

**AVAILABILITY INDICES OF BORON IN
MAJOR SOIL GROUPS OF KERALA**

By

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THESIS

**Submitted in partial fulfilment of the
requirement for the degree of**

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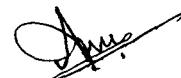
2011

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I, hereby declare that this thesis entitled “**Availability indices of boron in major soil groups of Kerala**” is a bona-fide record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award to me of any degree, diploma, fellowship or other similar title, of any other University or society.

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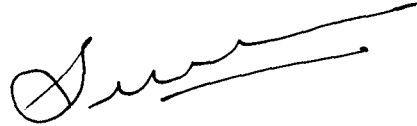


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CERTIFICATE

Certified that this thesis, entitled “**Availability indices of boron in major soil groups of Kerala**” is a record of research work done independently by **Ms. Anu George** under my guidance and supervision and that it has not previously formed the basis for the award of any degree, diploma, fellowship or associateship to her.



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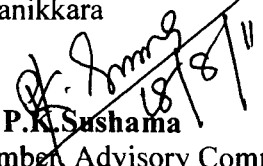
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Anu George 

*Dedicated to my dearest
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Introduction

1. Introduction

Boron is essential in plants for cell wall formation, cell division and extension. Deficiency of boron causes changes in chemical composition and structure of cell wall, accumulation of toxic phenols, inhibition of lignin synthesis and decrease in production of indole acetic acid (IAA). The decrease in IAA is responsible for induction of Ca deficiency. Such typical B-Ca deficiency syndrome is most often observed in banana in soils of Kerala. Boron is also essential for pollen tube growth which affects seed/fruit set and hence yield. It is also reported to impart drought tolerance. Regular boric acid sprays help in mitigating harmful effect of drought.

The availability of boron in soil is affected considerably by soil pH. At low pH most of the boron compounds are soluble and thus boron remains available as boric acid. But in acid soils, especially in coarse textured soils, where most of the boron forms become soluble, it is expected to be lost by leaching under the influence of high rainfall. Thus there is all probability of loss of boron and its deficiency in Kerala soils which are developed under typical tropical humid climate. These soils are highly acidic and subjected to rain induced leaching of soluble soil boron. In Kerala, though typical B deficiency symptoms are being observed in coconut, banana, nutmeg etc., detailed soil fertility investigations with respect to B, is limited. Boron, one of the essential micronutrients, is reported to be deficient in soils from many parts of the country. The deficiency is most common in Bihar, West Bengal, Orissa, Assam, Jharkand, Gujarat, Karnataka, Madhya Pradesh, Chattisgarh and Uttar Pradesh (Singh, 2004).

Boron exists and absorbed as boric acid (H_3BO_3) in highly acidic soils. As the pH increases, the ions $H_2BO_3^-$ dominates. As the pH becomes alkaline BO_3^- will be the dominant ion. In acid soils application of lime causes temporary locking up of boron in the freshly precipitated aluminium and iron hydrous oxides inducing boron deficiency. B also occurs complexed with organic matter.

Rice crop is reported to be affected by boron deficiency especially at fertilization as well as at the grain filling stages resulting in chaffy grains (Garg *et al.*, 1979).

Management of boron fertility in Kerala soils becomes pertinent under the above circumstances. For judicious management, a clear understanding of B dynamics in these soils is absolutely essential. The factors influencing boron availability, influence of different soil parameters on retention and supply of boron, the different forms of boron contributing to plant available pool etc. are to be studied in detail. Since no such investigations with respect to the above aspects of boron in Kerala soils, have been done so far, the present study was under taken with the following objectives:

1. To characterize major soil groups of Kerala with respect to their boron supplying power.
2. To study the adsorption characteristics of B in these soils.
3. To quantify the major fractions contributing to B fertility.

Review of literature

2. REVIEW OF LITERATURE

Boron is one of the essential elements for plant growth and development and its deficiency is known to reduce quantity and quality of agricultural products (Gupta, 1993). The element is distributed in various soil components including soil solution, organic matter and mineral fractions. It is one of the seven recognized essential micronutrients required for the normal growth of most plants. Among the known essential micronutrients, B deficiency in plants is reported to be the most wide spread.

2.1. Boron availability in soil

Phillipson (1953) reported the B solubility data, which were used to represent measured B levels for a large number of soils. Berger and Pratt (1963) reported that the total B content of most soils varies from 20-200 ppm. The adsorption of B on oxides of Fe and Al is believed to be an important mechanism governing B solubility in soils and clays (Sims and Bingham, 1968). Bingham *et al.* (1971) studied B deficiency in soils rich in Al oxides. B can be effectively leached from soil, although the rate of removal is much slower for B than for non-reacting elements (Bingham *et al.*, 1972). Gupta (1978) revealed that B deficiency in susceptible crops is a widespread problem in many countries and he also reported the various factors that affect B concentrations in soil solutions.

Bingham (1982) came into a conclusion that hot water extractable B can be regarded as a suitable index of plant available B. Keren & Bingham (1985) reported that boron is an essential element for normal plant growth but the range between B concentrations in soil solution causing deficiency or toxicity symptoms in plants is relatively narrow. They commended that B is readily adsorbed by soils and adsorbed B being unavailable to plants is considered not to be toxic. Also, maintaining B in the soil solution is important for plant nutrition and it is controlled by the pools of B in other soil fractions and their equilibration with the soil solutions. It was revealed that

soil properties that affect B adsorption were pH, surface area and content of clay, organic matter and oxy hydroxides.

Boron is unique among the essential mineral nutrients because it is the only element that is normally present in soil solution as a non-ionized molecule over the pH range suitable for plant growth (Oertli and Grgurevic, 1975). According to them, boric acid is the form of B that plant roots absorb most efficiently. Because of its non-ionic nature, once B is released from soil minerals it can be leached from the soil fairly rapidly and this explains why soils in high rainfall areas are often deficient in boron (Marschner, 1995). It was reported that soil B deficiency causes decline in crop quality and yields in >70 countries (Shorrocks, 1997). In general, the symptoms of B deficiency first appear in the growing regions of plants, and progress to the cessation of root elongation, reduced leaf expansion, and a loss of fertility (Dell and Huang, 1997; Marschner, 1995).

In crop plants, the requirement for B is often higher in the reproductive stage than in the vegetative stage (Dell and Huang, 1997). During the reproductive stage, B deficiency damages flower development, fertilization and fruit growth. Boron deficiency decreases seed yields in wheat, even in the absence of observable symptoms in the vegetative growth. The amount of boron in most soils is usually low to meet the crop requirements when modern agro-techniques adopted with the use of high analysis chemical fertilizers (Das and Saha 1999).

2.1.1. Factors influencing boron availability in soil

Jin *et al.* (1987) reported that a variety of factors such as pH, macronutrients, methods of application, soil texture, soil organic matter, stage of plant growth and plant part sampled, environmental factors, plant genotypes may change the content of extractable B, and transformations among different soil B fractions.

Soil pH

Gupta (1972) and Bennett and Mathias (1973) reported that soil pH is one of the most important factors affecting the availability of B in soil and plants. Generally B becomes less available to plants with increasing soil pH. . The content of water soluble B in soils tends to increase with soil pH, but not always in a consistent manner, probably because B adsorption by soil components also increases with the increase of soil pH, and reaches a maximum in the alkaline pH range. The availability of B to plants decreases sharply at higher pH levels, but the relationship between soil pH and plant B at soil pH values below 6.5 does not show a definite trend (Gupta, 1968). Eck and Campbell (1962) found that liming decreased B uptake when soil B reserves were high. They attributed this effect to high Ca content. Robertson and Loughman (1975) found that soil test levels of B in a calcareous soil decreased rapidly after B application. Lehto and Malkonen (1994) reported that liming soils may result in a significant decrease of B uptake presumably because of increased B sorption.

Macronutrients and sulphur

Nitrogen is of utmost importance in affecting B uptake by plants(Chapman and Vanselow,1955).It is found that large applications of N to the growing medium result in decreased uptake of B by crops. It is also reported that application of N is helpful in alleviating B toxicity on soils low in available N content (Gupta *et al.*, 1976). They also reported that high phosphorus increased the severity of B deficiency in tobacco. Tanaka (1967) speculated that there may be a slight effect of sulphate ion on the accumulation of B in plant tissues.

Methods of application

Two principal methods of applying B are by adding it directly to the soil or by foliar spraying. Soil applications of B made alone or with mixed fertilizers are

common, and most data reported on the B uptake have been obtained with fertilizers containing B added through broadcasting or in bands. Touchton and Boswell (1975) and Peterson and MacGregor (1966) on corn indicated that band-or foliar-applied B resulted in greater B uptake in plants than B applied by broadcast. Early foliar spray application result in greater absorption of B than those applied at later stages of growth (Gupta and Cutcliffe, 1978). Mortvedt *et al.* (1991) stated that early-morning applications of foliar-applied nutrients may result in increased absorption, as the relative humidity is high, the stomata are open, and photosynthesis is taking place.

Soil texture

Soil texture is an important factor affecting the availability of B (Wear and Patterson, 1962). Gupta (1968) in a study on soils from eastern Canada, found that greater quantities of hot water soluble B were found in the fine textured soils than in the coarse textured soils. The highest percentage of total B in the hot water soluble form occurred in the fine textured soils is attributed to the fact that some of boron in soils is adsorbed to clay particles. The observed relationship between B and soil texture could be attributed to the fact that some of the B in the soil is adsorbed to clay particles. The lower amounts of B in sandy soils are likely associated with higher leaching of B, which would also explain the lower percentage of total B that occurred in hot water soluble form in these soils.

Soil organic matter

Organic matter is one of the main sources of B in acid soils, as relatively little B adsorption on the mineral fraction occurs at low pH levels (Okazaki and Chao, 1968). The boron in soil has been found to be positively related to the organic matter content of the soil (Gupta, 1968). Addition of material rich in organic matter such as compost resulted in large concentrations of B in plant tissues and in phytotoxicity (Purves and Mackenzie, 1973). Berger and Pratt (1963) stated that a large part of the

total B in soil is held in the organic matter in tightly bound compounds that have been formed in the growing plants themselves. They also reported that B in organic matter is largely released in available form through the action of microbes. The significant interaction between organic matter and pH obtained by Miljkovic *et al.* (1966) indicates that the increase in B associated with an increase in pH is greater in soils with high, rather than low, organic matter content.

Stage of plant growth and plant part sampled

The part of the leaf, its position in the plant, the plant's age, and the plant part are some of the factors that affect the B composition of plants. The highest values of B occurred in the older leaves, while the lowest B content occurred in the fibrous and storage roots (Vlamiš and Ulrich, 1971). The boron concentration of corn leaves increased with age in seedling leaves, but decreased slightly in leaves at higher positions (Clark, 1975). Gupta and Cutcliffe (1978) reported that B levels in leaf tissue of cole crops were generally lower late in the growing season than they were in the early season.

Environmental factors

Intensity of light is one of the chief environmental factors affecting the availability of nutrients to plants. In an experiment on barley, Gupta *et al.* (1976) found that moisture had a significant effect on B uptake when B was applied to the soil.

Plant genotypes

Gorsline *et al.* (1965) observed that corn hybrids exhibited genetic variability related to B uptake and leaf concentration.

2.2. Dynamics of B in soil

2.2.1. Boron fractions in soil

Sequential fractionation procedure for separate extraction of soil B fractions was developed by Jin *et al.* (1987). They reported that the various fractions of B includes, nonspecifically adsorbed plus water soluble B (NSA-B), specifically adsorbed B (SPA-B), B occluded in Mn oxyhydroxide (MOH-B), B occluded in amorphous Fe and Al oxides (AMO-B), B occluded in crystalline Fe and Al oxides (CRO-B), and residual B (RES-B). They also reported that among the B fractions, NSA-B and SPA-B fractions may be most available to plants, and B fractions occluded in Al and Fe oxyhydroxides are relatively unavailable forms. It was also noted that the SPA-B fraction, which may be specifically adsorbed onto clay surfaces or associated with organic matter in soil showed the similar distribution with NSA-B fraction. Tsalidas *et al.* (1994) commended that boron is found in soils under various forms, which have a different availability to plant, such as nonspecifically and specifically adsorbed, occluded in Mn oxyhydroxides, and amorphous and crystalline Fe and Al oxides. They also reported that a variety of factors such as pH, organic matter, clay minerals, Fe & Al oxides, carbonates, and tillage management may change the content of extractable B and transformations among different soil B fractions.

Hot water extractable B has been regarded as a suitable index of plant available B (Bingham, 1982). But in some studies, levels of hot water extractable B have not been correlated with plant response (Sims and Johnson, 1991), suggesting that a better understanding is needed of the pools of soil be accessed by common soil B tests and their relationship to plant B uptake (Bell, 1997). Moreover, the available forms of soil boron vary with plant species (Tsadilas *et al.*, 1994). Jin (1987) found that the B concentration in corn tissue correlated positively with not only water soluble B, but also nonspecifically adsorbed B, specifically adsorbed B, and Mn-

oxyhydroxide occluded B. Tsalidas *et al.* (1994) showed that B content in olive tree leaves was well correlated with amorphous Fe-Al oxyhydroxide-occluded B, specifically adsorbed B and Mn-oxyhydroxide-occluded B besides water soluble B.

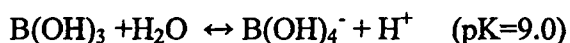
87.4 to 99.7% of soil B was in the residual fraction (RES-B), which generally did not relate well to the plant available B (Jin *et al.*, 1987 and Tsalidas *et al.*, 1994). The NSA-B fraction is mainly in solution or weakly adsorbed by soil particle, and is believed to be the most readily available fraction of B for plant uptake (Keren and Bingham, 1985). The SPA-B fraction may be specifically adsorbed on to clay surfaces or associated with OM in soil (Jin *et al.*, 1987). The $\text{NH}_2\text{-OH.HCl}$ extractable B fraction (MOH-B) may be mainly fixed with Mn oxyhydroxides, which are relatively easily dissolved with the release of occluded element, including possibly B (Chao, 1982). Several researchers have reported that Mn could accumulate in the surface horizon and was associated with the OM (Ellis *et al.*, 1982; Zhang *et al.*, 1997). Therefore, the release of OM bound with Mn by $\text{NH}_2\text{-OH.HCl}$ probably resulted in the MOH-B fraction being over estimated because of the release of B adsorbed by and incorporated in the OM (Keren and Bingham, 1985; Yermiyahu *et al.*, 1988).

Hou *et al.* (1996) developed a chemical fractionation scheme for soil B in which $\text{HNO}_3\text{-H}_2\text{O}_2$ was used to extract the organically bound B. However, this fraction was not significantly related to the amount of humic acid in the synthetic soil. It remains to be demonstrated that the Mn- reducible and organically bound B fractions can be clearly distinguished and that such a distinction is important for predicting plant response to soil B. Organic matter adsorbs B (Goldberg, 1997) and humus extracted from soils contains B (Parks and White, 1952). Hou *et al.* (1996) found that up to 23% of soil B was extracted by $\text{HNO}_3\text{-H}_2\text{O}_2$, and was therefore presumed to be organically bound. Marzadori *et al.* (1991) found that treating soils to remove OM increased B sorption by the soil. The fractionation procedure of Hou *et al.* (1996) may turn out to be more applicable than that of Jin *et al.* (1987) which does

not specifically extract an organically bound B fraction. Jin *et al.* (1987) developed a separate extraction scheme to determine the distribution of B between different fractions in soils. Hou *et al.* (1996) modified this scheme and developed a sequential fractionation method for partitioning total soil B among different distinct pools. The transformations among the forms (NSA-B, SPA-B, occluded in Mn oxyhydroxides, and amorphous and crystalline Fe and Al oxides) may be affected by a variety of factors such as pH, organic matter, clay minerals, and Fe and Al oxides was studied by Xu *et al.* (2001).

2.2.2. Reactions of boron in soils

Young soils and marine sediments are generally rich in B may also accumulate in alkaline soils even to levels which are toxic to plants. Highly weathered soils in humid areas are often absolutely low in B and crops on these soils may suffer from B deficiency (Ellis *et al.*, 1982). On such sites B can be easily leached out of the root zone. The soluble B in soils is mainly present in the form of boric acid $B(OH)_3$ or as $B(OH)_4^-$. The later anion is formed under alkaline pH conditions. Since boric acid is a Lewis acid, the anion is formed according to the following reaction.



The anion is adsorbed by Al/Fe oxides and clay minerals and the adsorption is the stronger the higher the soil pH (Goldberg and Forster, 1991). It is for this reason that B deficiency in crops frequently occurs on clay soils high in pH. On sandy soils a substantial portion of B is bound as ester to soil organic matter (Goldberg and Glaubig, 1986). Data on boron concentrations in sediments have been widely used as paleosalinity indicators, and several studies have been directed towards understanding adsorption and fixation reactions of this element on clay minerals (Harder, 1961; Couch and Grim, 1968; Jasmund and Lindner, 1972).

Boron is also one of the essential micronutrients for optimum plant growth, and the limits between essentiality and toxicity are rather narrow. Therefore, many investigations have focused on the adsorption of boron on clay minerals in competition with other ions (Hingston, 1964; Sims and Bingham, 1967; Singh, 1971; Keren and Mezuman, 1981; Keren and O'Connor, 1982). Several factors are known to influence boron adsorption reactions, including pH, initial boron concentration in solution, ionic strength, temperature, and presence of other metals and ligands, and the type of clay mineral surfaces. Although the adsorption of boron has been shown to differ with the form of the exchangeable cation, this effect has been attributed by some to the influence of the exchangeable cation on the thickness of the diffuse double layer and, thus, the accessibility of boron to potential adsorption sites (Keren and Gast, 1981; Keren and O'Connor, 1982). Reardon (1976) established that borate ions form soluble complexes with alkali and alkaline earth cations. Thus, the formation of borate complexes in solution may affect the adsorption of this element on mineral surfaces.

2.2.3. Relation between B in soil and plant uptake

There exists equilibrium between adsorbed B and soil solution B with most of the B being adsorbed. This distribution of boron between the soluble and adsorbed forms depends primarily upon the relation between total B, number of adsorption sites per unit weight of soil, and soil moisture content. Maas (1984) assumed that the principal factor controlling the response of plants was the concentration of boron in the solution bathing the root system, i.e., that the soil solution B which is available to plants irrespective of soil properties. This is based upon the findings of those who compared the availability of adsorbed and soluble boron (Ryans *et al.*, 1977; Bingham *et al.*, 1972).

2.2.4. Dynamics of B release from soil constituents

Leaching experiments (Bingham *et al.*, 1972) showed that a large fraction of soil B can be removed by percolating waters but that the remainder persists even after large amounts of water have been applied. Boron can be effectively leached from soil although the rate of removal is much slower for B than for non-reacting elements.

2.3. Q-I relations of B in soil

Boron present in soil solution and weakly adsorbed by soil components can be considered as a parameter of intensity. B adsorbed specifically on clay surfaces or associated with organic matter represents the quantity factor of the B supplying power of soils (Jin *et al.*, 1987).

Couch and Grim (1968) reported that a two step B retention mechanism where surface adsorption followed by a slow diffusion of B into the crystal lattice of clay mineral. The lack of reversibility of B adsorption/desorption reactions may be due to B diffusion into or from the clay mineral (Sharma *et al.*, 1989).

The B concentration in the soil solution is generally controlled by B adsorption reactions, as the amount of water soluble B becomes available for plant uptake. Plants respond only to the B activity in soil solution. B adsorbed by the soil surfaces is not perceived as toxic by plants (Keren and Gast, 1983).

2.3.1. B adsorption-desorption by different soil constituents

A variety of soil properties have been identified affecting the behavior of B in soils. Clay mineral types (Hingston, 1964; Keren and Mezuman, 1981), clay content and specific surface area (Biggar and Fireman, 1960), sesquioxides (Hatcher and Bower, 1967), organic matter content (Berger, 1947), soil pH (Keren and Talpaz, 1984), and soil salinity (Couch and Grim, 1968) have been reported to influence the B distribution between the liquid and the solid phases in soil. Clay content, organic carbon content, cation exchange capacity, specific surface, and electrical conductivity

of the saturation extract were significantly correlated with the adsorbed B (Elrashidi and O'Connor, 1982). They found that two types of B desorption reactions were observed. In the first type the adsorption was reversible, whereas in the 2nd type, desorption points deviated from the corresponding adsorption isotherm. They have also found that the tendency for desorption to exhibit hysteresis is not significantly correlated to any of the measured soil properties.

B adsorption by clay minerals

Boron can be specifically adsorbed by different clay minerals which vary in their adsorption capabilities (Keren and Mezuman, 1981). All the B adsorption by illite is much greater than by montmorillonite, although the total surface area of it is much greater than that of illite (McKercher, 1959). Boron adsorption is affected significantly by the particle size of the clay mineral. Boron adsorption (per clay mass) increases with decreasing clay particle size (Keren and Talpaz, 1984).

