

CHEMISTRY OF BORON IN SOILS-PLANTS-WATERS AND FACTORS AFFECTING ITS AVAILABILITY "A REVIEW" PART-I

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Introduction

Trace elements have long been recognized as "Essential Plant Nutrients". Many plant disorders have been recognized as trace element deficiencies. Recommendations have, therefore, been made to use minimal supplements of trace elements for all chemical fertilizers to minimize the fluctuations and availability of these elements to plants. Amongst the micro-nutrient elements, boron is perhaps the most important and plays a very important role in soil-plant relationship. It has a marked effect on crop growth, both from the standpoint of plant nutrition if it is deficient in soil, and of toxicity if it is present in excess. Boron is the 25th element in order of abundance on the earth's surface, and 12th in order of abundance in plants and animals (Robinson, 1953).

Boron was first used as a fertilizer in the mid sixteenth century (Berger, 1949; and Russel, 1957) when borax, under the name of "Tincal or Tincar" was shipped from Central Asia to Europe. It was during the First World War (1914), when use of American potash fertilizer containing considerable quantities of boron in form of borax caused much damage to crops, attention was first given to this element in plant nutrition. In the following year however, Maze (1915) in France, followed by Warrington (1923) at Rothamsted Experimental Station in England made an important contribution to our knowledge by suggesting that boron is an essential nutrient for normal vegetative growth.

It was also emphasized that boron is not only a growth stimulant but that in the absence of this element from mineral nutrient solutions, certain plant species develop characteristic deficiency symptoms and this results in abnormalities of normal plant growth. A number of studies on this subject has appeared since then, and supports the contention that green plants are unable to grow normally without boron.

Boron is needed by plants in smaller amounts than any other nutrient elements, except perhaps for chlorine and molybdenum (Jackson, 1958 and Singh, 1964). Investigation have shown that at low concentrations, boron is as necessary a food nutrient for normal development of many plant species (Eaton, 1935; Willis, 1935; Reeve and Shive 1944; Jackson, 1958). Concentrations greater than the desired amount are highly toxic to many plant species. Thus boron requirement of plants is confined to a narrow range of concentrations. To obtain optimum plant growth and a sustained high crop yield, it is thus essential to maintain regular boron availability within these narrow limits especially in young plantations.

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Relationship of boron with soil properties

Recognition of the practical importance of soil boron nutrition in relation to plants is one of the recent contribution to Soil Science. Application of boron is seen in the husbandry of many economic plant species. This has recently stimulated interest in boron nutrition which is likely to increase more deficiency and toxicity disorders and abnormalities. Considerable work has been done investigating boron starvation and several theories and possibilities have been proposed and valuable information obtained. There is abundant information concerning the occurrence of boron nutritional abnormalities traceable to soil characteristics. The present day knowledge of the exact behaviour of boron nutrients and factors affecting the release and the availability in soils to plants is still fragmentary and incomplete.

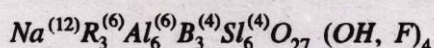
According to one estimate (Oram, 1961) the world extent of soil boron deficiency is close to six million hectares. The greatest areas of its occurrence in humid regions occur in sodic or overlimed soils (Midgley and Dunklee, 1939; Jones and Scarseth, 1944; Beeson, 1945 and Berger, 1949); soils low in organic matter and exchange capacity (Page and Coope, 1955); soils relatively high in free aluminum, iron and silicon (Parks and Shaw, 1941; Sims and Bingham, 1958; Hadas and Hagin, 1972); coarse textured soils low in clay content (Kubota, Berger and Truog, 1948; Baker and Cook, 1956) and soils that undergo prolonged dry period (Hobbs and Bertramson, 1949). The low levels of boron in the stoney and gravelly soils are probably associated with restricted soil exploration and low availability of boron during prolonged dry periods (Snowdon, 1971).

