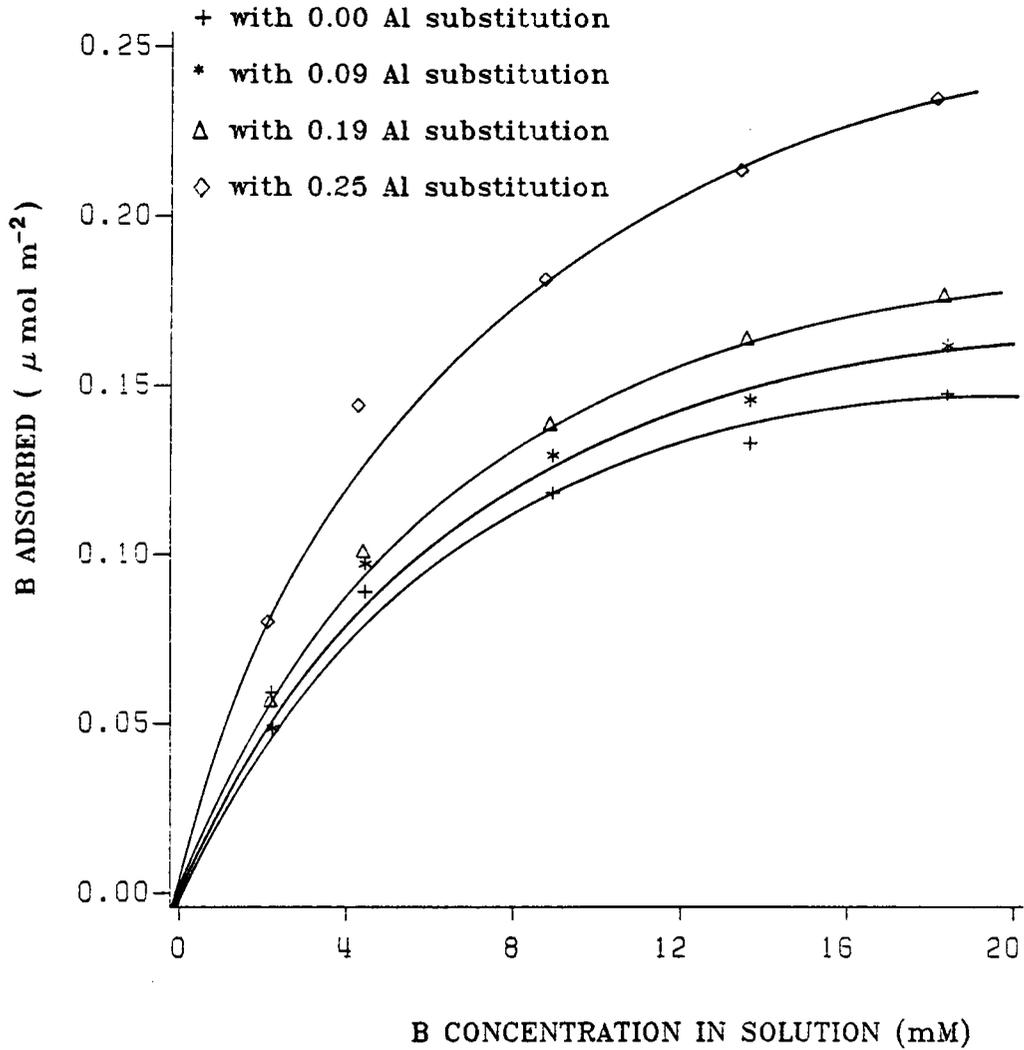


Figure 29: Boron adsorption by residues of slow oxidation Al-goethites after oxalate extraction.

The other possible reason is the removal of the fine crystal which has greater B adsorption capacity than the residue material. Further research is needed to answer this question.

Despite the unknown cause of the decrease of B adsorption power of the Al-goethite by the oxalate extraction, a correlation analysis was still performed to estimate the effect of Al substitution on B adsorption on a relative scale. A linear relationship was found between the maximum B adsorption and the mole fractions of Al in the slow oxidation Al-goethite after the oxalate extraction (Figure 30). It is evident that the Al substitution increases B adsorption, and the increase of B adsorption is a function of the mole fraction of Al in the Al-goethites. Sims and Bingham (1968) studied the formation of Al- and Fe-B complex using the mole ratio method and found that the retention of B by hydroxy Al was much greater than hydroxy Fe material. The Al incorporated into the goethite lattice may behaves differently than that in the hydroxy Al materials. However, our data did indicate an increase in B adsorption due to the Al substitution in the goethites.

