MECHANISMS OF BORON FIXATION IN SOME SOILS OF THE A. R. E.

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Boron had been shown to be an essential element for plant growth. Plant species vary in their requirements as well as tolerance to excess boron concentrations. Although boron toxicity is the major and widely spread problem frequently associated with salt-affected soils, boron deficiency is still reported in scattered areas. The occurrence of boron deficiency in many areas raised the question of a possible interaction between boron compounds in soils and soil constituents in such a way as to render boron unavailable to plants which was ascribed to the boron-fixing capacity of soil.

The problem of boron deficiency and the reactions of boron compounds with soil constituents received very little attention. Unfortunately, the limited work that has been done on boron reactions with soils and factors affecting boron retention presents a contradiction and the mechanism of boron fixation in soils remains to be investigated. To study these mechanisms and factors affecting boron sorption such as pH, effect of calcium, the specific effect of adsorbed cations, and drying and wetting, most of the work was done using soil systems. The complexity and varying characteristics of soils rendered the picture of boron fixation to be very contradictory. As to this contradiction and the lack of study of some other aspects of the problem, it is the object of this work to study the effect of these factors in relatively pure systems of clay minerals, pure suspensions of iron-and aluminum-hydroxides, silica gel, and humic acid. As these colloids were found to be the most active components of soil systems in relation to boron fixation. It was believed that a more detailed study with different clay minerals free from amorphous materials, saturated with different cations, and studied at different pH values, should provide a more complete picture of factors affecting boron fixation, and hence give a clue to the mechanisms involved. The infra-red spectra of boron treated and untreated samples of clays, amorphous oxides (iron- & Al- hydroxides and silica gel) and humic acid, was thought to help locating adsorption sites on these materials and to provide more conclusive evidence to the suggested mechanisms of boron retention.

2. REVIEW OF LITERATURE

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In the early twenties of this century, experimental evidence furnished by numerous workers showed that boron is an essential element for plant growth. Warington (1923) and Brenchley and Thornton (1925) proved boron to be an essential element for broad-bean plants. Sommer and Lipman (1962) in California, using highly refined techniques, showed that boron was a growth requirement for every kind of plant tested. However, it is well established now, that plant species vary in their requirement as well as in their tolerance to excess boron concentrations, as the high boron requirements of some plants may be toxic to others having very low boron requirements. It is also known that the range of boron concentrations in which most plant species can grow is very narrow.

Now, no doubt that the problem of boron nutrition is boron toxicity at one extreme and boron deficiency at the other. Although boron toxicity is the major and widely spread problem frequently associated with salt-affected soils, boron deficiency is still reported in scattered areas in laterites and podzols, also in widely separated areas as New Zealand, Europe, Colombia, and both Western and Northern United States.

Recent studies of the retention of boron by soils have indicated that movement of borate through the soil profile occurs by stepwise adsorption-desorption process similar to that occurs in chromatographic columns.

Eaton and Wilcox (1939); Reeve *et al.* (1944); Hatcher and Bower (1958), Biggar and Fireman (1960), and Singh (1964) found that the toxic levels of soluble boron may be removed from soils by leaching. However, excess boron in soils is not removed as ready by leaching as are excess chloride and sulfate salts. This phenomenon appears to be the result of an equilibrium that exists between dissolved and adsorbed boron in soils. Because of this equilibrium and because the amounts of adsorbed boron in soils are greater than the amounts of soluble boron present in their soil solutions, adsorbed boron is thought to act as a buffer that impedes the removal of toxic levels of soluble boron from soils with leaching.