B adsorption by hydroxides of Al, Fe and Mg

Hydroxyoxides of Al, Fe, and Mg adsorbed large amounts of B (Keren and Gast, 1983). Ageing the precipitates tended to reduce the amounts of B adsorbed, with this effect diminishing beyond 12 hours (McPhail *et al.*, 1972). B adsorption by hydroxyl-Al when montmorillonite is present depends on the nature and extent of the interaction between hydroxyl-Al and the clay surface. The higher the proportion of hydroxyl-Al that exist as interlayer, the lower the contribution of the hydroxyl-Al to B adsorption. However, when the hydroxyl-Al exist in suspension separate from the clay the amount of B adsorbed by the clay and hydroxyl-Al is additive without any reduction (Keren and Gast, 1983).

B adsorption by Organic matter

Organic matter is an active portion of a soil. Although most cultivated soils contain only 1 to 5% organic matter, this small amount can modify the soil's chemical properties of soil. Berger and Pratt (1963) stated that a large part of the total boron in soils is associated with the organic matter in tightly bound compounds. However, this B can be released to soil solution, in forms available to plants, by microbial activities (Lowe and Gu, 1990). Olson and Berger (1946) also found that oxidation of soil organic matter resulted in a significant release of B in forms available to plants and caused a slight decrease in B fixation.

B-CaCO₃ interaction

Injury symptoms on plants from B deficiency have been noted on limed, acid soils. The behavior of boron in a CaCO₃ solution has been studied by Kitano *et al.* (1978). They found that the amount of boron coprecipitated with CaCO₃ was proportional to the concentration of boron dissolved in the parent solution, and this relationship is affected by the crystal form of CaCO₃ precipitated and the concentration of NaCl dissolved in the parent solution.

2.3.2. Factors affecting B adsorption–desorption by soil constituents

B adsorption–desorption is affected by boron concentration and water content, suspension pH, anions, exchangeable ions and ionic Strength, wetting and drying cycles, and temperature.

B adsorption as affected by B concentration and water content

Within the tested range of solution–to-adsorbent ratio, the water content does not affect the B-adsorbent interaction (Keren and Mezuman, 1981).

Soil suspension pH

Soil pH is one of the most important factors affecting B uptake by plants. Studies by Peterson and Newman (1976) and Gupta and MacLeod (1977) have shown that a negative relationship between soil pH and plant B occurs when soil pH levels are higher than 6.5. Since the plants obtain their B from the soil solution (Hatcher *et al.*, 1959), these results indicate that boron distribution between the liquid and the solid phase is strongly dependent on soil pH.

Influence of some anions on B adsorption

The amount of boron adsorbed by hydrous oxides of Al and Fe and by amorphous soil was found to be affected by adsorption of silicon. Bingham *et al.* (1972) and McPhail *et al.* (1972) suggested that the reduced B adsorption could be caused by either direct competition between monosilicic acid and boric acid for adsorption sites, or by changes in the oxide surface following adsorption.

Exchangeable Ions and Ionic Strength

The effect of exchangeable ions on boron adsorption by clay minerals is dependent upon the conditions under which the clay suspension exists. Keren and Gast (1981) showed little effect of exchangeable cation species (Na^+ vs. Ca^+) on boron adsorption by montmorillonite at pH around 7. However, there was a significant exchangeable cation effect for pH greater than 8, with the Ca systems adsorbing more boron. Based on the reversibility of boron adsorption by Ca-montmorillonite, they suggested that Ca^{2+} had a nonspecific effect on B adsorption.

Wetting and drying cycles

Wetting and drying processes had a significant effect on B adsorption and desorption by soils and clay minerals (Keren and Gast, 1981). It was noted that

repeated wetting and drying increased B adsorption in soils (Biggar and Fireman, 1960).

Effect of temperature

Temperature may influence B adsorption by a) changing the dissociation constant, as the temperature of a boric acid solution rises, the activity of the borate ion increases (Owen and King, 1943) and b) through changes of the adsorbent-adsorbate interaction. Increasing temperature was also shown to be effective in increasing boron adsorption by illite (Couch and Grim, 1968).

The range of B soil solution concentrations between those causing deficiency or toxicity symptoms in plants is relatively narrow, so prediction of B concentration in soil solution is particularly important. Such a prediction is usually based on the assumption that B adsorption-desorption is a reversible process and B distribution between solid and liquid phases at equilibrium can be described by an adsorption isotherm (Communar and Keren, 2005). The parameters of such an isotherm depend upon mineral composition of soil as well as soil texture and pH. Boron can be removed from soil solution by reactions with mineral and organic surfaces in soils. These adsorption processes attenuate B concentrations. Since plants respond only to solution B, adsorption sites play an important role in managing phytotoxic B concentrations. The most important B adsorption surfaces in soils are Al and Fe oxides, clay minerals, CaCO₃ and organic matter (Corwin *et al.*, 1999)

Boudreau (1997) reported that various modeling approaches have been used to describe B adsorption reaction in soils. Interests in such models increased when profits from crop production are poor and when the marginal cost of any one or group of production input variables is similar to its margin of returns. Historically B adsorption by soils has been described using empirical models such as Langmuir and Freundlich adsorption isotherm equations. Both of these equations contain two

adjustable parameters and assume that adsorption occurs at constant solution pH. A sorption isotherm takes into account intensity (I), quantity (Q), and capacity factors, which are important for predicting the amount of soil nutrient required for maximum plant growth. As the amounts of nutrients required by a soil are effected by a) clay minerals, CEC, organic matter, soil texture, CaCO₃ and other properties which need not to be measured in order to determine soil requirements using sorption technique. (Shafiq *et al.*, 2008).

When B is released by minerals and organic matter during its mineralization or when it is added to soil by fertilization, a large part remains in solution, while another part is adsorbed by particles. Soil organic constituents also play an important role in soil B adsorption. Available B is associated mainly with organic matter and this explains the high available B contents in surface horizons (Lowe and Gu, 1990). Amount of B adsorbed increased as the quantities of added B increased in all the soils.

2.3.3. Adsorption isotherms with respect to B in soils

Boron adsorption reactions on oxides, clay minerals, and soil materials have historically been described using adsorption isotherm equations (Mondal *et al.*, 1993). The most popular adsorption isotherm models are the Langmuir and Freundlich but Tempkin and Brunauer-Emmett-Teller (BET) adsorption isotherm equations have also been used. Freundlich equation is an empirical equation and it corresponds to a model of adsorption in which the affinity term decreases exponentially as the amount of adsorption increases. Advantage of Freundlich isotherm is that it assumes unlimited sorption sites which correlated better with a heterogeneous soil medium having different chemical/physical properties (Mondal *et al.*, 1993). The Langmuir equation was first used to describe P adsorption by Watanabe and Olsen (1965). Main advantage of this equation is that it accounts the

adsorption maximum and bonding energy for an element and sorption can be calculated.

Watanabe and Olsen (1965), made use of the Langmuir isotherm to calculate phosphorus adsorption maxima in soils, while Hatcher and Bower (1958) and Biggar and Fireman (1960) concluded that over-limited concentration ranges the equilibrium between dissolved boron and adsorbed boron in soils and can be expressed approximately by the Langmuir isotherm.

The phenomenon of adsorption is usually described by either the Langmuir adsorption equation or by the empirical Freundlich equation when it is unimolecular layer adsorption and by the B.E.T. (Brunauer, Emmett and Teller) isotherm when it is multimolecular layer adsorption (Biggar and Fireman, 1960). When adsorbed boron (B_a) was plotted against boron in equilibrium solution (B_s) it was found to follow an almost linear curve and a simple adsorption isotherm in all the soils and clays. When B_s/B_a was plotted against B_s as required for fitting up of the Langmuir adsorption isotherm, it was seen that the isotherm was valid only approximately and in certain limits of boron concentration. Singh (1964) observed its validity within still more limited concentrations.

Since the temperature plays an important role in the adsorption, equilibrium greatly depended on it. As the heat of adsorption is mostly negative, all adsorption processes are exothermic - an increase in temperature will reduce the amount of the reaction product which means that the reaction forces are weak and the adsorption is physical. At high temperatures the heat of adsorption is positive, and there must be an increase in the amount of the reaction product; the term chemisorptions are then applied. Shafiq *et al.* (2008) reported that an increase in the adsorption of boron with increasing temperature, is there but the magnitude of the increase was not as high. This was probably due to the fact that adsorption first decreases with increase in temperature due to decreasing Van der Waals adsorption, and then begins to increase at temperatures where activated adsorption can take place.

Mathematical models accounting for the impact of different factors on B adsorption and transport in soils have been developed by Corwin *et al.* (1999) and Communar *et al.* (2004). The B adsorption isotherms for the loamy sand were obtained by Communar *et al.* (2004).

2.4. B nutrition in rice

Rice provides 35-60% of the dietary calories consumed by nearly 3 billion people (Guerra *et al.*, 1998). By the year 2025, it is estimated that it will be necessary to produce about 60% more rice than what is currently produced to meet the food needs of a growing world population (Balasubramanian, 1998). Match *et al.* (1996) reported that appreciable yield increase with B application has been observed in a number of crops including rice. Wheat (5-26%), Cotton (6-18%), Rice (5-26%), Maize (12-35%), Potato (15-18%). Mean yield increase of 19% in nine field experiments indicated severe B deficiency in rice. In rice, B content is up to 10-time lower than those of dicot plants (Match *et al.*, 1996). And thus rice young seedling is relatively resistant to B limited condition (Yu and Belle, 1998) compared to dicot plants (Miwa *et al.*, 2006). However, the effect of B limitation until the reproductive phase is little known in rice. Garg *et al.* (1979) reported that under sand cultures for rice plant, up to 2.5 mg L⁻¹ of boron content in nutrient solution can increase the yield of rice grain by improving the pollen vitality of rice flower, but inhibitory effects appeared beyond 5 mg L⁻¹ of boron content. Lewis (1980) reported that for pollen tube growth, high B levels in the stigma and style are required. The viability of pollen grains is also severely inhibited by B deficiency.

In Pakistan, the soil B contents are reported to be a key determinant in rice yields, and B is supplied in fertilizers to maintain sufficient yields (Rashid *et al.*, 2000). Aromatic fine grain Basmati rice is more sensitive to B deficiency than coarse grain IRRI types. B deficiency also delays flowering in rice.

Singh *et al.* (2001) reported that percent response over NPK controls of B in rice is 16.6%. Red lateritic soils (Alfisols) are highly deficient in boron, so application of 0.5-2 kg B ha⁻¹ increased the rice yield by 460-1500kg ha⁻¹ (12.5-37.2%) over controls (Sakal, 2001). Response of rice for B was greater in rabi (winter season) than in khariff (monsoon season) (Datta *et al.*, 1992). In 19 field trials in deltaic alluvial soils in Assam, application of 2 kg B ha⁻¹ to rice increased the grain yield significantly by 180-460 kg ha⁻¹ (25.2-39%) and that of the following wheat crop by 230-320 kg ha⁻¹ (23.1-35.8%) (Sakal *et al.*, 1996). B deficiency occurs in many plants when its concentration in the upper fully matured leaves is found to be below 15 mg B kg⁻¹. The sufficiency range of B is between 20 and 100 mg kg⁻¹ (Singh, 1998). B concentrations are higher in upper leaves than lower leaves and decrease with the age of plants.

B is generally applied through broadcasting and mixing into the soil prior to sowing or before transplanting the crop (Singh *et al.*, 2005). Band placement of B can lead to B toxicity in plants when it is applied in excess, or if it is placed too close to seedlings or shoots. Therefore, B should neither be placed in contact with seed or seedlings, nor should excessive doses be used because of potential toxicity problems. Regular use of higher doses of B can lead to its toxicity in crop plants (Singh, 2006). Optimum doses of B for light textured entisols ranged between 0.5 and 1.0 kg B ha⁻¹. Also Dangarwala (2001) reported that optimum requirements of B for wheat and rice were found to be between 0.75 and 1.5 kg B kg⁻¹

Frequency of B application depends upon doses of B applied and the nature of the crop. Regular applications of more than 2 kg B ha⁻¹ caused adverse effects on the growth and yield of crops. Therefore, one should apply the optimum dose of B at the desired frequency (Singh *et al.*, 2005). Among the various sources of B, the efficacy of borax Granubor II and boric acid was found to be almost equal in increasing the productivity of rice and maize (Sakal and Singh, 1995). Basal application of B, through broadcasting, gave the best response. However, if a basal

application is missed, foliar sprays of 2.0-2.5 g L⁻¹ of boric acid or solubor can be used for correcting the B deficiency quite efficiently (Singh, 2004).

2.4.1. Boron Toxicity

There is a relatively small range between levels of soil B causing deficiency and toxicity symptoms in plants. Of deficiencies of the known essential micro nutrients, B deficiency in plants is most widespread (Sparr, 1970). Excess and toxicity of B in soils of semi-arid and arid areas are more of a problem than deficiency. B toxicity occurs in these areas either due to high levels of B in soils or due to additions of B in irrigation water. During reclamation of saline soils, B moves more slowly than other salts. B removal from soil requires about three times more water than excess salt removal (U.S. Salinity Laboratory Staff, 1954).

Boron is adsorbed on the surface of particles from its aqueous solution and equilibrium between adsorbed and dissolved boron exists in soils. Boron adsorbed from the solution of the same concentration becomes injurious more quickly on coarse-textured soils than fine-textured ones. Similarly the boron toxicity on coarse-textured soils may be more easily overcome by application of low-boron water (Eaton, 1935). Since the plants respond only to water-soluble boron, the boron concentration of the soil solution on equilibrium would be equal to that of irrigation water. After equilibrium is attained, the effects on plant growth of boron in irrigation water can be predicted directly from the boron concentration of irrigation water (Hatcher *et al.*, 1959).

The first evidence of boron toxicity in rice was reported by Ponnampereuma and Yuan (1966) on a soil in the Silo region of Taiwan. The soil pH was 8.1. Soil solutions of the affected flooded soils contained 9.1 ppm boron compared with 1 ppm boron for two normal soils from the Philippines. In an experiment with the Taiwan soil and two soils from the Philippines, Ponnampereuma and Yuan (1966) induced foliar symptoms of boron toxicity in rice at 20-60 ppm of applied boron as borax.

These results suggested that the critical concentration of water-soluble boron for toxicity to rice may vary from soil to soil. Irrigation water with boron content greater than 2 ppm causes accumulation of boron in soils Ponnampereuma *et al.* (1979) summarized information on toxic limits of boron in a rice-growing soil.

- More than 3 ppm hot-water-soluble boron in soil is toxic (Hesse, 1971).
- High potassium content aggravates boron toxicity (Houng 1975).

Amelioration of excess boron in soil is difficult. However, if irrigation water from a well has high (more than 2 ppm) boron content, it should be diluted with surface water with less or no boron content. Internal drainage could also minimize accumulation of boron (Ponnampereuma *et al.*, 1979).

Materials and methods

3. MATERIALS AND METHODS

3.1. Collection of soil sample for analysis

In order to achieve the objectives of the present investigation representative surface samples (0-20 cm) of eight soil types each from three locations (total 25 samples-including one additional sample from Kuttanad) were collected. Kerala State has five agro-ecological zones and 23 agro-ecological units (Unpublished data: NBSS & LUP). The agro-ecological units, from which these soil samples were collected, cover 9 units out of 23, but represent the major rice growing tracts of Kerala. The details of soil samples collected are furnished in table 1.

Table 1. Locations of soil sampling, soil taxonomy and agro-ecological units

Soil sample No.	Soil type (Traditional Names)	Location	Soil taxonomy	Agro-ecological unit
1	Kuttanad (1)	Thiruvvarppu: Kayal (South)	Entisol	Kuttanad (AEU 4)
2	Kuttanad (2)	Thiruvvarppu: Kayal (North)	Entisol	Kuttanad (AEU 4)
3	Kuttanad (3)	Thiruvvarppu: Karappadam(Upper area)	Entisol	Kuttanad (AEU 4)
4	Kuttanad (4)	Thiruvvarppu: Karappadam (Upper area)	Entisol	Kuttanad (AEU 4)
5	Pokkali (1)	Palamattom padasekharam	Entisol	Pokkali lands (AEU 5)
6	Pokkali (2)	Paravoor south pokkali padam, North paravoor	Entisol	Pokkali lands (AEU 5)
7	Pokkali (3)	Cheppamamchattama padasekharam	Entisol	Pokkali lands (AEU 5)
8	Kole (1)	Jayanthikole padavu, Chazhoor, Kurumpilavu village	Entisol	Kole lands (AEU 6)

Soil sample No.	Soil type (Traditional Names)	Location	Soil taxonomy	Agro-ecological unit
9	Kole (2)	Kundankuzhi padasekharam, Maranchery panchayath, Ponnani taluk	Entisol	Kole lands (AEU 6)
10	Kole (3)	Padinjare karimpadam, Venkidangu panchayath, Chavakkad Taluk	Entisol	Kole lands (AEU 6)
11	Black cotton (1)	Chittoor	Vertisol	Palakad eastern plains (AEU 23)
12	Black cotton (2)	Ezhuthani, Perumatti	Vertisol	Palakad eastern plains (AEU 23)
13	Black cotton (3)	Alayar, Perumatti	Vertisol	Palakad eastern plains (AEU 23)
14	Onattukara (1)	Kappilmekku, Krishnapuram	Entisol	Onattukara sandy plains (AEU 3)
15	Onattukara (2)	Krishnapuram, Karthikappalli taluk	Entisol	Onattukara sandy plains (AEU 3)
16	Onattukara (3)	Krishnapuram, Karthikappalli taluk	Entisol	Onattukara sandy plains (AEU 3)
17	Midland laterite (upland)	Pattambi, RARS campus	Ultisol	North central laterite(AEU 10)
18	Midland laterite (upland)	Vellanikkara, Main campus	Ultisol	North central laterite (AEU 10)
19	Midland laterite (upland)	Kozhikode, Mavoor	Ultisol	Midland laterite (AEU 10)
20	Midland laterite (wetland)	Pattambi, RARS campus	Ultisol	North central laterite(AEU 10)

Soil sample No.	Soil type (Traditional Names)	Location	Soil taxonomy	Agro-ecological unit
21	Midland laterite (wetland)	Chalissery, Palakkad	Ultisol	North central laterite (AEU 10)
22	Midland laterite (wetland)	Ottappalam taluk, Palakkad	Ultisol	North central laterite (AEU 10)
23	Wayanad (1)	Padinjarathara, Vythiri taluk	Ultisol	Northern High hills (AEU 15)
24	Wayanad (2)	Vellamunda, Mananthavady taluk	Ultisol	Wayanad central plateau (AEU 20)
25	Wayanad (3)	Thondarnadu, Mananthavady taluk	Ultisol	Wayanad central plateau (AEU 20)

Collected soil samples were air dried under shade, sieved through 2mm sieve and used for laboratory characterization. The samples were analyzed for texture, pH, EC, CEC, exchangeable cations, percentage base saturation, available nutrients (organic carbon, P, K, Ca, Mg, Fe, Ca, Mn, Zn), available B and total B.

3.1.1. Physico-chemical analysis of soil

Soil texture

Texture of soils was determined by international pipette method (Robinson, 1922). 20 g soil samples were taken in 500 ml beaker. 60 ml, 6% H₂O₂ was added to remove the organic matter which acts as a binding material. 8 ml, 1N NaOH was added and stirred well for better dispersion of soil particles. Contents were transferred into a spoutless cylinder of 1000 ml capacity and from which 20 ml of suspension pipetted out to find out clay and silt particles based on their

sedimentation time. By repeated washing of the sediments and after oven drying, the weight of sand particles was also obtained.

Soil pH

The pH of the soils was determined in a 1:2.5 soil water suspension, potentiometrically using a pH meter (Jackson, 1958).

Electrical conductivity

Electrical conductivity was estimated in the supernatant liquid of the soil water suspension (1:2.5) used for pH estimation with the help of a conductivity meter (Jackson, 1958).

Organic carbon

Organic carbon of the soil was estimated by wet digestion method (Walkley and Black, 1934).

Available phosphorus

Available phosphorus in the soil samples were extracted using Bray No.1 reagent (Bray and Kurtz, 1945) and estimated colorimetrically by reduced molybdate ascorbic acid blue color method (Watanabe and Olsen, 1965) using a spectrophotometer (Model: Genesys 20)

Available potassium

Available potassium in the soil samples were extracted using neutral normal ammonium acetate and its content in the extract was estimated by flame photometry (Jackson, 1958).