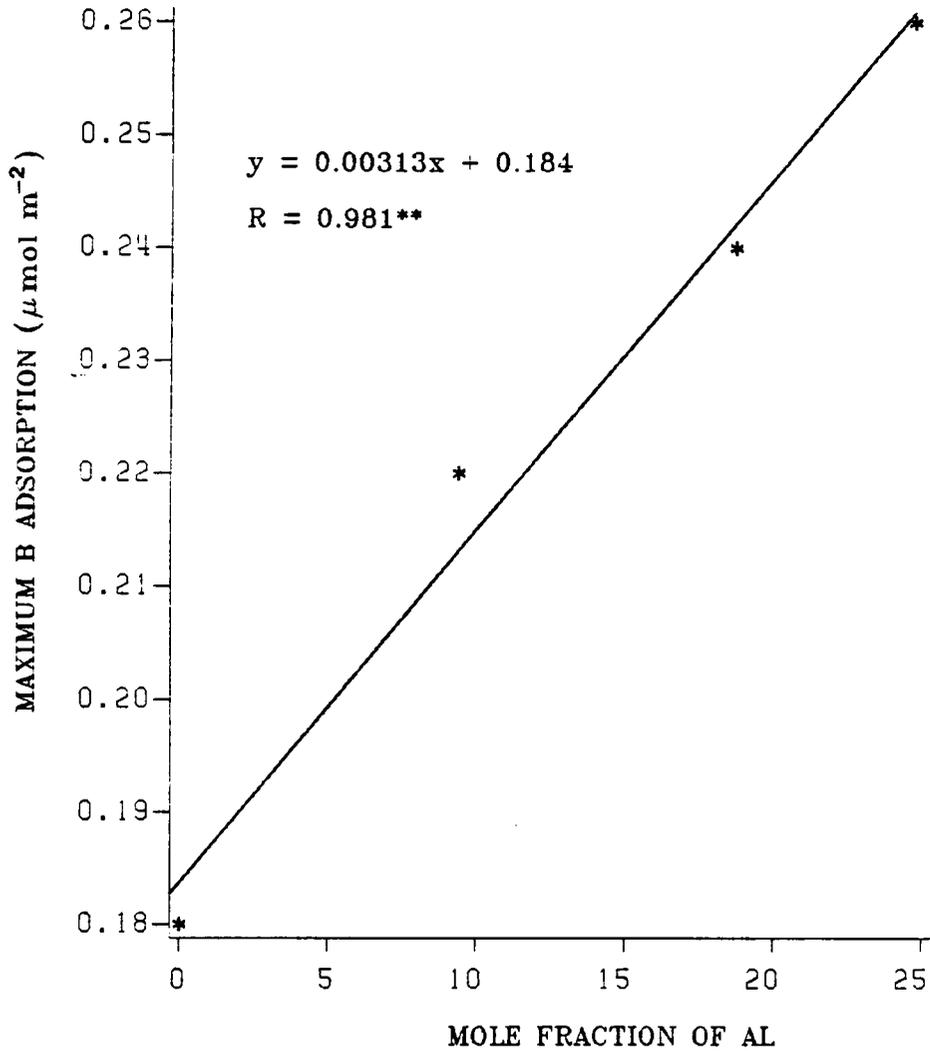


Figure 30: Plot of maximum B adsorption versus Al mole fractions in the residues of slow oxidation Al-goethites after oxalate extraction.

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Chapter VI

SUMMARY AND CONCLUSIONS

This study was conducted to ascertain the reactions of B in soil and hydroxy Al and Fe systems. During the investigation, basic information was obtained on the plant availability of native and applied B for 14 Virginia soils and on the specific reactions of B with the soils and Al and Fe minerals. The specific findings from this research are discussed below.

First, total B in the 14 Virginia soils under study ranged from 21.5 to 96.3 mg kg⁻¹. Distribution of the total B in different forms varied widely in the 14 Virginia soils. Only a small portion of the total B was in soil solution, in non-specifically or specifically adsorbed forms and in Mn minerals. These fractions of native B are readily available to plants. A large part of the total B was associated with non-crystalline and crystalline Al and Fe minerals or in soil layer silicates. These fractions of B contribute very little to B absorption by plants. Hot water soluble B, NH₄-acetate extractable B, mannitol exchangeable B and Mehlich III extractable B closely correlated with the tissue B concentration from native soil B. No B deficiency and yield response of corn plants to B application occurred on the 14

soils, although the HWS-B levels in some of the soils were below the suggested critical level of 0.1 mg kg^{-1} from literature. Further field research is necessary to calibrate the available B estimation procedures and to evaluate the critical levels for different crops.

Secondly, soil with high clay and Al- and Fe-oxide and hydroxide contents can adsorb much of the applied B in plant unavailable forms. In practice, if soils with high clay and Al- and Fe-oxide and hydroxide contents supply inadequate B, a greater amount of B fertilizer should be recommended in order to build up the available B levels as compared with sandy soils with low Al- and Fe-oxide and hydroxide contents. On the other hand, light textured soils have low B adsorption capacities and, therefore, intensive leaching of native B may result in B deficiency. The amount of B fertilizer required to correct B deficiency in these soils should be less than for soils with high clay and Al- and Fe-oxide and hydroxide contents.

Thirdly, B adsorption, either by soils or on gibbsite and goethite, is pH dependent and increases with an increase in pH. In practice, if a soil is over-limed, the increase in B adsorption by soil components will reduce the B availability to plants and, subsequently, a liming-induced B deficiency may occur.

Fourthly, B adsorption on both gibbsite and goethite is an exothermic process. It decreases with an increase in temperature. If this is true for B adsorption by all the soil components, more native B will be adsorbed in plant unavailable forms with a decrease of soil temperature. Therefore, an increase of plant availability of native soil B is expected with an increase in soil temperature. In early spring when the soil temperature is usually low, B fertilization for some spring crops, such as wheat and alfalfa, may be critical to obtain high yields.

Fifthly, Boric acid molecules in solution can be adsorbed on negatively charged surface of gibbsite and positively charged surface of goethite, while borate in solution can be adsorbed on negatively charged surfaces of gibbsite and goethite. The B adsorption on both gibbsite and goethite decreased the ZPC of the minerals. These findings indicate that B is specifically adsorbed on the surfaces.

Lastly, Al substitution affected particle size, crystallinity, surface area, color and B adsorption of the Al-goethites. Because many mineralogical properties change with Al substitution, it is not possible at this time to discuss the reason of the increase of B adsorption with Al substitution. In this research, B adsorption was calculated based on unit surface area to minimize, at least partially,

the influence of particle size and crystallinity. Therefore, the increase in B adsorption with Al substitution indicated an increase in affinity of the goethite surface for B adsorption. Further research on the effects of Al substitution on mineralogical and morphological properties of goethite and on B adsorption would add much insight into the knowledge of the adsorption mechanism of B in soils.

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