In humid areas, the available soil boron contents are usually less than one part per million (Berger and Truog, 1939), whereas Berger (1949) has reported water-soluble contents of humid region soils from 0.1 - 2.5 ppm. The mineral soils contain from 0.2 - 1.5 ppm and range up to 2.0 or more ppm for organic soils and down to 0.2 ppm in fairly sandy soils (Jackson, 1958). In regions of low rainfall, the boron content of soils is fairly high (Eaton, 1935; Russel, 1957; Berger, 1962). Boron in these soils probably exists largely as calcium and sodium borate, both of which are highly soluble (Berger, 1949). In these regions, the boron content of water is very high (1.0 - 3.00 ppm) and it cannot be safely used for irrigation purposes (Eaton, 1935; Russel, 1957 and Berger, 1962) as against 0.3 - 0.6 ppm in irrigation water on safe side. The soils of the semi-arid regions may fall in the same range as that of the humid regions (Jackson, 1958) but occasionally contain 10 - 40 ppm boron or more.

Source of boron in soils

Although boron is a component of about 56 minerals, in humid regions the principal source is the mineral Tourmaline (Berger and Truog, 1939). Tourmaline is a boro-aluminum silicate containing normally 10 - 11 % boron by weight (Deer, Wowie and

Zussman, 1966). It has a general formula;



where

12, 6, 6, 4, 4 represent the coordination numbers i.e. the number of other atoms at equidistant closest approach, and R represent various cations such as Al, Fe, Li, Mg, Mn etcetera (Deer, Howie and Zussman, 1966).

This mineral is highly insoluble, very hard, and resistant to weathering. It is considered to be one of the heavy detrital minerals. Tourmaline, although widespread, is a minor constituent of primary rocks (Richards, 1954). Boron also occurs in Crystalline schists, Gneiss, Clay slates, and is a common product of contact metamorphism of rocks of all types (Winchell and Winchell, 1909). Boron is also a constituent of Granite, Gabbros Meteorites and Argillaceous Sedimentary rocks (Goldschmit and Peters, 1932). Considerable amounts of unweathered tourmaline have been reported from the pyllite and micachist equivalent of the above sedimentary rocks. The boron content of igneous rocks is generally low, within the range 1-10 ppm boron (Rankama and Shahama, 1950; and Jackson 1958) while that of marine argillaceous sediments is usually high. 20-300 ppm boron (Rankama and Sahama, 1950). Snowden (1971) has likewise reported that *Pinus radiata* grown on soils derived from granite and volcanics commonly had boron contents less than 12 ppm and the trees suffered severely due to boron deficiency; while on sediments the boron content was usually greater than 16 ppm and the trees were much healthier.

Besides tourmaline, there are other primary boron minerals which however, are quite uncommon. This groups contain:

- Datolite - $2 CaO.B_2O_3.2 SiO_2. 2H_2O$, containing 3.1% B (Moldovan, Popovici and Chivu, 1969).
- Grandidieite - $2Na_2O_4.FeO.8 (Al, Fe, B)_2O_3.5SiO_2$, containing 1.0% B (Lacroix and Gramont, 1921).
- Kornerupine - $Mg_8 (Al, Fe, B) O_{12} (Si O_4)_7$; containing 0.8% B (Lacroix and Gramont, 1921).
- Sapphirine- $9MgO.10 (Al, Fe, B)_2 O_3.4SiO_2$; containing 0.2% B (Lacroix and Gramont, 1921).

The numerous watersoluble secondary boron minerals represent the most significant resources in arid regions. The most important are:

- Ashrite (Ashritic dolomite) $-2\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$; containing approximately 8% B (Moldovan, Popovici and Chivu, 1969).
- Bakerite and Borocite (Graham, 1957).
- Borax- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; containing 11.3% B (Muhr, 1940).
- Colemanite- $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$; a hydrated calcium borate containing 10% B (Russel, 1957).
- Howlite and Kernite- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$; containing 15% B (Winsor, 1950 and Graham, 1957).
- Milorganite containing 0.004% B (Muckenhirn, 1936).
- Resorite- $\text{Na}_2\text{B}_4\text{O}_7$ (anhydrous) containing 20% B (Mortvedt and Osborne, 1965).

Besides soil boron bearing minerals, boron is a constituent of practically all natural waters sources. The concentration varies from traces to several ppm B (from less than 0.10 to over 7 ppm Chapman and Pratt, 1961). Seawater is also a good source containing 4.5 ppm B (Jackson, 1958). Animal manure and plant debris when decomposed add a considerable amount of boron to the soil.