Available Micronutrients (Fe, Cu, Mn and Zn) in soil

Available micronutrients in soil samples were extracted using 0.1M HCl (Sims and Johnson, 1991). 2 g soil with 20 ml of 0.1M HCl was shaken for 5 minutes. It was filtered through Whatmann No. 42 filter paper and the filtrate was

collected and analysed for Fe, Cu, Mn and Zn using Atomic Absorption Spectrophotometer (Perkin Elmer Make Model: Analyst 400).

Available boron

Available boron in soil samples were extracted using hot water. (Gupta, 1975) and estimated colorimetrically by Azomethine-H method (Page *et al.*, 1982) using a spectrophotometer (Model: Genesys 20)

Cation exchange capacity, exchangeable cations, and percentage base saturation (PBS)

The cation exchange capacity in the soil was estimated by the method proposed by Hendershot and Duquette (1986). The cations (Ca, Mg, Na, K, Al, Fe, Mn, Cu and Zn) present in the exchangeable sites in the soil were replaced by 0.1M BaCl₂ solution and the extracted cations were estimated. Four grams of soil samples were taken in a centrifuge tube and 40 ml of 0.1M BaCl₂ was added. It was shaken for two hours and filtered through Whatman No. 42 filter paper. Filtrate was used for aspiration to a Perkin Elmer Atomic Absorption Spectrophotometer (Model: Analyst 400) for the determination of exchangeable Ca, Mg, Fe, Mn, Cu and Zn. Exchangeable Na and K were estimated with the help of flame photometer (Model: Elico CL361). Exchangeable Al was estimated colorimetrically using Aluminon (Jayman and Sivasubramanian, 1974). CEC of soils was computed by summing up the quantities of exchangeable cations expressed in cmol (p⁺) kg⁻¹. The PBS was computed from the quantities in cmol (p⁺) kg⁻¹ of exchangeable Ca, Mg, Na and K expressed as percentage of CEC.

Total sesquioxides in soil

The soil samples were digested with 8 N HCl and extract was made up to 250 ml. From which 50 ml extract was taken and concentrated HNO₃ was added to this extract and boiled. After cooling, concentrated ammonium hydroxide was added and again boiled. Residue was collected, dried and ignited in a muffle furnace. The

weight of the ignited residue was considered as the amount of sesquioxide present in the sample. (Jaiswal, 2003).

Total boron

0.1 g soil sample was taken in a platinum crucible and wetted by adding a few drops of conc. H_2SO_4 . Later 3 ml HNO_3 and 1 ml HClO_4 were added and digested in a hot plate. The contents were cooled and then 5 ml HF was added. It was boiled at 200°C . Finally, the yellowish white residue obtained was dissolved with 10 ml 6N HCl. Contents were transferred to a volumetric flask and made up to 100 ml using distilled water (Page *et al.*, 1982). Using this digest total B content in each soil was estimated colorimetrically by Azomethine-H method (Page *et al.*, 1982) using a spectrophotometer (Model: Genesys 20), at 420 nm.

3.2. Fractionation of soil Boron

Amount of soil boron in different forms (fractions) existing in soil were extracted and estimated. The major B fractions estimated were

- i) Nonspecifically adsorbed plus water soluble B (NSA-B)
- ii) Specifically adsorbed B (SPA-B)
- iii) B occluded in Mn-oxyhydroxide (MOH-B)
- iv) B occluded in amorphous Fe and Al oxides (AMO-B)
- v) B occluded in crystalline Fe-Al oxides (CRO-B) and
- vi) Residual B (RES-B).

Fractions of soil B were extracted by the method proposed by Jin *et al.* (1987). The extraction procedure involves extraction with

- i) 0.02M CaCl_2 to remove nonspecifically adsorbed plus water soluble B (NSA-B).
- ii) 0.02 M Mannitol in 0.02 M CaCl_2 to remove specifically adsorbed B (SPA-B).

iii) 0.1M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.01 M HNO_3 to remove B occluded in Mn-oxyhydroxide (MOH-B).

iv) 0.2 M NH_4 -oxalate to remove B occluded in amorphous Fe- Al oxides (AMO-B).

v) Sodium citrate–dithionate–bicarbonate to remove B occluded in crystalline Fe-Al oxides (CRO-B).

3.2.1. Fractionation procedure

Flow chart for the B fractionation is depicted in table 2.

10 g soil sample was taken in a 100 ml plastic beaker. 20 ml 0.02M CaCl_2 was added and shaken for 24 hours at 25 °C. After filtration nonspecifically adsorbed plus water soluble B (NSA-B) content in the filtrate was estimated. 6 g soil was shaken with 20 ml, 0.02 M Mannitol in 0.02 M CaCl_2 . After filtration specifically adsorbed B (SPA-B) content in the filtrate was estimated. 4 g soil samples was shaken for 30 minutes with 40 ml 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.01 M HNO_3 . After filtration, B occluded in Mn- oxyhydroxide (MOH-B) in each soil was estimated. 1g soil was shaken for 2 hours with 50 ml 0.2 M Ammonium-oxalate in the dark at 25 °C. B occluded in amorphous Fe-Al oxides (AMO-B) was estimated by using this technique. B occluded in crystalline Fe-Al oxides (CRO-B) was estimated by shaking 0.50 g soil with 20 ml Sodium citrate–dithionate–bicarbonate(CDB) for 15 minutes in water bath at 80 °C. The cycle was repeated once again and boron in the filtrate was estimated. Residual B (RES-B) content in the soils was estimated by subtracting the total amount of boron in all the above fractions from total boron.

3.2.2 Estimation of B fractions

For each fraction separated as above, 1 ml of the filtrate was taken in a polyethylene beaker to which 2 ml buffer solution and 2 ml azomethine-H prepared in ascorbic acid was added. The intensity was read in spectrophotometer at 420 nm. B

content in each fraction was calculated by subtraction of the B extracted in previous B fractions.

Table 2. Extraction procedures for various B fractions in soil (Jin *et al.*, 1987)

B fraction	Extraction procedure	Computation of actual fraction
A. Nonspecifically adsorbed plus water soluble B (NSA-B)	10 g soil, 20 mL 0.02 M CaCl ₂ , shaking for 24 h at 25 ⁰ C	Computed 'A' fraction itself
B. Specifically adsorbed B (SPA-B)	6 g soil, 20 mL 0.02 M mannitol in 0.02 M CaCl ₂ , shaking for 24 h at 25 ⁰ C	Amount of boron fraction obtained by this procedure – Amount of boron fraction obtained by procedure for A
C. B occluded in Mn oxy hydroxides (MOH-B)	4 g soil, 40 mL 0.1 M NH ₂ OH·HCl in 0.01 M HNO ₃ , shaking for 30 min at 25 ⁰ C	Amount of B fraction obtained by this procedure – Amount of boron fraction obtained by procedure for 'B'
D. B occluded in amorphous Fe and Al oxides (AMO-B)	1.00 g soil, 50 mL 0.2 M NH ₄ -oxalate, shaking for 2 h in the dark at 25 ⁰ C	Amount of B fraction obtained by this procedure – Amount of boron fraction obtained by procedure for C
E. B occluded in crystalline Fe and Al oxides (CRO-B)	0.50 g soil, 20 mL DCB, shaking 15 min in water bath at 80 ⁰ C, repeating the cycle once more or 1.00 g soil, 50 mL 0.2 M NH ₄ -oxalate, shaking for 2 h under ultraviolet light at 25 ⁰ C	Amount of B fraction obtained by this procedure – Amount of B fraction obtained by procedure for D
F. Residual B (RES-B)	Total B in soil – (sum of the B content in fractions A+B+C+D+E)	

3.3. Adsorption study

For adsorption study 2.5 g soil was shaken with 25 ml 0.01M CaCl₂ containing B concentrations of 0, 3, 4, 5, 6, 7, 8, 9, 10, 15 mg L⁻¹ as boric acid for 24

hours at 25⁰C (Shafiq *et al.*, 2008). This process was replicated thrice for each soil. After shaking, the soil solution was filtered through filter paper (Whatman No. 42). After filtration, B concentration in the filtrate was measured using Azomethine-H method by a spectrophotometer at 420 nm wavelength. Simple Q/I curve using the amount of adsorbed B and equilibrium boron concentration were drawn for each soil. Best fit curves were obtained by using regression equations (Cox, 1987). Slopes of these curves were considered as buffer power with respect to each soil. Further by using the data on adsorption the following three adsorption isotherms were fitted for each soil.

a) Langmuir adsorption isotherm

$x/m = KMC/1+KC$, which was modified to the curve fitting form as

$$C/x/m = 1/KM + C/M$$

Where, x/m =amount adsorbed per unit weight of soil, C = concentration, K = bonding energy coefficient, M =adsorption maximum.

b) Freundlich adsorption isotherm

$x/m = KC^{1/n}$, where 'K' and '1/n' are Freundlich constants.

The linear form of this equation used was

$$\log (x/m) = \log K + 1/n \log C$$

c) Tempkin adsorption isotherm

$$(x/m)/b = (RT)/a \ln AC$$

Where 'A' and 'a' are coefficients, 'R' is the universal gas constant, and 'b' is the Langmuir adsorption maximum.

3.4. Pot culture experiment

A pot culture experiment was carried out in the glass house of the Radiotracer Laboratory, College of Horticulture during October-January with rice variety Jyothi. The soil with the lowest available B status was selected to study the effect of three levels of B with and without organic manure on rice. Mud pots of uniform size were used for the study. These pots were filled with 5 kg of processed soil.

The treatments are detailed below:

A. Levels of B

- a) 0 kg ha⁻¹ (0 mg pot⁻¹)
- b) 10 kg ha⁻¹ (22 mg pot⁻¹)
- a) 20 kg ha⁻¹ (44 mg pot⁻¹)

B. Levels of organic manure

- a) 0 t ha⁻¹ (0g pot⁻¹)
- b) 5 t ha⁻¹ (11.2g pot⁻¹)

Treatment combinations: $3 \times 2 = 6$

The experiment was laid out in a completely randomized design with 6 treatment combinations and 5 replications. The treatment details are illustrated in table 3.

Table 3. Details of pot culture experiment

Treatment	Combination	Notation
T ₁	0 t FYM ha ⁻¹ , 0 kg B ha ⁻¹ (0 mg pot ⁻¹)	O ₁ L ₁
T ₂	0 t FYM ha ⁻¹ , 10 kg B ha ⁻¹ (22 mg pot ⁻¹)	O ₁ L ₂
T ₃	0 t FYM ha ⁻¹ , 20 kg B ha ⁻¹ (44 mg pot ⁻¹)	O ₁ L ₃
T ₄	5 t FYM ha ⁻¹ (11.2g pot ⁻¹), 0 kg B ha ⁻¹ (0 mg pot ⁻¹)	O ₂ L ₁
T ₅	5 t FYM ha ⁻¹ (11.2g pot ⁻¹), 10 kg B ha ⁻¹ (22 mg pot ⁻¹)	O ₂ L ₂
T ₆	5 t FYM ha ⁻¹ (11.2 g pot ⁻¹), 20 kg B ha ⁻¹ (44 mg pot ⁻¹)	O ₂ L ₃

All the soils in the pots were treated with lime initially. Lime requirement was calculated using ΔpH value. ΔpH was the difference in pH of the soil from a pH value 6.5. Thus ΔpH value for Onattukara soil with a pH value of 5.02 was $6.5-5.02=1.48$. Based on this per plot lime requirement was calculated as 1.1 g ($1.48 \times 0.3375 \text{ t ha}^{-1}$). The soils in T₄, T₅ and T₆ were treated with FYM (5 t ha⁻¹) as per the Package of Practices recommendations. The soils were kept under submerged condition for 2 weeks so as to ensure possible decomposition and other chemical changes as in a wetland paddy system.

Nitrogen, Phosphorus and potassium were applied in the form of Urea (0.44g pot⁻¹), Rajphos (0.5 g pot⁻¹) and Muriate of potash (0.17g pot⁻¹) in 3 splits as per the Package of Practices Recommendations (KAU, 2007) of 90:45:45 kg ha⁻¹ N:P₂O₅:K₂O. One week old Rice seedlings were transplanted at 3 seedlings pot⁻¹ and it was assured that three seedlings were maintained in each pot.

Both soil and plant samples were drawn at panicle initiation and at the time of harvest. Biometric observations were also recorded at the above two stages. The soil samples were assayed for hot water soluble boron content at both stages.

3.4.1. Plant analysis

Plant samples were collected from different treatments on P.I. and harvesting stages. The samples were oven dried at 70 ± 5 °C, powdered and used for analysis. Total B, P, K, Ca, Mg, Fe, Mn, Cu, and Zn, in different plant parts, namely grain, leaf and straw were estimated after digestion of the sample with 2:1 nitric – perchloric acid mixture.

Boron

B in the digest was determined colorimetrically by Azomethine-H method (Page *et al.*, 1982) using a spectrophotometer (Model: Genesys 20)

Nitrogen

N in the plant samples were determined by using block digester cum distillation unit (Model: Kel Plus). Digestion was done by using concentrated H₂SO₄ and digestion mixture of K₂SO₄ and CuSO₄ (10:1) at 450 °C. Digested samples were distilled by using 40% NaOH and distillate was collected to 2% boric acid. This was titrated against 0.02 N H₂SO₄. By using this titre value N content in the plant samples were calculated (Hesse, 1971).

Potassium

K content in the digest was estimated by flame photometry (Jackson, 1958).

Phosphorus

P in the digest was determined by the Vanado molybdate yellow color method (Koenig and Johnson, 1942) measuring the colour intensity in a spectrophotometer (Model: Analyst 400).

Secondary and micronutrients (Ca, Mg, Fe, Cu, Mn, and Zn)

The digested samples were analyzed for Ca, Mg, Fe, Cu, Mn and Zn using Atomic Absorption Spectrophotometer (Perkin Elmer Make Model: Analyst 400).

3.5. Statistical analysis

Correlation studies of data were carried out by the method suggested by Panse and Sukatme (1978). Correlation and regression analysis of soil data generated were carried out based on the method suggested by Cox (1987). Path coefficient analysis was carried out using SPSS package Analysis of variance in CRD was done using MSTAT C package.

Results

4. Results

The data generated from the characterization of selected soils and analytical data from the pot culture experiments are presented in this section.

4.1. Electrochemical properties, texture and available nutrient status

4.1.1. pH

The pH of the soils under present investigation is given in table 4a. The pH ranged from 2.3 to 6.7. The lowest pH was recorded in *Pokkali* soil and highest in black cotton soil.

4.1.2. Electrical conductivity

The electrical conductivity ranged from 0.03 to 4.3 dS m⁻¹. Lowest EC was recorded in Onattukara soil and highest in *Pokkali* soil. EC of *pokkali* soils are >4 dS m⁻¹ justifying its classification as acid saline soil.

4.1.3. Texture

The texture of the soils was found to be Clay loam for *Kuttanad* (1) and *Kuttanad* (2), *Kole* (10) soils, Sandy clay loam for *Kuttanad* (3), *Kole* (7 and 8) *Wayanad* (23) and, Silty clay for *Kuttanad* (4), Sandy for Onattukara (14, 15 & 16) and Sandy loam for *Pokkali*. (Table 4a).

4.1.4. Available nutrient status

The organic carbon content of the soils varied from 0.33 to 3.7%. The lowest organic carbon content was recorded in Onattukara sandy soil and highest was in *Kuttanad*.

The available phosphorus of the soils ranged from 6.14 to 52.8 kg ha⁻¹. The lowest available phosphorus was recorded in *Kuttanad* and the highest was recorded in *Pokkali* soil (Table 4a). Out of the 25 soil samples 9 samples were P deficient soil with <10 kg P ha⁻¹ i.e., 36% soils with severe P deficiency.

Table 4a. Electrochemical properties, texture and available nutrient status of soils under study

Soil No.	Soil type	pH	EC (dS m ⁻¹)	Sand (%)	Silt (%)	Clay (%)	Textural class	OC (%)	Available Nutrient status					
									kg ha ⁻¹		mg kg ⁻¹			
									Av.P	K	Fe	Mn	Cu	Zn
1	Kuttanad-1	3.0	1.0	30.0	28.2	42.4	Clay loam	3.7	6.8	311.4	138.5	5.2	2.5	1.1
2	Kuttanad-2	3.2	0.7	39.0	22.8	38.2	Clay loam	3.6	7.8	294.6	191.9	17.6	2.9	1.4
3	Kuttanad-3	3.3	0.6	52.9	23.4	23.8	Sandy clay loam	3.7	13.9	217.3	245.6	42.2	4.9	3.6
4	Kuttanad-4	3.0	0.7	10.9	45.5	43.6	Silty clay	3.7	6.1	284.5	170	23.7	3.6	1.6
5	Pokkali-1	2.8	4.0	78.2	15.7	6.8	Sandy loam	1.6	52.8	95.2	356	3.4	2.9	24.2
6	Pokkali-2	2.3	4.3	82.7	7.1	10.2	Sandy loam	1.4	22.7	112	412.5	5	2.3	18.5
7	Pokkali -3	3.1	3.9	71.6	12.3	16.1	Sandy loam	2.3	37.9	127.7	461	14.6	2.3	5.6
8	Kole- 1	2.8	0.2	60.9	18.6	20.2	Sandy clay loam	2.7	13.1	186	480	11.4	5.1	8.4

Soil No.	Soil type	pH	EC (dS m ⁻¹)	Sand (%)	Silt (%)	Clay (%)	Textural class	OC (%)	Available Nutrient status					
									kg ha ⁻¹		mg kg ⁻¹			
									Av.P	K	Fe	Mn	Cu	Zn
9	Kole-2	3.5	0.20	66.8	14.3	18.3	Sandy clay loam	3.4	13.8	434.6	101.4	35.9	5.5	3.1
10	Kole -3	3.4	0.20	44.9	23.2	32.0	Clay loam	2.1	26.0	222.9	240.9	11.1	2.1	1.2
11	Black cotton-1	5.2	0.20	70.5	5.2	15.3	Sandy clay loam	1.1	15.0	114.2	194.1	63.7	4.6	1.3
12	Black cotton-2	6.7	0.30	54.7	12.0	32.0	Sandy clay loam	0.62	7.2	84	74.9	39.5	3.8	1.2
13	Black cotton-3	6.2	0.10	71.5	20.2	8.05	Sandy loam	0.72	8.3	241.9	22.1	41.6	3.4	1.4
14	Onattukara -1	5.0	0.04	90.1	5.2	4.8	Sandy	0.47	29.6	43.7	22.2	40.2	1.2	0.9
15	Onattukara -2	5.1	0.03	92.3	4.3	3.2	Sandy	0.33	17.6	45.9	18.9	32.1	0.75	0.6
16	Onattukara -3	5.0	0.04	97.4	1.9	0.6	Sandy	0.52	20	41.4	15	35.6	1.1	1.1
17	Vellanikkara	4.7	0.08	59.8	24.1	16.1	Sandy loam	1.08	6.3	230.7	3.8	158.1	2.0	2.5

Soil No.	Soil type	pH	EC (dS m ⁻¹)	Sand (%)	Silt (%)	Clay (%)	Textural class	OC (%)	Available Nutrient status					
									kg ha ⁻¹		mg kg ⁻¹			
									Av.P	K	Fe	Mn	Cu	Zn
18	Kozhikode	4.8	0.04	53.6	26.3	20	Sandy loam	1.2	14.9	135.5	4.7	69.3	2.3	2.5
19	Pattambi (upland)	4.0	0.20	66.1	15.2	19.1	Sandy loam	1.7	21.3	423.4	7.0	878.6	3.0	2.2
20	Chalissery	4.3	0.05	57.4	29.3	13.3	Sandy loam	1.6	8.3	68.3	46.2	25.1	2.8	0.8
21	Ottappalam	4.7	0.16	74.7	20.5	7.0	Sandy loam	1.6	9.1	178.1	63.3	184.8	7.0	1.4
22	Pattambi (wetland)	4.6	0.05	74.0	9.2	16.8	Sandy loam	1.5	18.4	229.6	66.2	166.5	5.9	1.8
23	Wayanad-1	4.6	0.07	49.9	27.0	23.1	Sandy clay loam	1.8	6.9	113.1	48.4	383.4	4.9	0.68
24	Wayanad-2	4.6	0.08	70.8	14.4	14.9	Sandy loam	1.8	8.3	126.6	47.2	325.6	4.6	0.67
25	Wayanad-3	4.3	0.04	85.2	10.2	4.6	Sandy loam	2.3	15.1	53.8	82.9	55.5	3.7	0.73

The available potassium content of the soils ranged from 41.4 to 434.6 kg ha⁻¹. The lowest available potassium was recorded in Onattukara soil and highest was recorded in *Kole* soil (Table 4a). It was found that 15 soil samples (60%) showed medium to high fertility status with >125 kg K ha⁻¹

4.1.4. Available micronutrient status

The available (0.1N HCl extractable) micronutrient status (Fe, Mn, Cu and Zn) of the soils is given in table 4a. Available Fe content of the soils ranged from 3.8 to 480 mg kg⁻¹. The lowest available Fe content was noted in Vellanikkara soil and highest value was in *Pokkali* soil. Available Mn content of the soils ranged from 3.4 to 878 mg kg⁻¹. Lowest available Mn content was observed in *Pokkali* and the highest value was recorded in Pattambi soil. Available Cu content of the soils varied from 0.75 to 7.04 mg kg⁻¹. Onattukara recorded the lowest available Cu content and laterite soil from Ottappalam recorded the highest value. The amount of available Zn in the soils ranged from 0.57 to 24.2 mg kg⁻¹. The lowest available Zn was noted in Onattukara soil and the highest value was observed in *Pokkali* soil.