The pH of the system was reported as the main factor controlling boron retention. Eaton and Wilcox (1939) and Eaton (1935) investigated boron fixation in four San Fernands Valley, California soils and reported that boron sorbed increased with increasing pH of the soil. Similar results were reported by Olson and Berger (1946). Their work on two different soils ..Carington silt loam (a prairie soil formed on calcareous glacial drift) and Spencer silt loam (an acid soil formed under forest).. shows that very little boron was fixed below pH 7.0. At pH values above 7.0, the quantity of boron fixed increased rapidly with the increase in pH up to values beyond 10.0. It is not clear from their article whether the pH values reported are the equilibrium pH or the initial pH measured before the addition of boron as boric acid. Drake _et al._ (1941) did some work on boron sorption using electrodialyzed colloids isolated from Miami soil. At 16 pH values ranging from 4.1 to 11.5 they were able to recover all the boron added at all the pH levels studied and reported that no boron was fixed by the clay fraction. They obtained similar results on humus extracted from Brookston silt loam. Midgley and Dunklee (1940) studied the injurious effect induced by overliming of podzol soils, which was possibly due to boron defficiency. They found that podzol soils fix very little boron in their acid state, but their capacity to fix boron increased by raising their pH through liming up to slightly beyond neutrality (pH 7.4). The amount of boron fixed decreased with any further pH increase. Hingston (1964) saturated the clay fraction extracted from soil samples in Australia, with calcium and suspended it in 0.01 M $CaCl_2$. He found that the amount of boron fixed by this clay is very sensitive to pH changes, particularly in the range (5.0-8.5) for samples which are dominantly illite, and (7.0-9.5) for samples which are dominantly bentonite; but boron sorbed decreased with further pH increase. His samples, however, were mixtures of more than two clay types and were not treated for iron or aluminum oxides removal. Okazaki and Chao (1968) indicated that the adsorption capacities of soils were related to soil pH, as boron adsorption increased with the increase of the pH values. They used in their work low humic latosol soils taken from pineapple plantations on the island of Oahu, Maui, Molokai, and Kauai, which represent dry and moderately humid areas of Hawaii, and composed of high percentage of clays, mainly kaolinite. Sims and Bingham (1968a) Metwally (1966) found that boron retention by hydroxy iron and aluminium materials was found to be pH dependent with maximum retention in the alkaline range.

The role of calcium in relation to boron sorption by soils is again uncertain and the results published on that are contradictory. In the work of Midgley and Dunkley (1940), their results show that overliming greatly increased boron retention by soils, especially acid ones, and this caused plant injuries as a result of boron deficiency. Olson (1947) and Metwally (1966) observed that the calcium was shown to increase boron sorption only at high pH. On the other hand, Parks (1944) obtained completely opposite results, when he found that lime added with boron, or before the addition of boron, to Dunkirk fine sandy loam soils drastically decreased boron sorption by this soils. Such result may be obtained if calcium is added to highly dispersed systems at neutral or slightly alkaline pH. Under these conditions there is a reduction of the surface area which decreases the boron sorption, and in the meantime the pH is not high enough to introduce the calcium effect. Olson (1947) found that the addition of $CaCl_2$ up to 30 meq. Ca/100g. of soil, in Carrington silt loam, had no effect on boron retention, but when calcium was added as $Ca(OH)_2$ or $CaCO_3$ to raise the pH, a considerable increase of boron fixation capacity existed. Parks and Shaw (1942) mixed solutions of Si, Al, Fe, Ca, Mg, and a suspension of electrodialyzed humus and bentonite, alone and in various combinations, with boric acid, then titrated to pH values varying form 5.0 to 9.0. In some cases precipitates were formed, and the only two systems in which boron precipitate was insoluble in boiling water were a synthetic Ca-alumino silicate and Ca-unsaturated bentonite. This work shows that Ca plays a major role in boron sorption by alumino-silicate systems at high pH values.

The specific effect of the exchangeable cations on the surface of the colloidal systems in relation to boron sorption by these systems has not been thoroughly investigated, however, it is claimed by Parks and White (1952) to overshadow the pH effect. They studied boron sorption by Georgia kaolinite, and Wyoming bentonite treated for the removal of iron and aluminum oxides and saturated with Ca, Mg, NH_4, K, and hydrogen. Both clay minerals showed almost the same capacity to fix boron when saturated with the same cation. In fact, it is hard to conclude from their work whether the boron sorption by clay minerals is largely controlled by the specific saturating cation or the pH of the clay suspension or both, since they made no study of the sorption by homoionic clays as a function of the pH. In this article the amount of boron reported to be fixed by clays is very low (1-5 Ugm B/g clay) and in fact it lies within the experimental error of the analytical methods of boron determination, if the fact is taken into consideration, that the boron fixed was calculated as the difference