The weathering of rocks and minerals and its relationship to plant nutrition has been studied in many ways since the beginning of Soil Science. It is now evident that the acidity in the soils created by plant roots and by soil microbes is one of the major chemical reagents for the breakdown of minerals, converting them to plant nutrients. Humus colloids are the means of passing the hydrogen, accumulated from the roots, onto the minerals; and in turn passing the nutrient in the opposite direction from the mineral to clay surfaces and then to the plant root.

In addition to this phenomenon, the roots and soil microbes may secrete organic compounds with chelation properties which form stable complexes with multivalent cations, initially held in the mineral and pass these soluble molecular complexes of organo-metallic combination on to the plant (Graham, 1957). The removal of cations from minerals either by some colloidal system or by organic chelation results in the release of soluble anions which then become available to plants as nutrient ions. The soil nutrients in the form of exchangeable and water-soluble electrolytes may facilitate

germination and productive growth for a few years. However, if the soil is to continue its productivity over an extended period of time, it must have reserves of nutrients which commonly are contained in the rather stable, rock-derived minerals. It is these nutrients reservoirs that are the sustaining fertility of our major, constantly productive soils.

In the light of this evidence it seems plausible that boron may occur in large numbers of primary and secondary soil minerals with varying degrees of stability and solubility, release available nutrient boron, replenishing its supply to plants under normal geoclimatic conditions in the biotic system. If conditions favouring the availability of boron are good, the amount of boron released by the sources will probably be adequate for normal plant growth.

Much progress has been made in the control of soil nutrient boron. Regions of severe crop losses have been transformed into regions of maximum sustained crop yields by these considerations. Today we have many commercial boron fertilizers in single as well as in mixed form, both as slowly available and as readily available sources of nutrient boron.

The boron cycle in soils

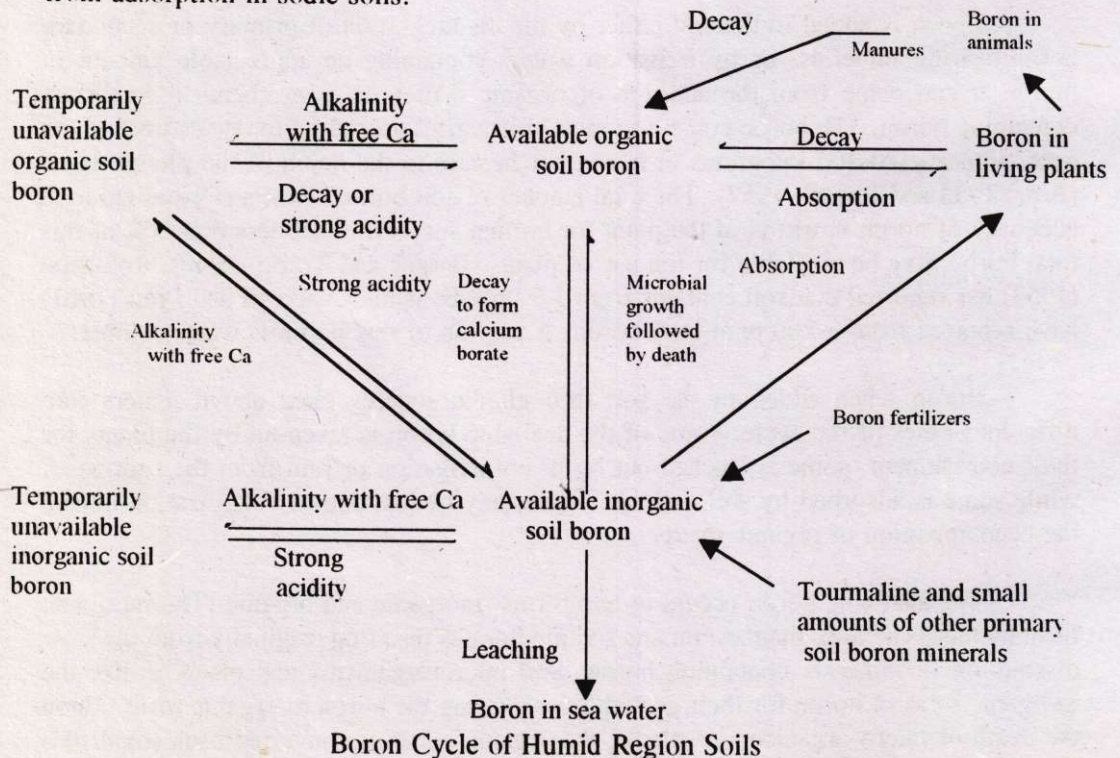
Boron is added to the soil either by the disintegration of primary or secondary boron-bearing minerals, or by irrigation waters containing an appreciable amount of boron. It can come from the addition of organic matter or from chemical fertilizers containing boron. The boron content in most soils varies according to one estimate from approximately 20-200 kilograms of boron per hectare to the depth of the plough layer (Bear, 1953 and Russel, 1957). The total amount of soil boron is not a reliable guide to adequacy of boron nutrition of the plant for normal survival, since less than 5% of this total boron may be available for the use of plants (Berger and Truog, 1940). Robinson (1953) has reported that soil contains from 3-9 ppm B, while Chapman and Pratt (1961) have reported from 3-200 ppm total boron. A portion of this boron is water soluble.