4.2.1. Exchangeable cations

The BaCl₂ exchangeable cation status of the soils under study is given in table 4b. The exchangeable Na content of the soils varied from 0.13 to 1.4 cmol (p+) kg⁻¹. Exchangeable K content of the soils ranged from 0.13 to 0.43 cmol (p+) kg⁻¹.

The amount of exchangeable Ca in the soils noticed was in between 0.47 to 5.8 cmol (p+) kg⁻¹. Exchangeable Magnesium content of the soils ranged from 0.04 to 1.38 cmol (p+) kg⁻¹.

Exchangeable Al content of the soils were 0.004 to 2.4 cmol (p+) kg⁻¹. Fe content in the exchangeable pool varied from 0.0004 to 0.6 cmol (p+) kg⁻¹. Mn content of in the exchangeable pool in soils varied from 0.07 to 1.46 cmol (p+) kg⁻¹.

Table 4b. CEC and exchangeable cations of the soils

Soil No.	Soil type	CEC [cmol(p+)kg ⁻¹]	Exchangeable cations [cmol(p+)kg ⁻¹]									PBS (%)
			Na	K	Al	Ca	Mg	Fe	Mn	Cu	Zn	
1	Kuttanad-1	7.78	0.5	0.4	2.05	2.8	0.69	0.42	0.92	0.0009	0.003	56.4
2	Kuttanad -2	7.49	0.53	0.43	1.93	2.9	0.69	0.05	0.96	0.0004	0.002	60.7
3	Kuttanad -3	7.01	0.55	0.32	2.07	2.5	0.35	0.004	1.2	0.0007	0.006	53.1
4	Kuttanad -4	6.94	0.4	0.26	2.4	2.6	0.36	0.006	0.91	0.0007	0.005	52.1
5	Pokkali-1	7.36	1.4	0.22	2.4	1.9	0.69	0.04	0.66	0.002	0.05	57.2
6	Pokkali-2	6.88	1.2	0.2	2.2	1.9	0.7	0.07	0.57	0.002	0.04	58.1
7	Pokkali -3	9.33	1.4	0.22	1.89	3.8	0.69	0.6	0.72	0.001	0.01	65.5
8	Kole -1	4.08	0.86	0.21	1.13	1.2	0.22	0.02	0.43	0.001	0.01	61
9	Kole -2	9.16	1.04	0.34	0.87	5.1	0.34	0.01	1.46	0.0007	0.003	74.4
10	Kole- 3	6.03	0.3	0.13	1.87	2.5	0.26	0.16	0.81	0.0006	0.002	52.9
11	Black cotton-1	9.29	0.67	0.31	0.11	5.0	1.38	0.02	1.8	0.0003	0.0004	79.2
12	Black cotton -2	9.22	0.87	0.28	0.15	6.8	0.69	0.03	0.4	0.0004	0.0002	93.7
13	Black cotton -3	7.90	1.02	0.4	0.07	5.2	0.38	0.05	0.78	0.0003	0.0002	88.6
14	Onattukara-1	1.97	0.6	0.13	0.004	1.0	0.09	0.03	0.12	0.0002	0.0006	92.2

Soil No.	Soil type	CEC [cmol(p+)kg ⁻¹]	Exchangeable cations [cmol(p+)kg ⁻¹]									PBS (%)
			Na	K	Al	Ca	Mg	Fe	Mn	Cu	Zn	
15	Onattukara -2	1.46	0.3	0.13	0.004	0.8	0.07	0.04	0.12	0.0001	0.0006	88.8
16	Onattukara -3	2.50	0.33	0.13	0.11	0.76	0.05	0.03	0.09	0.0004	0.0006	50.8
17	Vellanikkara	3.76	0.64	0.32	0.18	2.1	0.2	0.02	0.3	0.0003	0.0009	86.7
18	Kozhikode	3.78	0.6	0.18	0.004	2.4	0.2	0.03	0.36	0.0002	0.001	89.5
19	Pattambi (upland)	7.59	1.19	0.5	0.52	2.1	0.25	0.005	3.03	0.0004	0.001	53.2
20	Chalissery	1.87	0.24	0.27	0.76	0.47	0.04	0.02	0.07	0.0005	0.0006	54.5
21	Ottappalam	3.35	0.13	0.36	0.19	2	0.23	0.01	0.43	0.0003	0.0004	81.2
22	Pattambi (wetland)	3.27	0.63	0.41	0.17	1.5	0.16	0.03	0.37	0.0003	0.0005	82.5
23	Wayanad-1	5.12	1.15	0.25	0.14	2.2	0.23	0.0004	1.15	0.0003	0.0007	74.8
24	Wayanad-2	5.38	0.9	0.26	0.05	2.9	0.23	0.0007	1.04	0.0004	0.0007	79.7
25	Wayanad-3	2.41	0.44	0.16	0.76	0.78	0.1	0.007	0.17	0.0003	0.0006	61.2

Exchangeable Cu content of the soils was negligible ranging from 0.0001 to 0.001 cmol (p+) kg⁻¹ and lowest value was recorded in Onattukara soil. Percentage Base Saturation also recorded the same trend which varied from 50.8 to 93.7%.

4.3. Availability indices of B

4.3.1. Available B

Table 5 shows the data on available B status of the soils. Available B status varied from 0.04 to 4.21 (mg kg⁻¹). Highest value noted in *Pokkali* and the lowest was in Onattukara soil. Out of 25 soils 15 (60%) were severely deficient in B with <0.5 mg kg⁻¹

4.3.2. Fractions of boron

The data on various B fractions and that of total B are presented in table 5. The water soluble B fraction in the soils ranged from 0.05 to 1.92 mg kg⁻¹. The soluble B fraction of Kozhikode soil recorded the lowest value. Specifically adsorbed fraction of the soils varied from 0.01 mg kg⁻¹ to 0.95 mg kg⁻¹. The MOH-B fractions were in the range of 0.06 to 1.78 mg kg⁻¹. The amorphous Fe-Al occluded fraction ranged from 0.13 to 4.2 mg kg⁻¹. The crystalline occluded B fraction in the soils varied from 0.14 mg kg⁻¹ to 8.0 mg kg⁻¹.

The residual B content of the soils ranged from 10.4 mg kg⁻¹ to 56.8 mg kg⁻¹. The total B content of the soils varied from 11.8 mg kg⁻¹ to 69.2 mg kg⁻¹. Highest total B content was recorded in *Kuttanad* soil and lowest was in Onattukara soil.

The B fractions in quantitative terms existed in the following order

Residual > CRO-B > AMO-B > MOH-B > SPA-B > NSA-B

4.3.3. Correlation of available boron with boron fractions and other soil parameters

Correlation coefficients for available boron with soil parameters and boron fractions are given in table 6a.

Table 5. Available B and B fractions

Soil No.	Soil type	Av.B (mg/kg)	B fractions (mg kg ⁻¹)					Residual B (mg/kg)	Total B (mg/kg)
			NSA-B	SPA-B	MOH-B	AMO-B	CRO-B		
1	Kuttanad-1	3.12	0.31	0.52	0.88	3.64	7.8	55.3	68.5
2	Kuttanad -2	0.26	0.18	0.06	0.94	3.7	7.5	56.8	69.2
3	Kuttanad -3	0.6	0.49	0.07	0.79	4.2	7.5	33.8	46.8
4	Kuttanad -4	0.98	0.14	0.22	0.64	4.0	8.0	27.7	40.7
5	Pokkali-1	3.8	1.26	0.22	1.28	1.27	0.93	17.6	22.6
6	Pokkali- 2	3.27	1.92	0.03	1.78	0.72	0.98	33.4	38.83
7	Pokkali- 3	4.21	1.48	0.02	1.4	1.2	0.9	37.48	42.48
8	Kole-1	0.57	0.4	0.67	0.53	2.3	2.5	31.5	37.9
9	Kole-2	1.07	0.1	0.46	0.44	2.1	3.3	37.2	43.6
10	Kole-3	0.39	0.45	0.95	0.12	2.48	1.0	15.9	20.9
11	Black cotton-1	0.35	0.12	0.31	0.19	1.5	0.8	41.2	44.1

Soil No.	Soil type	Av. B (mg/kg)	NSA-B	SPA-B	MOH-B	AMO-B	CRO-B	Residual B (mg/kg)	Total B (mg/kg)
12	Black cotton -2	0.1	0.12	0.27	0.16	0.94	0.96	45.8	48.3
13	Black cotton -3	0.29	0.06	0.26	0.17	1.23	0.9	27.7	30.3
14	Onattukara-1	0.04	0.11	0.06	0.24	0.36	0.67	10.4	11.8
15	Onattukara -2	0.18	0.44	0.01	0.29	0.21	0.63	19.7	21.3
16	Onattukara -3	0.05	0.11	0.13	0.17	0.13	0.14	18.7	19.4
17	Vellanikkara	0.47	0.16	0.01	0.13	1.07	1.53	40.8	43.7
18	Kozhikode	0.26	0.05	0.14	0.06	1.74	1.86	24.7	28.5
19	Pattambi (upland)	0.45	0.34	0.09	0.27	1.73	2.6	41.1	46.1
20	Chalissery	0.45	0.22	0.12	0.08	1.33	1.47	18.9	22.1
21	Ottappalam	0.49	0.05	0.29	0.24	0.86	2.04	35.35	38.83
22	Pattambi (wetland)	0.1	0.49	0.09	0.11	1.69	2.7	41.02	46.1
23	Wayanad-1	0.6	0.3	0.04	0.39	1.2	1.8	34.0	37.7
24	Wayanad-2	0.65	0.26	0.29	0.41	1.5	2.0	37.0	41.5
25	Wayanad-3	0.48	0.44	0.14	0.36	1.34	2.0	44.3	48.5

Table 6a. Correlation coefficients of available B with B fractions and soil parameters

Sl. No.	Parameters	Av. B	NSA-B	SPA-B	MOH-B	AMO-B	CRO-B	Resid. B	Total B
1	pH	0.627(**)	0.581(**)	-0.194	-0.732(**)	-0.528(**)	-0.471(*)	-0.077	-0.237
2	EC	0.902(**)	0.921(**)	-0.167	0.910(**)	-0.044	-0.056	-0.016	0.031
3	Sand	-0.032	0.244	-0.313	-0.05	-0.816(**)	-0.738(**)	-0.339	-0.482(*)
4	Silt	0.022	-0.251	0.187	-0.013	0.669(**)	0.621(**)	0.086	0.23
5	Clay	0.06	-0.175	0.353	0.121	0.809(**)	0.740(**)	0.470(*)	0.599(**)
6	OC	0.203	0.111	0.252	0.407(*)	0.885(**)	0.840(**)	0.461(*)	0.619(**)
7	Av.K	-0.306	-0.383	0.304	-0.2	0.606(*)	0.570(**)	0.435(*)	0.499(*)
8	Av.P	0.689(**)	0.658(**)	0.063	0.517(**)	-0.132	-0.266	-0.196	-0.184
9	Fe	0.724(**)	0.735(**)	0.302	0.783(**)	0.323	0.151	0.131	0.216
10	Mn	-0.159	-0.127	-0.154	-0.188	-0.025	0.014	0.284	0.237
11	Cu	-0.052	-0.112	0.298	-0.007	0.395	0.358	0.572(**)	0.586(**)
12	Zn	0.786(**)	0.779(**)	0.016	0.752(**)	-0.033	-0.102	-0.08	-0.039
13	Sesquioxide	-0.108	-0.231	-0.038	0.025	0.630(**)	0.590(**)	0.469(*)	0.546(**)
14	Av. B	1.0	0.804**	-0.02	0.855**	0.071	0.067	0.101	0.158

Table 6b. Correlation coefficients of available B and B fractions with CEC and exchangeable cations

Sl.No.	Parameters	Av. B	NSA-B	SPA-B	MOH-B	AMO-B	CRO-B	Resid. B	Total B
1	CEC	0.444*	0.229	0.217	0.438*	0.406*	0.28	0.457*	0.497*
2	Na	0.560**	0.556**	-0.152	0.519**	-0.145	-0.22	0.132	0.095
3	K	-0.044	-0.227	-0.075	-0.026	0.406*	0.467*	0.663**	0.669**
4	Al	0.668**	0.572**	0.21	0.774**	0.634**	0.555**	0.104	0.285
5	Ca	0.064	-0.134	0.218	0.008	0.149	0.046	0.401*	0.361
6	Mg	0.448*	0.297	0.096	0.459*	0.212	0.127	0.435*	0.437*
7	Fe	0.686**	0.433*	0.119	0.464*	0.124	0.091	0.211	0.237
8	Mn	0.051	-0.042	0.098	0.077	0.354	0.266	0.357	0.382
9	Cu	0.823**	0.816**	0.118	0.840**	0.11	0.047	-0.068	0.016
10	Zn	0.730**	0.804**	-0.059	0.766**	-0.075	-0.113	-0.192	-0.139

B, CRO-B, residual B and total B. With respect to organic carbon MOH-B, AMO-B, CRO-B, residual B and total B were correlated significantly. Available K content had significant correlation with AMO-B, CRO-B, residual B and total B. Available boron, NSA-B, and MOH-B are significantly correlated with available P content, available Fe and Zn in these soils. Available Cu had significant correlation with residual and total B. Sesquioxide contents had significant correlations with AMO-B, CRO-B, residual B and total B.

Correlation coefficients for available boron and fractions are given in table 6a. Available B content was significantly correlated only with water soluble fraction (NSA-B) and MOH-B.

Correlation coefficients of available B and B fractions with CEC and exchangeable cations are given in table 6b. Available boron, MOH-B, AMO-B, residual B and total B was correlated significantly with CEC. Exchangeable Na, Al, Mg, Fe, Cu, Zn had significant correlation with available boron MOH-B and water soluble plus NSA-B fractions.

Path coefficients indicating direct and indirect effects on available boron are given in table 7. Direct effect of water soluble plus NSA-B fraction as well as its indirect effect through MOH-B is significant. Similarly the direct effect of MOH-B and its indirect effect through water soluble plus NSA-B with available B are also significant. This means that NSA-B plus water soluble fraction and MOH-B are directly contributing to available B. At the same time these fractions are contributing indirectly to available boron through each other.

Table 7. Path coefficients indicating direct and indirect effects on available boron

	NSA-B	MOH-B	Simple correlation coefficients (r)
NSA-B	0.2893*	0.5148*	0.8041**
MOH-B	0.2430*	0.6127*	0.8557**

** Significant at the 0.01 level

* Significant at the 0.05 level

Note: Direct effects are in main diagonal. Values on horizontal rows are indirect effects.

'r' value represents the simple correlation coefficients of factors listed with available boron.

4.4. Quantity- Intensity studies

Quantity- Intensity relationships with respect to boron in the above soils were studied. From the data obtained from the adsorption study, Q-I curve was plotted with amount of B adsorbed on Y axis and the equilibrium B concentration on X axis. The Quantity and Intensity parameters were calculated from the adsorption experiments with increasing concentrations of B added to a fixed weight of soil samples (2.5g) as detailed in chapter 2. The equilibrium concentration after equilibration for 24 hrs was considered as Intensity factor. The amount of B adsorbed on solid phase per unit weight basis was considered as quantity factor. The Q/I curves were fitted with these data and the intercept and slope were computed from best fit curve using regression analysis. The slope of the curve is taken as buffer power of soil with respect to boron supplying power.

The simple linear equation, $\Delta Q = b X c + K$ was used to obtain the best fit curve where, b is the buffer power (slope of the curve), and K is the intercept. The derived equations are given in table 8a.

4.4.1. Adsorption isotherms

The data obtained from the above said experiment were tried to be fitted in to different adsorption isotherms like Freundlich, Langmuir and Tempkin isotherms. The data for two soils could be described by Langmuir equation; the same two soils followed Tempkin equation also. The data in table 8b give different parameters of Langmuir adsorption isotherm such as bonding energy coefficient (K) and adsorption maxima (M). The data for 22 soils could be described by linear form of Freundlich equation. The Freundlich equations are given in table 8c.

Correlation coefficients of Langmuir adsorption maxima (M) with available B and other soil parameters are given in table 9a. Adsorption maxima correlated significantly and positively with AMO-B, CRO-B and silt, and correlated negatively with sand. The adsorption maxima (M) correlated significantly and positively with bonding energy coefficient (K). Correlation coefficients of Freundlich constant ($1/n$) with available B and other soil parameters (Table 9a) showed that the $1/n$ significantly and positively correlated with available boron.

Table 8a. Buffer power (b) and intercept of Q/I curve of the soils for boron adsorption

Soil No.	Soil	Intercept of the Q/I	Buffer power (b) (L kg ⁻¹)
1	Kuttanad-1	-17.35	0.12
2	Kuttanad- 2	-17.64	0.02
3	Kuttanad -3	7.23	0.45
4	Kuttanad -4	-6.02	0.36
5	Pokkali-1	-8.7	0.21
6	Pokkali-2	-5.93	0.12
7	Pokkali -3	-3.96	0.07
8	Kole-1	-4.36	0.44
9	Kole-2	-4.27	0.51
10	Kole-3	-6.62	0.42
11	Black cotton-1	1.42	0.11
12	Black cotton -2	-10.04	0.43
13	Black cotton -3	-3.62	0.25
14	Onattukara-1	-0.73	0.07
15	Onattukara -2	0.51	0.27
16	Onattukara -3	-3.85	0.31
17	Vellanikkara	-6.76	0.27
18	Kozhikode	-5.08	0.23

Soil No.	Soil	Intercept of the Q/I	Buffer power (b) (L kg ⁻¹)
19	Pattambi (upland)	-5.59	0.25
20	Chalissery	-8.5	0.28
21	Ottappalam	-9.35	0.25
22	Pattambi (wetland)	-1.27	0.21
23	Wayanad-1	-8.77	0.21
24	Wayanad-2	-6.36	0.12
25	Wayanad-3	-4.03	0.11

Table 8b. Langmuir and Tempkin adsorption characteristics of the soils for boron adsorption

Adsorption characteristics	Black cotton 1	Onattukara 2
i) Langmuir equation	$C/(x/m) = 2.8860 + 0.0557C$	$C/(x/m) = 1.5392 + 0.0353C$
K(mL g ⁻¹)	0.3465	0.6497
M (mg kg ⁻¹)	17.95	28.3
Variance explained (%)	57.72	31.73
ii) Tempkin equation	$(x/m)/b = 128.31C$	$(x/m)/b = 127.49C$
A (mL g ⁻¹)	-0.1931	-0.1953
a (mg kg ⁻¹)	0.99	0.99
Variance explained (%)	89.1	69.1

Table 8c. Freundlich adsorption characteristics of the soils for boron adsorption

Soil No.	Soil group	Freundlich equation	K	1/n	Variance explained (%)
1	Kuttanad-1	NS			
2	Kuttanad -2	NS			
3	Kuttanad- 3	$\log x/m=0.6102+1.1635 \log c$	0.6102	1.1635	59.62
4	Kuttanad -4	$\log x/m=0.0124+3.0467 \log c$	0.0124	3.0467	74.50
5	Pokkali-1	$\log x/m=0.0003+4.3203 \log c$	0.0003	4.3203	74.18
6	Pokkali-2	$\log x/m=0.0009+3.8300 \log c$	0.0009	3.8300	75.57
7	Pokkali -3	$\log x/m=0.0009+3.6587 \log c$	0.0009	3.6587	58.1
8	Kole-1	$\log x/m=0.4559+1.1970 \log c$	0.4559	1.1970	85.25
9	Kole-2	$\log x/m=0.2541+1.5460 \log c$	0.2541	1.5460	78.32
10	Kole-3	$\log x/m=0.0608+2.2357 \log c$	0.0608	2.2357	73.1
11	Black cotton-1	$\log x/m=0.6562+0.7644 \log c$	0.6562	0.7644	93.12
12	Black cotton -2	$\log x/m=0.0187+2.8113 \log c$	0.0187	2.8113	89.77

Soil No.	Soil group	Freundlich equation	K	1/n	Variance explained (%)
13	Black cotton -3	$\log x/m=0.0842+1.9400 \log c$	0.0842	1.9400	89.07
14	Onattukara-1	NS			
15	Onattukara -2	$\log x/m=0.7910+0.8099 \log c$	0.7910	0.8099	56.35
16	Onattukara -3	$\log x/m=0.3029+1.3377 \log c$	0.3029	1.3377	84.66
17	Vellanikkara	$\log x/m=0.2079+1.3574 \log c$	0.2079	1.3574	60.7
18	Kozhikode	$\log x/m=0.0679+1.9700 \log c$	0.0679	1.9700	77.66
19	Pattambi (upland)	$\log x/m=0.0826+1.8856 \log c$	0.0826	1.8856	89.74
20	Chalissery	$\log x/m=0.0529+2.0177 \log c$	0.0529	2.0177	68.66
21	Ottappalam	$\log x/m=0.0039+3.2742 \log c$	0.0039	3.2742	85.6
22	Pattambi (wetland)	$\log x/m=0.3695+1.1450 \log c$	0.3695	1.1450	91.83
23	Wayanad-1	$\log x/m=0.0977+1.7315 \log c$	0.0977	1.7315	88.47
24	Wayanad-2	$\log x/m=0.0004+4.0580 \log c$	0.0004	4.0580	55.31
25	Wayanad-3	$\log x/m=0.0306+2.1769 \log c$	0.0306	2.1769	94.28

Table 9a. Correlation coefficients of Langmuir adsorption maxima (M), Freundlich constant (1/n) and buffer power (b) with Av. B, Bonding energy coefficient (K) and other soil parameters

	K	M	Av. B	NSAB	SPAB	MOHB	AMOB	CROB	Sand	Silt	Clay	Ex. Cu	Ex. Zn
M	0.443*	1.0	0.020	-0.172	0.118	0.052	0.408*	0.445*	-0.470*	0.474*	0.390	0.067	-0.032
1/n	0.412*	0.056	0.678**	0.530*	-0.016	0.600**	-0.08	-0.065	0.021	0.308	0.108	0.586*	0.576*
b	0.321	0.413*	0.014	0.231	-0.025	0.119	0.328	0.265	-0.032	0.056	0.067	0.121	-0.221

** Significant at the 0.01 level

* Significant at the 0.05 level

4.5. Pot culture experiment

The experiment was conducted as detailed in section 3.4. The soil with low available B status was selected for the pot culture experiments (Onattukara soil with available B status 0.04 mg kg^{-1}).

Both soil and plant samples were taken and analysed at 2 stages of the experimentation viz. i) Panicle Initiation (PI) stage, ii) Harvest stage. The available boron content in soil and content of B, N, P, K, Ca, Mg, Fe, Mn, Cu, and Zn in grain, straw and leaf were analyzed. The data are presented in tables 10a to 23c.

4.5.1. Available boron in soils

Available B content in the soil sample was estimated at this stage. Available B content in the initial soil sample was 0.04 mg kg^{-1} . The data on available B status at PI stage is given in table 10a. At this stage, the available B status increased from the initial content. The levels of B and organic manure had significant influence on the available B at this stage. The available B content of the soil increased significantly from $0.044 \text{ mg B kg}^{-1}$ to $0.314 \text{ mg B kg}^{-1}$ as the applied B level was enhanced from 0 to 20 kg ha^{-1} . At highest level of B the available B content was reported as 0.286, without organic matter addition. By organic matter addition it was increased up to 0.314 mg kg^{-1} .

Table 10b shows the data on available B in soil, at harvest stage. The levels of B and organic manure had significant influence on increasing the available soil B. The available B content of the soil increased significantly from $0.035 \text{ mg B kg}^{-1}$ to 0.2 mg B kg^{-1} as the applied B level was enhanced from 0 to 20 kg ha^{-1} . By organic matter addition an increase from 0.182 to $0.201 \text{ mg B kg}^{-1}$ was also recorded.

Table 10a. Effect of levels of B and organic manure on available soil B (mg kg⁻¹) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	0.038	0.064	0.051
L ₂ (10 kg B ha ⁻¹)	0.098	0.074	0.086
L ₃ (20 kg B ha ⁻¹)	0.286	0.314	0.300
Mean	0.141	0.151	0.146
C.D	L = 0.005	O = 0.004	O*L = 0.007

Table 10b. Effect of levels of B and organic manure on available soil B (mg kg⁻¹) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	0.025	0.075	0.05
L ₂ (10 kg B ha ⁻¹)	0.133	0.177	0.155
L ₃ (20 kg B ha ⁻¹)	0.182	0.201	0.192
Mean	0.113	0.151	0.132
C.D	L = 0.025	O = 0.021	O*L = 0.036

4.5.2. Biometric Observations at PI and harvest stage

B application of 20 kg ha⁻¹ along with FYM increased plant height significantly at this stage. Highest treatment combination of 20 kg B ha⁻¹ plus 5 tones of FYM yielded best result of 60.13 cm. The data are shown in table 11a.

The levels of B and organic manure did not show any significant influence on the height at harvest stage

The data on number of tillers at PI stage are presented in table 11b. The levels of B and organic manure increased the number .of tillers significantly. At this

stage, maximum number of tillers was noticed in 10 kg B ha⁻¹ applied pot with and without organic manure application.

The levels of B and organic manure did not show any significant influence on the number of tillers at harvest stage.

Table 11a. Effect of levels of B and organic manure on height (cm) of the plants at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	54.87	55.4	55.1
L ₂ (10 kg B ha ⁻¹)	50.93	53.93	52.3
L ₃ (20 kg B ha ⁻¹)	58.17	60.13	59.4
Mean	54.6	56.4	55.6
C.D	L = 2.55		

Table 11b. Effect of levels of B and organic manure on number of tillers of the plants at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	19	14	16
L ₂ (10 kg B ha ⁻¹)	20	20	20
L ₃ (20 kg B ha ⁻¹)	19	18	18
Mean	19.4	17.2	18.3
C.D	L = 1.79	O = 5.47	O*L = 2.53

4.5.3. Yield at PI and at harvest stage

The data on total dry weight, at PI stage are presented in table 12a. The levels of B and organic manure had significant influence on the total dry weight at

this stage. The total dry weight per pot increased as the levels of B increased from 0 to 10 kg ha⁻¹. The highest total dry weight was observed in this treatment without organic manure application. However FYM application without boron also could yield better dry matter production (11.3 g pot⁻¹) in comparison with the control (9.6 g pot⁻¹).

At harvest stage, highest total dry matter yield (15.9 g pot⁻¹) was noticed in treatment with 20 kg boron ha⁻¹ without organic manure application (Table 12b). By organic manure application dry matter yield was decreased from 15.9 g pot⁻¹ to 10.1 g pot⁻¹ at highest level of boron (20 kg ha⁻¹).

The levels of B and organic manure did not show any significant influence on the straw yield at PI stage.

The data on straw yield, at harvest stage are presented in table 13a. The levels of B and organic manure had significant influence on the straw weight at this stage. Straw yield at this stage enhanced directly with organic manure addition but decreased with B application.

Table 14a depicts the data on grain yield, at harvest. Grain yield at this stage is significantly influenced by the levels of B and organic manure. At this stage, highest total grain yield was recorded for 20 kg ha⁻¹ boron application without organic manure. It was noticed that by FYM application grain yield was decreased from 5.7 to 4.15 g pot⁻¹ with 20 kg B ha⁻¹

Table 12a. Effect of levels of B and organic manure on total dry matter yield (g pot⁻¹) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	9.6	11.3	10.45
L ₂ (10 kg B ha ⁻¹)	15.6	10.7	13.23
L ₃ (20 kg B ha ⁻¹)	12.1	10.13	11.12
Mean	12.45	10.77	11.6
C.D	L = 0.183	O = 0.149	O*L = 0.259

Table 12b. Effect of levels of B and organic manure on total dry matter yield (g pot⁻¹) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	11.37	14.4	12.85
L ₂ (10 kg B ha ⁻¹)	13.4	11.85	12.63
L ₃ (20 kg B ha ⁻¹)	15.9	10.1	12.98
Mean	13.6	12.1	12.82
C.D	O*L = 3.19		

Table 13a. Effect of levels of B and organic manure on straw yield (g pot⁻¹) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	2.25	4.05	3.15
L ₂ (10 kg B ha ⁻¹)	2.6	3.4	3.0
L ₃ (20 kg B ha ⁻¹)	3.9	2.0	2.96
Mean	2.9	3.1	3.0
C.D	O*L = 1.05		

Table 14a. Effect of levels of B and organic manure on grain yield (g pot⁻¹) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	4.14	5.66	4.9
L ₂ (10 kg B ha ⁻¹)	5.0	4.04	4.5
L ₃ (20 kg B ha ⁻¹)	5.7	4.15	4.9
Mean	4.9	4.6	4.8
C.D	L = 0.005	O = 0.004	O*L = 0.007

4.5.4. Nutrient content in plants at PI and harvest stage

The data on B content in grains, at harvest stage are presented in table 15a. At this stage, highest B content in grains noticed in 10 kg B ha⁻¹ without organic manure application. Here also OM application decreased B content.

The data on B content in leaves, at PI stage are shown in table 15b. Boron @10 kg ha⁻¹ along with FYM resulted highest B content in leaves at this stage. Here also OM application significantly declined B content from 5.7 to 4.7 mg kg⁻¹ as above.

The data on B content in straw, at PI stage are presented in table 15c. 20 kg B ha⁻¹ without FYM resulted in highest B content in straw at this stage. OM application had significantly reduced B content from 6.05 to 1.17 mg kg⁻¹.

Table 15a. Effect of levels of B and organic manure on B content in grains (mg kg^{-1}) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	1.2	0.58	0.863
L ₂ (10 kg B ha ⁻¹)	6.1	1.0	3.6
L ₃ (20 kg B ha ⁻¹)	3.98	1.9	2.94
Mean	3.76	1.16	2.5
C.D	L = 0.13	O = 0.11	O*L = 0.2

Table.15b. Effect of levels of B and organic manure on B content in leaves (mg kg^{-1}) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	2.64	2.34	2.49
L ₂ (10 kg B ha ⁻¹)	3.12	5.37	4.25
L ₃ (20 kg B ha ⁻¹)	6.05	1.17	3.61
Mean	3.94	2.96	3.45
C.D	L = 0.034	O = 0.028	O*L = 0.049

Table 15c. Effect of levels of B and organic manure on B content in straw (mg kg^{-1}) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	2.8	2.5	2.65
L ₂ (10 kg B ha ⁻¹)	5.18	6.94	6.06
L ₃ (20 kg B ha ⁻¹)	5.75	4.76	5.3
Mean	4.57	4.7	4.67
C.D	L = 0.092	O = 0.07	

The data on N content in grains, at PI stage are presented in table 16a. The levels of B and organic manure had significant influence on the N content in grains. At this stage, highest N content in plant grains was noticed in organic manure added pot without any boron application.

The levels of B and organic manure was not having any significant influence on the N content in grains at harvest stage

Application of 10 kg B ha⁻¹ along with FYM resulted in highest B content in leaves at PI stage (Table 16a). At highest level of B (20 kg ha⁻¹) along with FYM significantly increased the N content from 0.45 to 0.51%.

The levels of B and organic manure was not having any significant influence on the N content in leaves at harvest stage

The data on N content in straw, at PI stage are presented in table 16b. 20 kg B ha⁻¹ without FYM resulted in highest B content in straw at this stage. B application at 20 kg ha⁻¹ along with FYM significantly declined the N content from 0.6 to 0.24%

The levels of B and organic manure did not have any significant influence on the N content in straw at harvest stage.

Table 17a shows the data on P content in leaves, at PI stage. 10 kg B ha⁻¹ along with FYM resulted highest P content in leaves at this stage. At highest level of B with FYM had significantly declined the P content from 1.23 to 0.56 %.

The data on P content in leaves, at harvest stage are presented in table 17b. Only levels of boron application had significant influence on P content in leaves at this stage. However the highest P content was noticed in control pot.

Table 17c shows the data on P content in straw, at PI stage. B at 10 kg ha⁻¹ with FYM resulted in highest P content in straw (0.36 %). By application of organic manure P content declined in highest B applied pot (0.33 to 0.23 %). K content did not show significance in any of the plant parts either at PI or harvest stage.

Table 16 a. Effect of levels of B and organic manure on N content in leaves (%) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	0.637	0.72	0.68
L ₂ (10 kg B ha ⁻¹)	0.85	0.74	0.79
L ₃ (20 kg B ha ⁻¹)	0.45	0.51	0.48
Mean	0.64	0.66	0.651
C.D	L = 0.06	O*L = 0.09	

Table 16 b. Effect of levels of B and organic manure on N content in straw (%) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	0.18	1.3	0.74
L ₂ (10 kg B ha ⁻¹)	0.97	0.77	0.87
L ₃ (20 kg B ha ⁻¹)	0.6	0.24	0.42
Mean	0.58	0.77	0.68
C.D	L = 0.14	O = 0.12	O*L = 0.21

Table 17 a. Effect of levels of B and organic manure on P content in leaves (%) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	0.56	0.45	0.51
L ₂ (10 kg B ha ⁻¹)	0.64	1.3	0.97
L ₃ (20 kg B ha ⁻¹)	1.23	0.56	0.9
Mean	0.81	0.77	0.79
C.D	L = 0.13	O*L = 0.18	

Table 17b. Effect of levels of B and organic manure on P content in leaves (%) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	0.34	0.3	0.32
L ₂ (10 kg B ha ⁻¹)	0.3	0.3	0.28
L ₃ (20 kg B ha ⁻¹)	0.19	0.21	0.2
Mean	0.27	0.25	0.26
C.D	L = 0.06		

Table 17c. Effect of levels of B and organic manure on P content in straw (%) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	0.28	0.36	0.32
L ₂ (10 kg B ha ⁻¹)	0.3	0.32	0.31
L ₃ (20 kg B ha ⁻¹)	0.33	0.23	0.28
Mean	0.3	0.23	0.30
C.D	O*L = 0.09		

Highest Ca content in leaves was noticed in control pot at PI stage (Table 18a). Ca content was decreased significantly from 14150 to 5910 mg kg⁻¹ and from 8230 to 5910 mg kg⁻¹ respectively with increasing levels of B and FYM.

The data on Ca content in straw, at PI stage are given in table 18b. Here also same trend was observed as above. Highest Ca content was observed in control pot with 3048 mg kg⁻¹

Table 18c depicts the data on Ca content in straw, at harvest stage. 10 kg B ha⁻¹ without FYM resulted in highest Ca content in straw. By FYM application the content was declined from 1309 to 1067.3 mg kg⁻¹

Table 18a. Effect of levels of B and organic manure on Ca content in leaves (mg kg^{-1}) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	18755	14150	16452.5
L ₂ (10 kg B ha ⁻¹)	8215	8535	8375
L ₃ (20 kg B ha ⁻¹)	8230	5910	7070
Mean	11733	9532	10632.5
C.D	L = 11.8	O = 9.6	O*L = 16.6

Table 18b. Effect of levels of B and organic manure on Ca content in straw (mg kg^{-1}) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	3048	2225	2638.5
L ₂ (10 kg B ha ⁻¹)	2057	2155	2106
L ₃ (20 kg B ha ⁻¹)	2275	1925	2100.3
Mean	2460.2	2101.7	2280.9
C.D	L = 8.2	O = 6.7	O*L = 11.6

Table 18 c. Effect of levels of B and organic manure on Ca content in straw (mg kg^{-1}) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	1106.3	1946.3	1526.3
L ₂ (10 kg B ha ⁻¹)	2215.8	1292.5	1754.1
L ₃ (20 kg B ha ⁻¹)	1309.0	1067.3	1188.1
Mean	1543.67	1435.3	1489.5
C.D	O = 214.1		

At PI stage, highest Mg content in leaves was noticed at 10 kg B ha⁻¹ with organic manure (Table 19a). By organic manure application Mg content was increased from 521.7 to 540 mg kg⁻¹ at 20 kg B ha⁻¹. Table 19b shows the data on Mg content in straw, at PI stage. 10 kg B ha⁻¹ without FYM resulted in highest Mg content in straw at this stage. By organic matter application Mg content was decreased from 521.3 to 511 mg kg⁻¹ at highest B applied pots.

Table 19a. Effect of levels of B and organic manure on Mg content in leaves (mg kg⁻¹) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	524.7	503.3	514
L ₂ (10 kg B ha ⁻¹)	523.7	555.3	539
L ₃ (20 kg B ha ⁻¹)	521.7	540	530.8
Mean	523.3	532.9	528.1
C.D	L = 7.21	O = 5.9	O*L = 10.2

Table 19b. Effect of levels of B and organic manure on Mg content in straw (mg kg⁻¹) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	530	510	520
L ₂ (10 kg B ha ⁻¹)	547	536	541.5
L ₃ (20 kg B ha ⁻¹)	521.3	511	516.2
Mean	532.8	519	525.9
C.D	L = 1.7	O = 1.4	O*L = 2.34

Table 20a shows the data on Fe content in leaves, at PI stage. Boron at 10 kg ha⁻¹ along with FYM resulted in highest Fe content in leaves (671 mg kg⁻¹). Application of 10 kg B without FYM resulted in highest Fe content in straw at this stage (1263 mg kg⁻¹). Organic matter addition declined the Fe content from 626 to 464 mg kg⁻¹ at this stage.

The data on Mn content in leaves, at PI stage presented in table 21a indicated that highest Mn content (1975.7 mg kg⁻¹) was obtained in the control pot compared to other treatment combinations. The manganese content in leaves, at harvest stage (Table 21b) showed the control treatment giving highest Mn content (652.6 mg kg⁻¹) followed by 20 kg B applied pot (646.6 mg kg⁻¹). Application of 10 kg boron ha⁻¹ with FYM recorded highest Mn content in straw at this stage (1630 mg kg⁻¹).

Table 20a. Effect of levels of B and organic manure on Fe content in plant leaves (mg kg⁻¹) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	425	402.3	413.7
L ₂ (10 kg B ha ⁻¹)	580.3	358	469.2
L ₃ (20 kg B ha ⁻¹)	475	671	573
Mean	327.2	509.7	418.5
C.D	L = 3.7	O = 3.02	O*L = 5.24

Table 20b. Effect of levels of B and organic manure on Fe content in straw (mg kg⁻¹) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	466.6	525.8	496.2
L ₂ (10 kg B ha ⁻¹)	1263	735	999
L ₃ (20 kg B ha ⁻¹)	626	464	545.3
Mean	785.2	575.1	680.2
C.D	L = 3.42	O = 2.8	O*L = 4.8

Table 21 a. Effect of levels of B and organic manure on Mn content in leaves (mg kg⁻¹) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	1975.7	1067.7	1521.7
L ₂ (10 kg B ha ⁻¹)	607	1537.3	1072.2
L ₃ (20 kg B ha ⁻¹)	1016	816.3	916.2
Mean	1199.6	1140.4	1170
C.D	L = 7.2	O = 5.84	O*L = 10.2

Table 21 b. Effect of levels of B and organic manure on Mn content in leaves (mg kg⁻¹) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	652.6	492.7	572.6
L ₂ (10 kg B ha ⁻¹)	483.2	442.4	464.8
L ₃ (20 kg B ha ⁻¹)	380.1	646.6	513.3
Mean	505.3	527.2	516.2
C.D	O*L = 227.7		

Table 21 c. Effect of levels of B and organic manure on Mn content in straw (mg kg⁻¹) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	1415.3	973	1194.2
L ₂ (10 kg B ha ⁻¹)	579.3	1630	1104.7
L ₃ (20 kg B ha ⁻¹)	430	534.8	482.4
Mean	808.2	1045.9	927.1
C.D	L = 6.8	O = 5.5	O*L = 9.4

Table 22a shows the data on Cu content in grains, at harvest stage. The levels of B and organic manure had significant influence on the Cu content in plant grains. The highest Cu content in grains noticed in 10 kg B ha⁻¹ added pot with organic manure application. Organic matter application increased the Cu content from 5 to 6.6 mg kg⁻¹ at 20 kg B ha⁻¹ applied pots.

The data on Cu content in leaves, at PI stage are presented in table 22b. Compared to treatments control gave good result with respect to Cu content (21.7 mg kg⁻¹). By organic matter addition Cu content declined at this stage. An enhancement of boron application to 10 kg ha¹ along with FYM resulted in highest Cu content in leaves at harvest stage (Table 22 c).

The data on Cu content in straw, at PI stage are shown in table 22 d. Control pot recorded highest Cu content at this stage. 10 kg B ha⁻¹ with FYM resulted in highest Cu content in straw at harvest stage (Table 22 e). FYM application also significantly improved Cu content at this stage.