Boron when added to the soil through the sources cited above, enters into different phases of the cycle. Some of the available boron is taken-up by the plants for their nourishment, some is leached-out by heavy irrigation or rain from the root-zone, while some is adsorbed by soil colloids. Some may be lost due to volatilization during the decomposition of organic matter.

The available boron occurs in two forms, inorganic and organic. The inorganic form includes calcium, magnesium and sodium borates resulting originally from the slow dissolution of minerals containing boron. Soil micro-organisms and plants utilize the inorganic form of boron for their growth transforming the boron to organic form. Upon the death of micro-organisms or plants, the organic boron is converted back (oxidized)

to inorganic boron. Thus there is always equilibrium existing between these two temporarily unavailable forms. However, these are in equilibrium with available forms but often the tendency is for the reaction to shift towards the temporarily unavailable form. In acid soils, much of the boron remains in the inorganic form and is leached out. This causes acid sandy soils to be low in available boron. Generally in the humid region soils low in available boron are the light colored acid soils and alkaline sodic soils regardless of their organic matter content (Berger, 1949). In arid and semi-arid regions, because of the absence of leaching, quantities of inorganic borates occur, probably as sodium and calcium salts.

The amount of boron available for re-use, plus that made available through the continual weathering of minerals, is adequate for normal plant growth in some soils. The losses of available boron through crop removal, leaching, and reversion of the available boron to the unavailable form (adsorption or fixation); and volatilization losses coupled with greater boron requirements for higher crop yields result in an inadequate supply of nutrient boron for crop growth on many soils of the humid regions. Losses of boron through crop removal is unavoidable and must be replenished eventually by application of chemical fertilizers or manures. The most serious losses are leaching losses encountered in coarse textured and acid soils of the humid region, and the losses resulting from adsorption in sodic soils.



It has been observed that boron, when coming into contact with other minerals, forms a compound which is intractable, unless disturbed by plant roots or soil microbes able to create conditions leading to the decomposition of the mineral (Parks and White 1952; Graham, 1957). This process, called the "Mechanism of boron Adsorption or Fixation", plays an important role in soil boron nutrition. Boron is fixed more readily than it is leached out and then it accumulates or is fixed by soil colloids. The excess soil boron cannot be readily removed by leaching by low boron waters as is the case with excess amounts of other soluble salts present in the soil (Hatcher and Bower, 1958). The importance of the mechanism of boron fixation lies in the fact that plants tend to obtain their boron nutrients from the soil solution and are not directly influenced by the presence of adsorbed or fixed boron in the soil (Biggar and Fireman, 1960). Equilibrium between boron in the soil solution and fixed boron partly determines the instantaneous supply of nutrient boron to plants. Furthermore, the rate at which boron in soil solutions is replenished by desorption or released from soil, determines the effectiveness of a soil for controlling the concentration of available boron (Biggar and Fireman, 1960).

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