Table 22 a. Effect of levels of B and organic manure on Cu content in grains (mg kg⁻¹) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	21.7	19	20.3
L ₂ (10 kg B ha ⁻¹)	20.3	21.3	20.83
L ₃ (20 kg B ha ⁻¹)	20	17.97	18.98
Mean	20.67	19.4	20.05
C.D	O = 2.52		

Table 22 b. Effect of levels of B and organic manure on Cu content in leaves (mg kg⁻¹) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	4.2	6.1	5.1
L ₂ (10 kg B ha ⁻¹)	2.2	7.0	4.6
L ₃ (20 kg B ha ⁻¹)	5.0	6.6	5.8
Mean	3.8	6.6	5.2
C.D	O = 1.3		

Table 22 c. Effect of levels of B and organic manure on Cu content in leaves (mg kg⁻¹) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	3.1	4.98	4.0
L ₂ (10 kg B ha ⁻¹)	2.8	5.3	4.0
L ₃ (20 kg B ha ⁻¹)	3.3	4.4	3.8
Mean	3.02	4.9	3.95
C.D	O = 1.2		

Table 22 d. Effect of levels of B and organic manure on Cu content in straw (mg kg⁻¹) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	18.3	13.7	15.97
L ₂ (10 kg B ha ⁻¹)	16.3	16.0	16.2
L ₃ (20 kg B ha ⁻¹)	12.7	13.9	13.3
Mean	15.8	14.5	15.14
C.D	L = 1.69	O*L = 2.4	

Table 22 e. Effect of levels of B and organic manure on Cu content in straw (mg kg^{-1}) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	4.4	5.5	4.9
L ₂ (10 kg B ha ⁻¹)	2.2	5.5	3.9
L ₃ (20 kg B ha ⁻¹)	4.2	5.5	4.8
Mean	3.6	5.5	4.54
C.D	O = 1.14		

Table 23 a. Effect of levels of B and organic manure on Zn content in grains (mg kg^{-1}) at harvest stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	30.2	23.7	26.9
L ₂ (10 kg B ha ⁻¹)	24.1	29.9	26.98
L ₃ (20 kg B ha ⁻¹)	31.5	20.9	26.2
Mean	28.6	24.8	26.7
C.D	L = 1.45	O = 1.19	O*L = 2.05

Table 23 b. Effect of levels of B and organic manure on Zn content in plant leaves (mg kg^{-1}) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	20.9	22.3	21.6
L ₂ (10 kg B ha ⁻¹)	23.3	36	29.7
L ₃ (20 kg B ha ⁻¹)	24.3	28.3	26.3
Mean	22.9	28.9	25.9
C.D	L = 1.5	O = 1.2	O*L = 2.12

Table 23 c. Effect of levels of B and organic manure on Zn content in straw (mg kg^{-1}) at PI stage

Level	O ₁ (0 FYM)	O ₂ (5 t FYM ha ⁻¹)	Mean
L ₁ (0 B)	44.7	32.3	38.5
L ₂ (10 kg B ha ⁻¹)	27.5	51.6	39.5
L ₃ (20 kg B ha ⁻¹)	39.3	22.0	30.7
Mean	37.2	35.3	36.23
C.D	L = 1.4	O = 1.1	O*L = 1.9

Table 23a shows the data on Zn content in grains, at harvest stage. The levels of B and organic manure had significant influence on the Zn content in grains at this stage. The highest Zn content in grains noticed in 20 kg B ha⁻¹ application without organic manure. Here also organic manure application reduced the Zn content from 31.5 to 20.9 mg kg⁻¹.

An increase in B application from 0 to 10 kg ha⁻¹ along with FYM recorded highest Zn content in leaves at PI stage (36 mg kg⁻¹). FYM application also significantly improved Zn content at this stage (Table 23b). The data on Zn content in straw, at PI stage are presented in table 23c. Here also same trend was recorded as above.

Discussion

5. Discussion

The results obtained from present investigations are discussed in detail with the support of literature available in this chapter.

5.1. Electrochemical properties, texture and available nutrient status

5.1.1. pH

Data on pH presented in table 4a varied from 2.3 to 6.7. All the acid sulphate /acid saline soils (Kuttanad, Kole and Pokkali soils) were ultra acidic with pH below 3.5. The laterite soils came under the pH range of 4 to 4.8 which are either extremely acidic or very strongly acidic. In terms of acidity the sandy soils of Onattukara region comes under strongly acid (pH: 5-5.5) category. The Wayanad soils were similar to laterite soils in acidity. The black cotton soils of Chittoor area come under the slightly acidic or near neutral. The data on soil pH clearly indicated that the acid sulphate /acid saline soils as well as the lateritic soils were confronted with the problem of soil acidity.

5.1.2. Electrical Conductivity

With respect to EC all the three acid saline soils of Pokkali area were having an EC of more than 4 dS m^{-1} . Soil salinity in Pokkali lands is due to periodic inundation with sea water. Unlike in Kuttanad and Kole lands, Pokkali lands do not have any protection against sea water inundation. The acid sulphate soils of Kuttanad showed higher salinity in comparison with Kole soils. The laterite and lateritic soils as well as Onattukara soils were found to have negligible salinity.

5.1.3. Texture

The texture of Kuttanad soils was mainly clay loam, whereas that of Kole soils are mainly sandy clay loam and that of Pokkali soils are sandy loam in nature. The Onattukara soils, as expected are sandy in texture with $> 90\%$ sand. Black cotton

soils are sandy clay loam while the laterite, lateritic and Wayanad soils were sandy loams.

5.1.4. Available nutrient status

All the soils from Kuttanad, Kole and Pokkali area are rich in organic carbon which was reported by many workers earlier (Thampatty and Padmakumar, 1999). The black cotton soils are medium in organic carbon whereas sandy soils of Onattukara tract are low in organic carbon and hence in organic matter. Wayanad soils are rich in organic carbon whereas the laterite and lateritic soils are medium or high in organic carbon status.

Majority of soils under present study i.e., 10 soils are low or medium in available P status. Only Pokkali soils were found to be rich with respect to P status.

Available K status showed a mixed trend with Kuttanad and Kole soils showing high fertility, Pokkali and black cotton soils low to medium in fertility. The sandy soils of Onattukara are very low in K status whereas the available K status of laterite and lateritic soils varied from low to medium in fertility with one soil (Pattambi) showing high K status.

Among the micronutrients (Fe, Mn, Cu and Zn), Zn was found to be critical (with 0.1 N HCl extractable Zn $< 1 \text{ mg kg}^{-1}$) in 6 soils which included sandy soils of Onattukara tract, one lateritic soil (Soil no. 20) and all the Wayanad soils (Soil no. 23, 24 and 25).

It is also noted that sandy soils of Onattukara were low in all the nutrients except available P.

5.2. Cation Exchange Capacity, exchangeable cations and Percentage Base Saturation

The cation exchange capacity ranged from 1.46 in Onattukara tract to 9.33 cmol (p+) kg^{-1} in Pokkali soil. In all the soils the CEC values were low and were < 8 except in one Pokkali soil and two black cotton soils.

The PBS was highest for black cotton soils. The PBS was lower than 75% in majority of the soil which is an indication of lower status of base elements especially K, Ca, and Mg. Sajnanath (2000) also got similar results.

A perusal of the data on exchangeable ions (Table 4b) showed that the most dominant cation in the exchange complex was Ca followed by Mg and then by Al. It was also noted that exchangeable Ca content was inversely related to exchangeable Al content. In other words Ca saturation was adversely affected by the exchangeable Al content. Further it was noticed that though the PBS was 92 in one of the soils from Onattukara (soil no.14) exchangeable Ca as well as CEC of these soils were very low (1 and 1.974 cmol (+) kg⁻¹ respectively) which would mean that the nutrient retention power of this soil is very low. Seena (2000) also reported the lower CEC values of the tropical Kerala soils with misleading PBS data due to this.

5.3. Available boron and fractions

The data on available boron content (table 5) showed that 15 soils out of the 25 soils under study were having hot water extractable boron content of less than the critical limit (< 0.5mg kg⁻¹). The Pokkali soils were rich in boron. Some of the Kuttanad, Kole and Wayanad soils were also found to have sufficient plant available form of boron. However, all the soils of lateritic origin and all the sandy tracts of Onattukara were critically deficient in available boron. This might be due to leaching of soluble forms of boron along with silica and bases under the influence of tropical humid climate.

The present study aimed at identifying the major soil groups with boron deficiency. The most dominant fraction in which boron exists in soil was residual. The next dominant fraction was amorphous and crystalline oxide occluded fractions. However, non specifically absorbed plus water soluble fraction (NSA- B) was highest in Pokkali soils.

5.4. Correlation studies

Available boron was correlated positively and significantly with EC, available P, Fe, and Zn. Negative significant correlation were obtained for available boron with pH(table 6 a). The negative significant correlation of available boron with pH would mean that availability increases with increase in acidity. This would suggest the possibility that as the pH decreases there might be solubilization of boron occluded in crystalline and amorphous Mn, Fe and Al oxides. This is further supported by the significant negative correlation of pH with non specifically adsorbed and water soluble boron($r = -0.581^{**}$), MOH-B ($r = -0.732^{**}$), AMO-B ($r = -0.528^{**}$), CRO-B($r = -0.477^{*}$).

The significant positive correlation of available boron with EC ($r = 0.902^{**}$) indicated the clear role of boron salts in increasing salinity. In other words, as depicted in Pokkali soils, available boron was the highest in these soils; so also the EC. Further high significant positive correlation EC with NSA plus water soluble boron also endorses this fact. That is, water soluble boron is mainly contributed by the soluble salts from sea water. MOH-B showing a negative significant correlation with pH and positive significant correlation with EC also support the fact that this fraction is also contributing to the water soluble boron under extremely low pH.

The CEC is significantly and positively correlated to available boron as well as to MOH-B, AMO-B and residual B. Among the exchangeable ions exchangeable Na, Al, Mg, Fe, Cu and Zn showed significant positive correlation with available boron as well as with water soluble and MOH-B.

5.4.1. Contribution of boron fractions to available boron

The data in table 6a showed that among the fractions only NSA-B and MOH-B were significantly and positively correlated with available boron. That is water soluble fraction and manganese oxide occluded fractions are contributing to the available pool.

The partial coefficients indicating the direct and indirect effects of NSA-B and MOH –B on available boron opened up that both these fractions are contributing to available pool. The direct and indirect effects of MOH-B are more in quantitative terms (table 7) suggesting the contribution to available pool is mainly from MOH-B through water soluble pool. The data on available boron and fraction also support this argument. That is plants absorb boron from water soluble pool and the depleted water soluble pool is enriched from the manganese oxide occluded pool.

A multiple regression equation including all the parameters significantly correlated with available boron finally yielded the following equations.

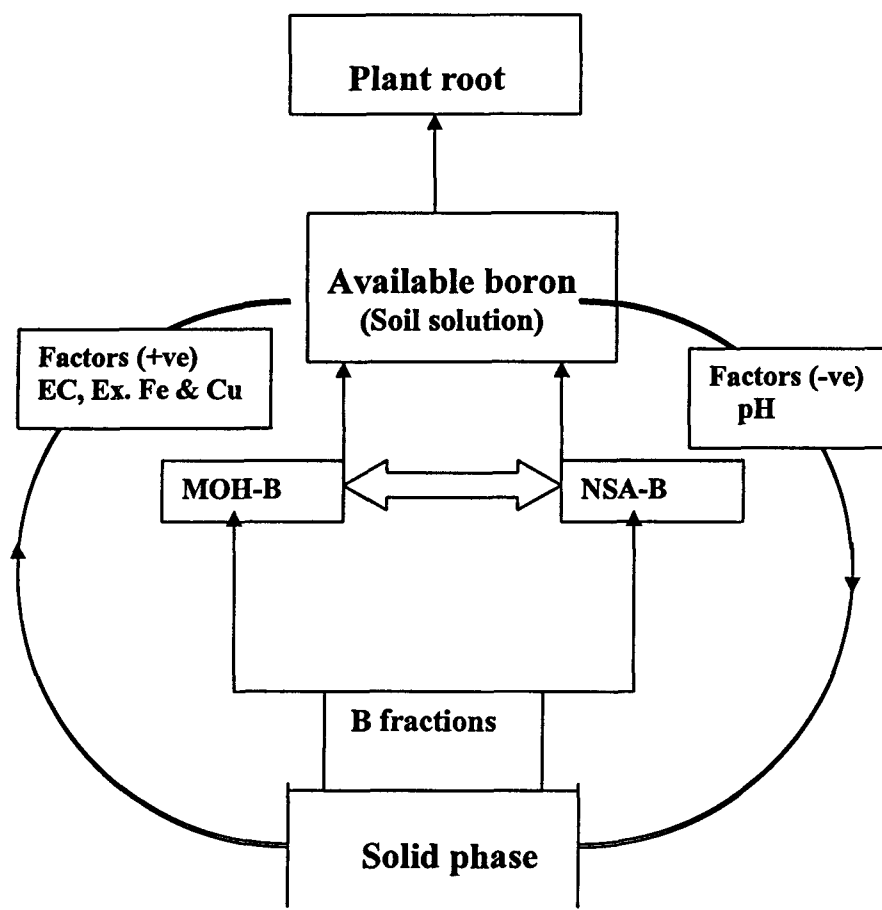
- i) Available B=0.333+0.894 EC, (R²=0.814)
- ii) Available B=0.229+0.738 EC+3.051 exFe, (R²=0.908)
- iii) Available B= -0.116+0.38 EC+3.628 exFe+926.9 exCu, (R²=0.932)
- iv) Available B= -1.47+ 0.345 EC+4.17exFe+1400.02 exCu-0.002 av.Fe, (R²=0.949)
- v) Available B= -0.448+0.403EC+4.48 ex.Fe+1380.5 ex.Cu-0.002 av.Fe+0.09 av.Cu
(R²=0.961)

The above equations clearly indicate that EC is the single most important factor indicating the available boron status explaining 81.4% of variability since soluble boron is the main source contributing to both salinity as well as available B. Inclusions of exchangeable Fe (equation 2) improves the predictability from 84.1 to 90. 8%. By including exchangeable copper the R² value improved from 90.8 – 93.2%. Further inclusion of available Fe and available Cu still improved the predictability to 94.9 and 96.1%.

The above data on contribution of fraction on available pool and on parameters influencing boron availability led to the conclusion that soluble salts of boron are the main source of plant nutrition and that the level of boron in soil solutions is mainly supplemented by the solid phase namely manganese oxy-

hydroxide B. The complete picture of boron dynamics in soils under the present investigation could be depicted as follows.

Fig.1. B dynamics in tropical Kerala soils



5.5. Adsorption study

Among the 25 soils two of the Kuttanad soil did not show any linear relationship between Q and I (Fig.2). In fact there was desorption from the solid phase with increase in concentration of boron. Only at a concentration of 150 mg B L⁻¹ adsorption was observed.

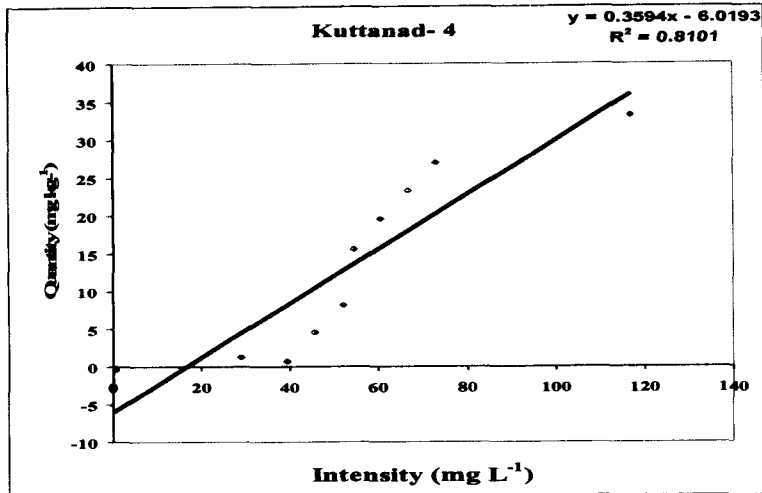


Fig.2a

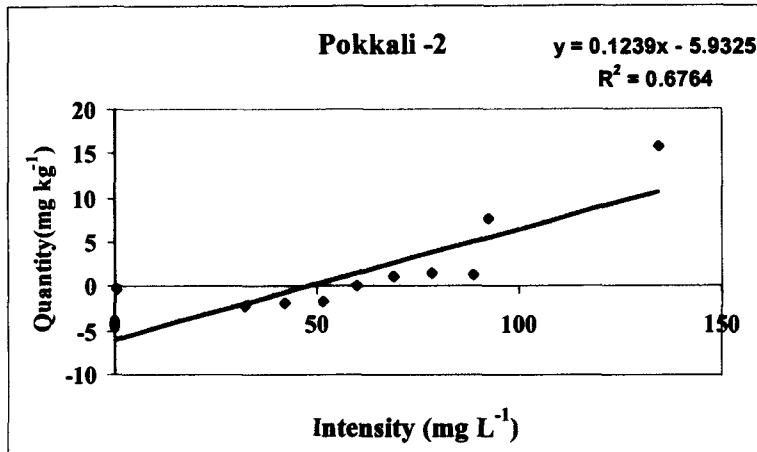


Fig.2b

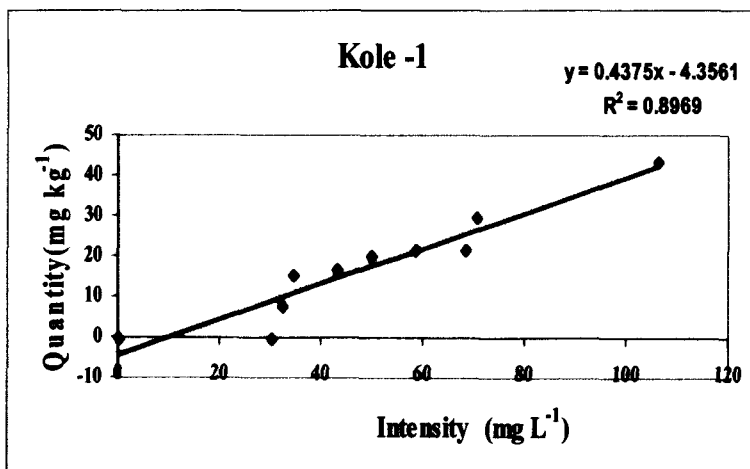


Fig.2c

Fig.2. Quantity- Intensity curves for the soils under study

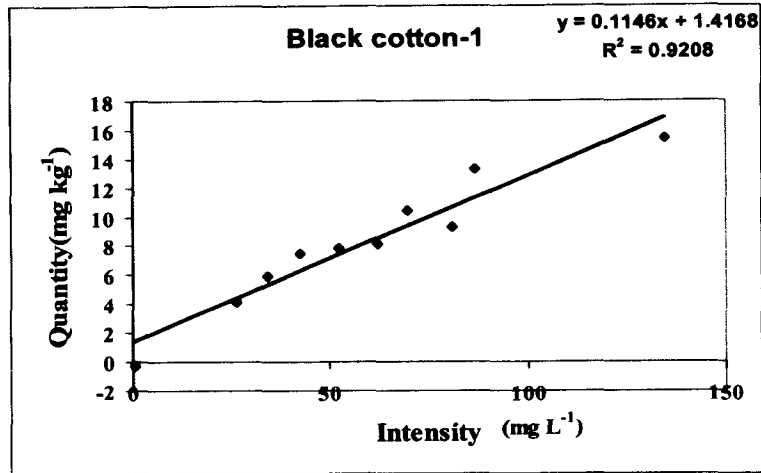


Fig.2d

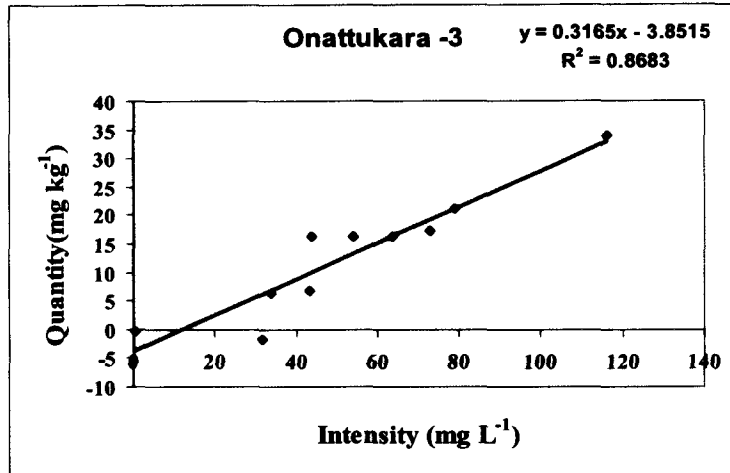


Fig.2e

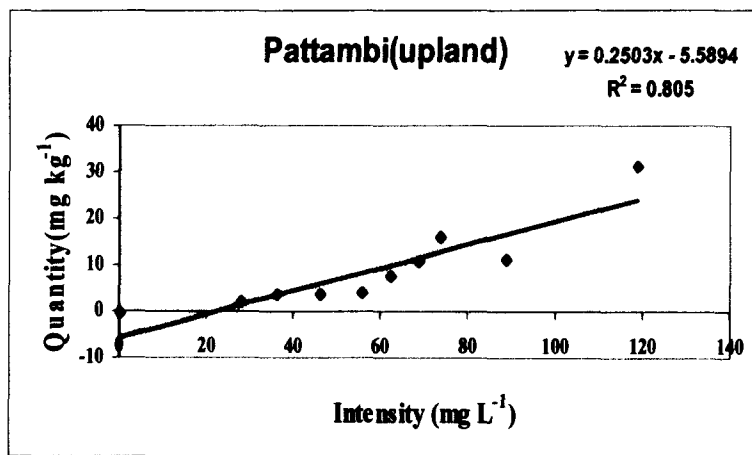


Fig.2f

Fig.2. Quantity- Intensity curves for the soils under study

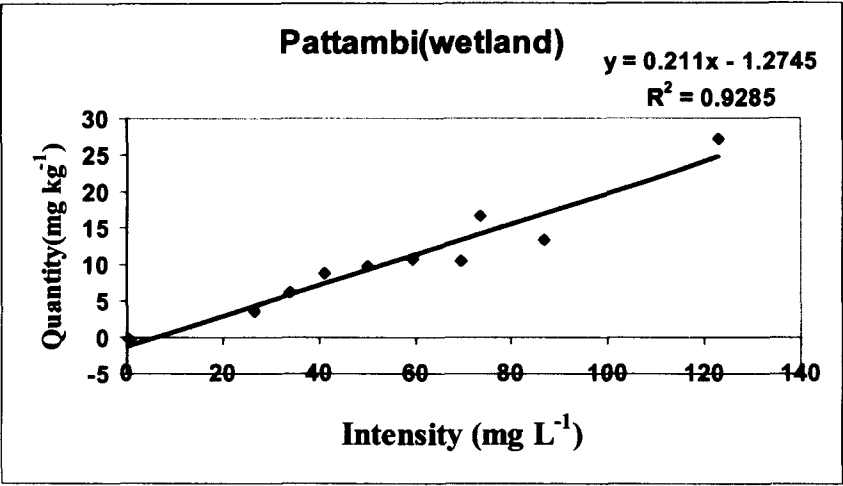


Fig.2g

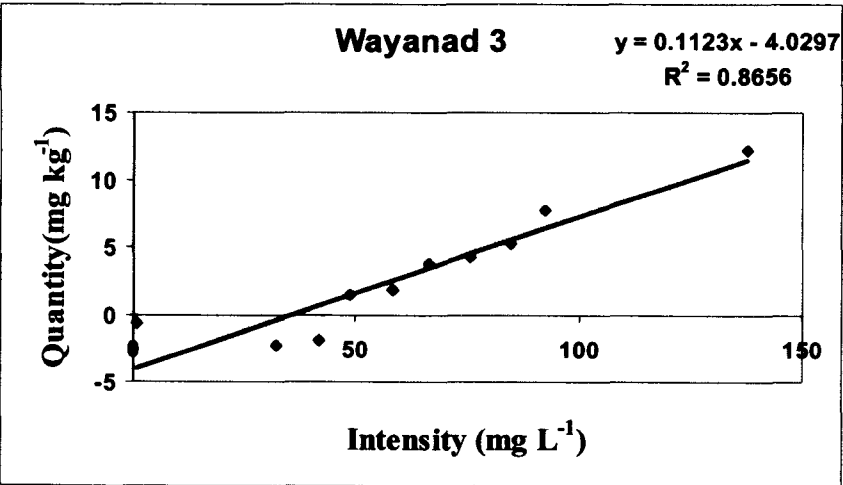


Fig.2h

Fig.2. Quantity- Intensity curves for the soils under study

This might be probably due to higher amounts of reserve of boron on solid phase. One of the Pokkali soils (Soil no. 4) showed the same trend. All the remaining soils except two lateritic soils (Soil no.19 and 20) could give best fit curves with more than 50% variability explained; majority of them could explain more than 80% variability. This could mean that a typical linear relationship existed between the solid phase solution phase B equilibrium. A perusal of the data (Table 8a) clearly indicated that in majority of the soils intercept values were negative which in turn meant that if the intensity factor *viz.* concentration in the equilibrium solution will be maintained by the soil if it is decreased below a particular concentration by the desorption of boron in the solid phase. On the other hand positive value for the intercept would suggest that there should be a minimum amount of boron on the solid phase only above which the solid phase will supplement boron to the solution as depicted in black cotton soil (soil No11). However the individual factors influencing boron adsorption/desorption and boron supplying power of soil are to be further investigated.

The adsorption pattern were further analyzed using three adsorption isotherms namely Freundlich, Langmuir, and Tempkin. The Freundlich ($x/m=KC^{1/n}$) although empirical was interpreted later by Sposito (1980) as to give that the affinity (Bonding energy) decreases exponentially with increasing surface coverage of adsorption which is perhaps nearer to the reality than the assumption of constant bonding energy as in the simple Langmuir equation ($C/x/m= 1/Km+C/M$). The Langmuir equation on the other hand has the advantage that it provides a measure of the adsorption maximum. But as already said bonding energy is uniform for all the sorption sites and remains unaltered throughout the adsorption process. Tempkin equation is based on assumption that the bonding energy of adsorption decreases linearly with increasing surface coverage.

All the soils except Kuttanad 1, 2 and Onattukara 1 were found to follow linear form of Freundlich pattern of adsorption, namely $x/m= K C^{1/n}$ (Fig. 3). The Freundlich constants (K and 1/n) are presented in table 8a. The constant K is defined

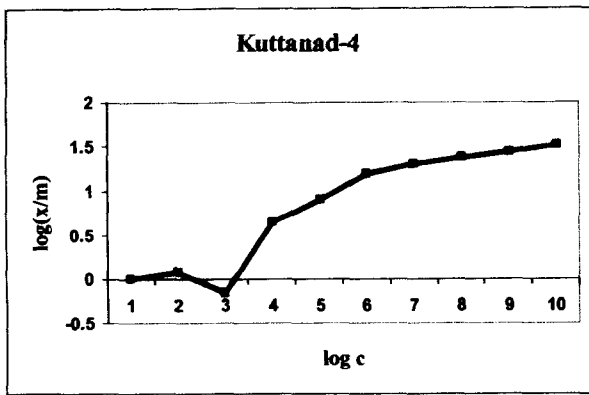


Fig.3a

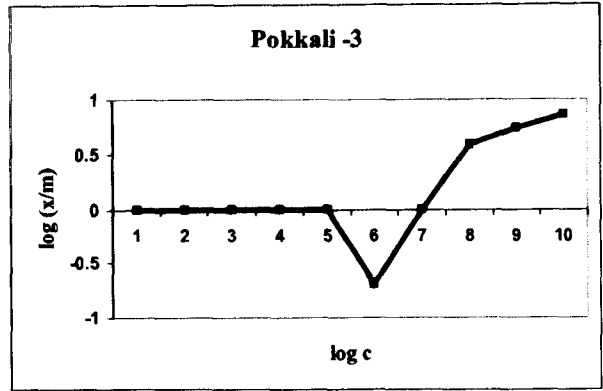


Fig.3b

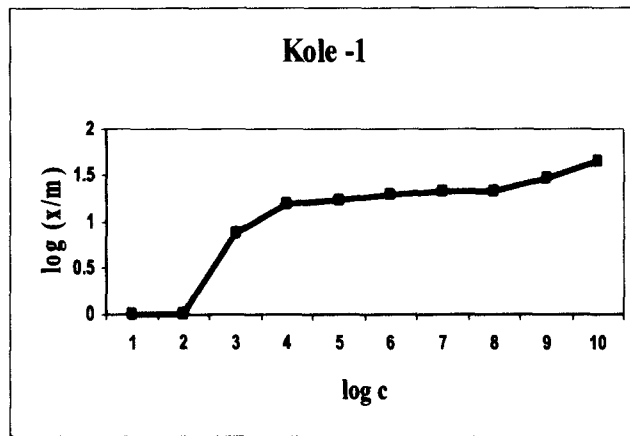


Fig.3c

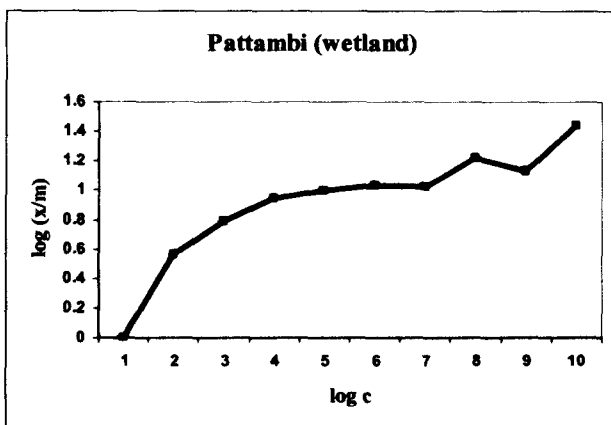


Fig.3d

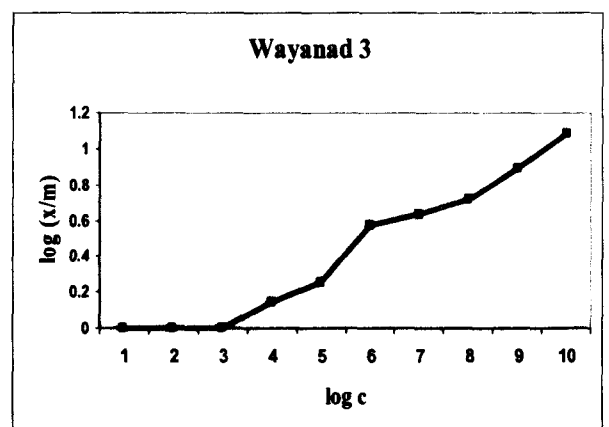


Fig.3e

Fig.3. Freundlich adsorption pattern of soils under study

as the amount of boron adsorbed at unit soil solution concentration. The fraction $1/n$ being the slope of linear form of Freundlich curve ($\log x/m = \log K + 1/n \log c$) which is less than 1 (fraction) only in the case of one each of black cotton and Onattukara soil (soil no12 and 15).

Incidentally the data on adsorption in these two soils could be described by Langmuir adsorption (Fig.4). The adsorption maxima (M) was positively and significantly correlated with AMO-B, CRO-B and silt content while it was significantly and negatively correlated with sand content (Table 9a). This would mean that the adsorption site for B on solid phase might be amorphous and crystalline oxides of Fe and Al and silt fractions of the soil separates. The negative significant correlation of sand fraction would suggest that sand content and hence sandy soils might have low B retention.

The Freundlich parameter $1/n$ was positively and significantly correlated with available B, water soluble B, MOH-B, exchangeable Cu and Zn. Hence $1/n$ is governing available boron in such a way through the fractions contributing to available B. Surprisingly the bonding energy coefficient (K) was found to have no significant correlation with any of the parameter. However significant correlation of Freundlich K with adsorption maximum in Langmuir curve (M) might be considered as an indication of increase in adsorption with increase in concentration until maximum possible surface coverage is attained.

Tempkin equation is based on the assumption that bonding energy of adsorption decreases linearly with increasing surface coverage. The resulting concentration depends for the middle range of surface coverage and should yield a straight line for a plot of x/m against $\log c$. Such plots for soil in many cases however yield gentle curve rather than straight line (Saha *et al.*, 1999).

In the present study only those soils following simple Langmuir type of adsorption (monolayer adsorption) were following Tempkin equation (Fig.5). This

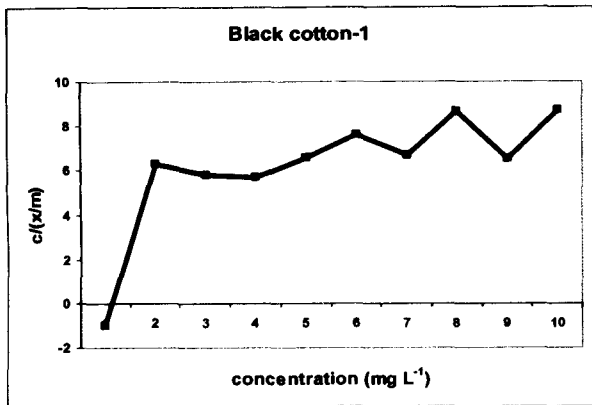


Fig.4a

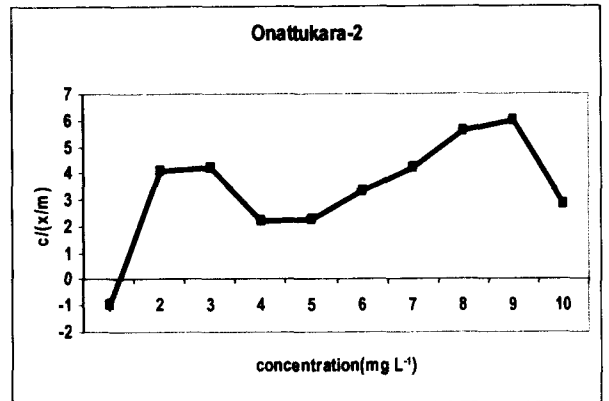


Fig.4b

Fig.4. Langmuir adsorption pattern of soils under study

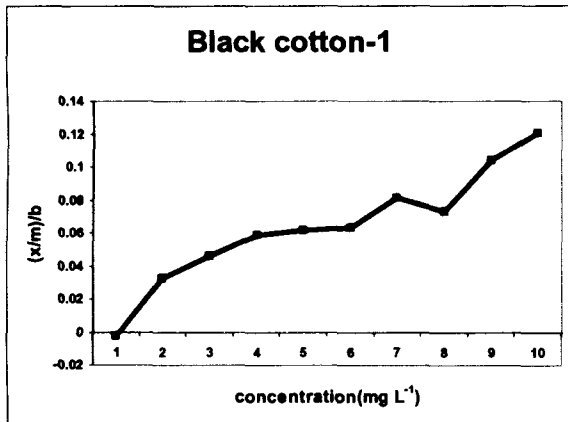


Fig.5a

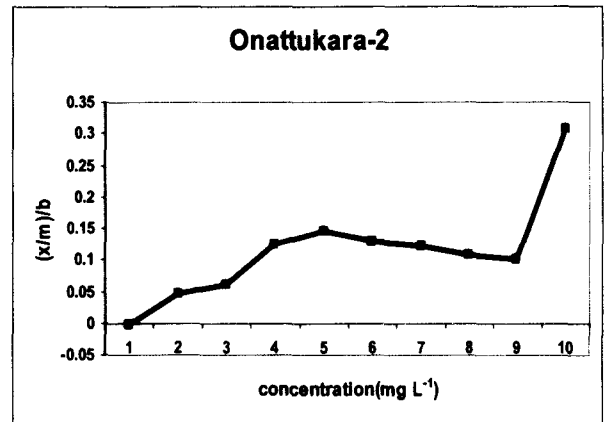


Fig.5b

Fig.5. Tempkin adsorption pattern of soils under study

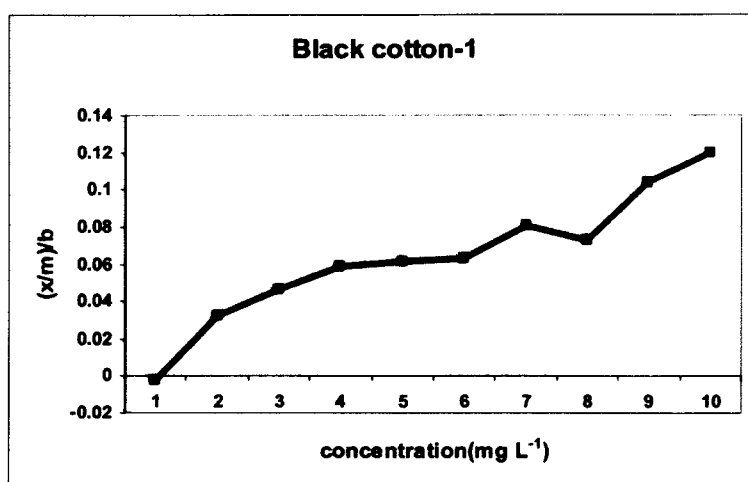
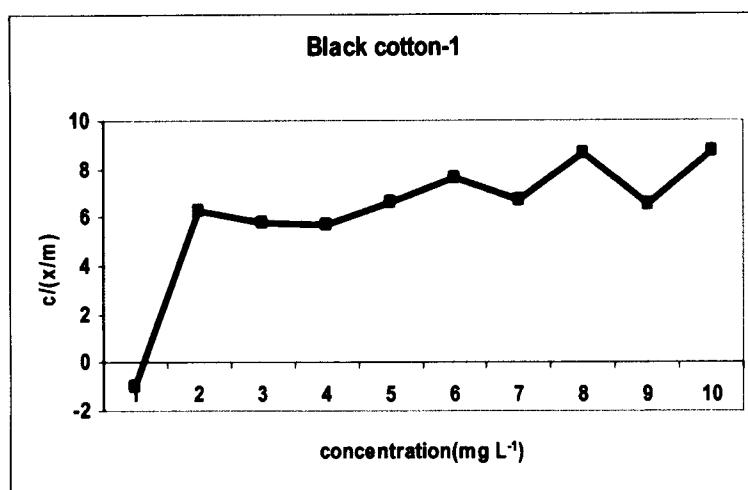
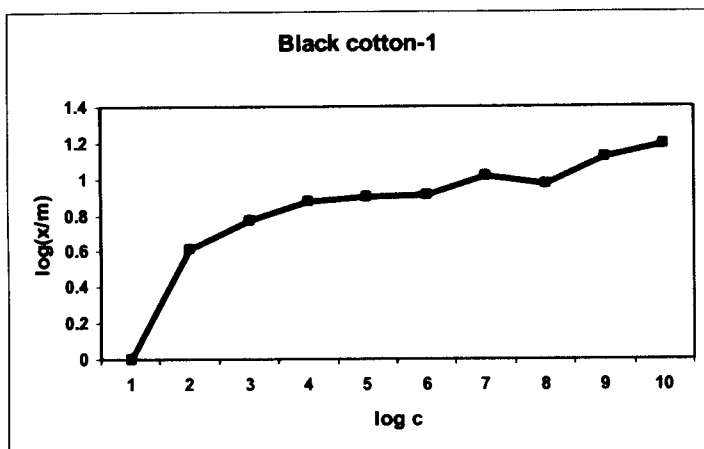


Fig.6a. Comparison of Freundlich, Langmuir and Tempkin adsorption isotherms for Black cotton soil

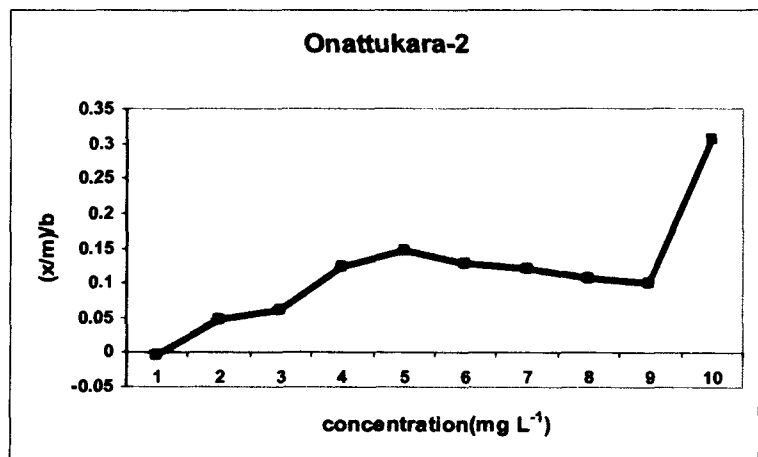
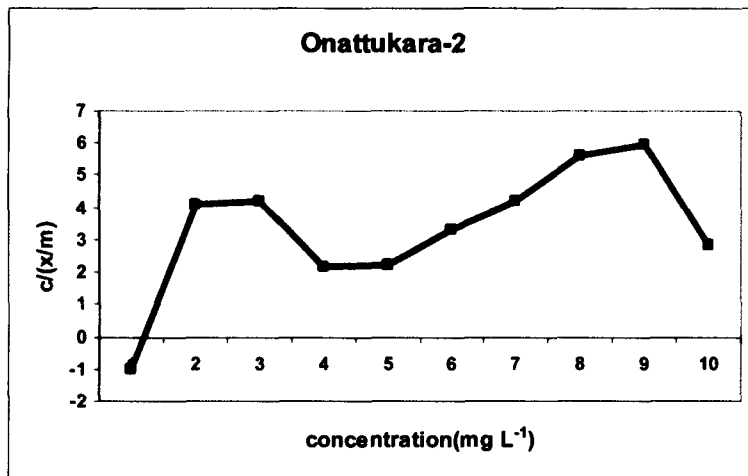
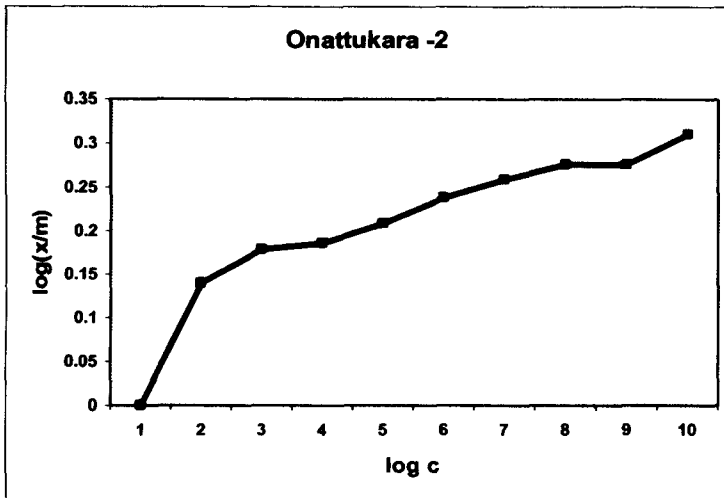


Fig.6b. Comparison of Freundlich, Langmuir and Temkin adsorption isotherms for Onattukara soil

clearly indicated these two soils could adsorb boron as a monolayer over the surface of the adsorbent (Soil solids).

Comparing the three equations the best fit for maximum number of soils to Freundlich equation implies that the affinity (bonding energy) decreased exponentially with increasing surface coverage, a condition which is perhaps nearer to the reality than the assumption of constant bonding energy as in simple Langmuir equation. The best fit for Freundlich equation for majority of the soils over Langmuir and Tempkin could lead to the conclusion that as the surface coverage is more the affinity and strength for further adsorption is decreasing exponentially. In fact this might be the reason why the Kuttanad soils which could not be described by any of the adsorption isotherms. These soils must have large quantity of adsorbed boron covering the entire soil surface that too on the broken edges of oxy-hydroxy bonds of sesquioxides or similar type of minerals in the silt and clay fractions. It can also be concluded that in all other soils the adsorption followed linear form of Freundlich equation.

5.6. Pot culture

5.6.1. Available boron in soil at PI and harvest stage

The data in table 10a and 10b showed the available boron content in soils at panicle initiation stage and at harvest stage. The data revealed that application of B increased the available boron status of soil in comparison with no B fertilization. In FYM applied plots lower level of boron at 10 kg ha⁻¹ could not improve the available boron status in comparison with the treatment of same level of boron without organic manure at panicle initiation. But higher levels of boron i.e., at 20 kg ha⁻¹ improved the available B status to a higher level in FYM applied treatment. i.e., B at 20 kg ha⁻¹ with 5 t of FYM improved available boron status from 0.044 to 0.314 at this stage. The trend was same at harvest stage also. Highest available B was noticed at application of 20 kg B ha⁻¹ along with FYM. This clearly showed that FYM also act

as a source of B, supplying boron at a slower rate. In this context it may be noted that B content of FYM used in the present study was 4.8 mg kg^{-1} which definitely contributed to available boron status at a slower release rate.

5.6.2. Biometric Observations at PI and harvest stage

B application at 20 kg ha^{-1} along with FYM increased plant height significantly at PI stage. Maximum number of tillers was recorded at a boron level of 10 kg ha^{-1} whereas number of tillers was minimum (ie, 14) when FYM was applied without boron (Table 11b). At harvest stage there was no significant effect for any of the treatment combination. As already known any influence on height, number of tillers or any other growth parameter could be depicted at vegetative stage of the crop (Fageria, 2004)). This might be the probable reason the treatments were influencing the growth parameters positively only at PI stage.

5.6.3. Yield at PI and at harvest stage

Data on total dry matter yield at panicle initiation stage showed that highest total dry weight was obtained for 10 kg B ha^{-1} without FYM. However FYM alone without B could yield better dry matter in comparison with the control (14.4 g pot^{-1}). At harvest stage application of boron without FYM increased the dry matter yield with increase in B level. Application of FYM along with different levels of B was found to reduce the total dry matter yield (Fig.7a). i.e., the interaction effect of FYM and boron was antagonistic which lead into reduction in dry matter production. However due to this effect the main effects of neither levels of boron nor that of FYM has any significant effect. The same trend was observed in the case of straw yield also.

Data on grain yield at harvest (table 14b and fig. 7b) also showed the same trend .ie, grain yield increased significantly with increase in B addition in treatments without FYM whereas maximum grain yield was obtained when FYM was applied

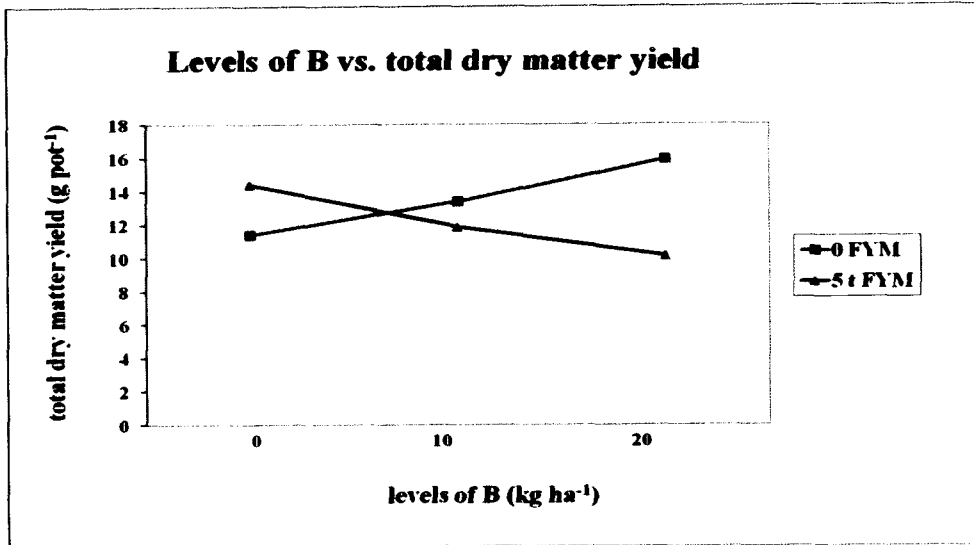


Fig.7a. Response curve showing effect of levels of boron and FYM on total dry matter yield

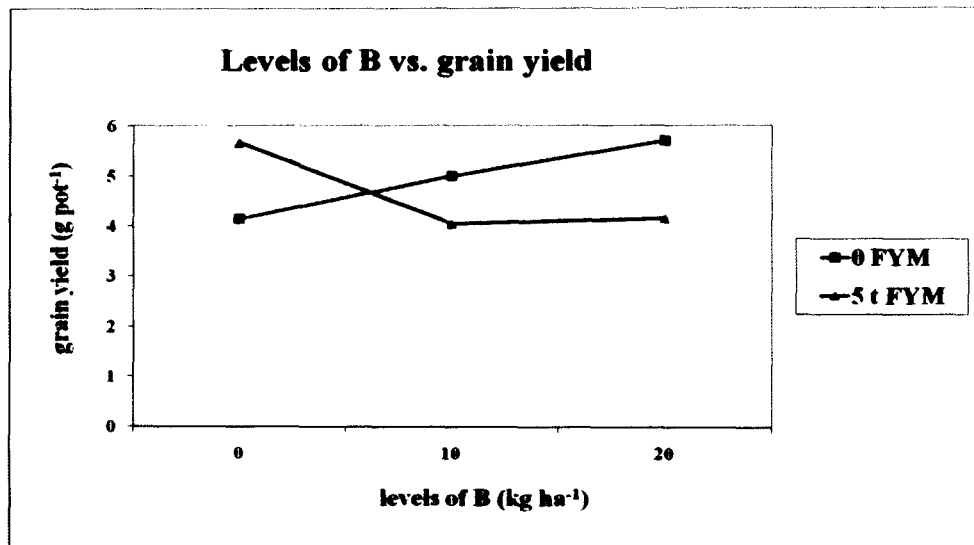


Fig.7b. Response curve showing effect of levels of boron and FYM on total grain yield

without B. Because of these opposing treatment effects of levels of boron and FYM main mean grain yield without B and with highest level of B were on par and significantly superior to B at 10 kg ha⁻¹. Organic matter addition with application of B could only lead to reduction in grain yield (Fig. 7b). These results points to the fact that application of FYM alone could solve the problem of B deficiency. However if B is applied it should not be along with FYM. This also opened up the necessity for detailed investigation on interaction of organic matter with labile boron. Application of soluble forms of B along with FYM might have resulted in formation of insoluble complexes temporarily decreasing the level of boron in soil solution which might have affected B availability when required by the plant for yield forming metabolic process. On the other hand if FYM alone was applied which contained sufficient amount of B to support plant growth was being released slowly as and when needed. The decrease in plant B content in treatments with application of a combination of borax and FYM might also be due to inhibition of B absorption by plant roots due to the antagonistic effect of unknown reasons in the rhizosphere. The same trend of decreasing the absorption of ions was noticed in the case of N, Fe and Mn.

5.6.4. Nutrient content in plants at PI and harvest stages

The B content increased with increase in rates of B in leaf and straw at PI stage. However highest B content in leaves was observed in treatment with 10 kg B ha⁻¹. In B applied treatments the content was highest in leaves and straw when it was applied along with FYM whereas in grains it was highest in boron applied treatments without FYM.

The data on B content in straw and leaves showed that there was no significant difference between treatments at harvest stage. However B content increased with increased level of application in grains. The content was significantly lower in FYM applied treatments, when compared with levels of B without FYM. As already indicated earlier there was definitely antagonistic effect affecting B absorption due to application of borax and FYM together, the reasons are yet to be traced out.

The N content given in table 16a and b in leaves and straw at PI stage increased significantly with application of 10 kg B ha⁻¹ while decreased with highest level of boron, i.e., 20 kg B ha⁻¹ in treatments without organic manure. The N content did not differ significantly in any of the plant part at harvest stage.

The data on P content showed that it was highest when B was applied at 10 kg ha⁻¹ with or without organic matter. P content in leaves at PI stage increased significantly with increasing level of boron without organic manure. The treatment with 10 kg ha⁻¹ with 5 t FYM recorded highest P content in plant leaves (1.3%). The P content in plant leaves at harvest stage was lowest at highest level of boron, i.e., at 20 kg ha⁻¹ (Table 17b). The P content in straw decreased significantly with increase in boron when applied along with FYM. Similarly lowest P content was recorded when 20 kg B ha⁻¹ applied along with FYM.

K content was not significant in any of the plant parts either at PI or harvest stage.

Ca content decreased with increasing levels of B and FYM in case of leaves and straw at PI stage. Organic matter addition reduced the Ca content in leaves and straw at this stage. At harvest stage Ca content was significant only in straw (Table 18c). The Ca content increased significantly at 10 kg B ha⁻¹ application whereas it decreased at highest level of B. Organic matter addition along with B application was found to decrease Ca content. Thus highest Ca content in straw was observed in treatment without any B or FYM application.

As the B level increased content of Mg in straw and leaves increased (Table 19 a & b). Organic matter addition decreased the Mg content in straw while the same was found to get increased with addition of FYM in case of grains and leaves. In straw at PI stage Fe content was highest when applied at 10 kg ha⁻¹ with or without organic manure. When B was applied along with organic manure Fe content in straw at this stage was significantly decreased.

The data on Mn content in different plant parts (Table 21a, b and c) at PI stage showed that highest content of Mn was obtained at higher level of B (20 kg ha⁻¹) while along with organic matter this level of B application recorded lowest Mn content at this stage. In leaves at PI stage Mn content decreased with increased levels of B. The Mn content was found to get decreased with FYM application. In straw Mn content at PI stage was decreasing with increasing levels of boron while it increased with application of organic matter. Thus highest Mn content in straw was recorded when B was applied 10 kg ha⁻¹ along with FYM.

The Cu content in plant grains at harvest stage showed that it decreased significantly with application of B. While the content of Cu decreased in plant leaves at PI stage with application of B and FYM. There was no significant effect for B application on Zn content at grains at harvest stage. Incorporation of FYM decreased Zn content in grains at harvest stage. Zn content in leaves at PI stage increased with increasing levels of boron when boron was applied without FYM. FYM incorporation increased Zn content in leaves significantly at PI stage. The Zn content in straw was significantly decreased by FYM application (Table 23 c).

A perusal of the data on different nutrient contents in different plant parts of rice at PI and harvest stage, could deduce the following trends:

1. Increasing boron levels increased the content of B, N, P, Ca, Mg, Cu and Zn.
2. Addition of FYM along with boron reduced the content of these elements.
3. Application of FYM alone resulted in an increasing trend in nutrient content in different plant parts.

The practical implication of these observations is that good quality organic manure can definitely supplement the micronutrient requirements of the crops. Application of manure could modify the rhizosphere in such a way to restrict nutrient ions luxuriously. However this aspect needs a detailed investigation especially with respect to application of FYM with soluble fertilizers (borax in the present study).

Summary

6. SUMMARY

Representative surface samples (0-20 cm) of eight soil types each from three locations (total 25 samples-including one additional sample from Kuttanad) representing the major rice growing tracts of the state were collected for the present study on ' Availability indices of boron in major soil groups of Kerala'. Samples of these soils were collected from the agro-ecological units (AEU) Kuttanad (Kuttanad, AEU 4), Kole (Kole lands, AEU 6), Pokkali (Pokkali lands, AEU 5), Black cotton (Palakkad eastern plains, AEU 23), Onattukara (Onattukara sandy plains, AEU 3), Palakkad rice soil (North central laterite, AEU 10), Laterite soils from Kozhikode, Vellanikkara and Pattambi (Midland laterite, AEU 11 and North central laterite, AEU 10) and Wayanad Plateau soils (Wayanad central plateau, AEU 20). The soils were characterized with respect to pH, EC, CEC, PBS and exchangeable cations, total sesquioxide and available nutrient status (Organic carbon, available B, P, K, Fe, Mn, Cu and Zn).

Fractionation of soil Boron was done to separate the different forms of boron existing in soil *viz.* nonspecifically adsorbed plus water soluble B (NSA-B), specifically adsorbed B (SPA-B), Manganese oxy-hydroxide bound B (MOH-B), B occluded in amorphous Fe- Al oxides (AMO-B), B occluded in crystalline Fe-Al oxides (CRO-B) and residual boron.

Adsorption studies were conducted with each of the soils to study the adsorption pattern of B in the above soils. The data obtained from boron adsorption experiments were fitted into different adsorption isotherms like Freundlich, Langmuir and Tempkin isotherms. From Freundlich equation, Freundlich constants ($1/n$ and K) were calculated. From Langmuir equation, bonding energy coefficients and adsorption maxima values were calculated.

Among the 25 soils, sandy soils of Onattukara (soil no.14) recorded the lowest available B (0.04 mg kg^{-1}), as well as all other available nutrients except available P.

Based on the lowest available B content this soil was selected for pot culture experiments. The pot culture experiment was carried out at Radiotracer laboratory, College of Horticulture to study the effect of three levels of B with and without organic manure on rice.

The salient results of the present study along with the practical implications are summarized below:

1. 15 soils out of the 25 soils under study were having hot water extractable boron content of less than the critical limit ($<0.5\text{mg kg}^{-1}$), among which the Onattukara sandy soil recorded the lowest available B of 0.04 mg kg^{-1} . Kuttanad, Pokkali, Kole and Wayanad soils have adequate levels of plant available boron, while laterite and black cotton soils were deficient.
2. The total boron content was highest in Kuttanad soil and was lowest in Onattukara soil.
3. The most dominant fraction in which boron existing in soil was residual.
4. The B fractions in quantitative terms existed in the following order
 $\text{Residual} > \text{CRO-B} > \text{AMO-B} > \text{MOH-B} > \text{SPA-B} > \text{NSA-B}$
5. Water soluble fraction (NSA-B) and manganese oxide occluded fraction (MOH-B) were contributing to the available pool.
6. EC is the single most important factor influencing the available boron status indicating the clear role of boron salts in increasing salinity as well as soil solution concentration of boron. This relationship is exclusively due to sea water inundation of Pokkali soils.
7. Available boron correlated negatively and significantly with pH *viz.*, the availability of B increased with increase in acidity

8. Adsorption of boron for 22 soils could be described by Freundlich equation.
9. Both Langmuir and Tempkin equations could be used to describe the adsorption of boron by two soils (Soil No.11-Black cotton & Soil No. 15 - Onattukara).
10. Soils from Kuttanad agro-ecological unit (soil No.1&2) could not be described by any of the adsorption isotherms. As the soils were already rich in Boron there was no adsorption reaction and it led to even desorption.
11. The adsorption maxima (M) from Langmuir equation was positively and significantly correlated with silt content while it was significantly and negatively correlated with sand content. Hence sandy soils will have low B retention.
12. Pot culture experiments revealed that the levels of B and organic manure increased the number of tillers and height significantly at panicle initiation stage.
13. Increasing boron levels increased the content of nutrients at PI and harvest stages. Content of these elements was reduced by the addition of FYM along with boron. FYM contains 4.8 mg kg^{-1} B. Application of FYM alone resulted in increasing nutrient content in different plant parts at the above two stages.

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AVAILABILITY INDICES OF BORON IN MAJOR SOIL GROUPS OF KERALA

By

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ABSTRACT OF THE THESIS

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Abstract

Representative surface samples (0-20 cm) of eight soil types each from three locations (total 25 samples-including one additional sample from Kuttanad) covering nine agro-ecological units representing the major rice growing tracts of the state were collected for the present study on "Availability indices of boron in major soil groups of Kerala". The agro-ecological units (AEU) included were Kuttanad (Kuttanad, AEU 4), Kole (Kole lands, AEU 6), Pokkali (Pokkali lands, AEU 5), Black cotton (Palakkad central plains AEU 23 and Palakkad eastern plains, AEU 10), Onattukara (Onattukara sandy plains, AEU 3), Palakkad rice soil (North central laterite, AEU 10), Laterite soils from Kozhikode, Vellanikkara and Pattambi (Midland laterite, AEU 11 and North central laterite, AEU 10) and Wayanad Plateau soils (Northern High hills, AEU 15 and Wayanad central plateau, AEU 20). The soils were characterized with respect to pH, EC, CEC, PBS and exchangeable cations, total sesquioxide and available nutrient status (Organic carbon, available B, P, K, Fe, Mn, Cu and Zn). Among the 25 soils, 15 soils showed acute boron deficiency chances (Critical limit: $<0.5 \text{ mg kg}^{-1}$ soil).

Fractionation of soil boron was done to separate the different forms of boron existing in soil viz. nonspecifically adsorbed plus water soluble B (NSA-B), specifically adsorbed B (SPA-B), manganese oxy-hydroxide bound B (MOH-B), B occluded in amorphous Fe-Al oxides (AMO-B), B occluded in crystalline Fe-Al oxides (CRO-B) and residual boron. Amount of boron existed in different fractions was in the following order, Residual > CRO-B > AMO-B > MOH-B > SPA-B > NSA-B. Among these fractions, MOH-B and NSA-B contributed to available B directly as well as indirectly through each other. Electrical conductivity or rather salinity is the single most important factor influencing B availability.

Adsorption studies were conducted with all the soils to study the adsorption pattern of B in the above soils. The data obtained from boron adsorption experiments were fitted into different adsorption isotherms like Freundlich, Langmuir and Tempkin

isotherms. 22 soils followed Freundlich adsorption pattern where as only one each of Black cotton soils (Black cotton 1) and Onattukara soils (Onattukara 2) fitted with Langmuir and Tempkin as well.

Onattukara 1, the soil which recorded the lowest available B of 0.04 mg kg^{-1} was used to conduct a pot culture experiment using rice as test crop with three levels of B (0,10 and 20 kg ha^{-1}) with and without 5t of FYM per hectare. The data on soil as well as plant analysis at panicle initiation and harvest stages indicated that available B status improved with increasing levels of B. Grain and total DM yield increased with the increase in boron doses without FYM. It was also noted that FYM alone could meet the B requirement. FYM with borax was found to have antagonistic effects with respect to yield as well as the nutrient contents in rice.