CHEMISTRY AND TRANSFORMATION OF BORON IN SOILS OF KERALA

By

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THESIS

Submitted in partial fulfillment of the
Requirement for the degree of

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COLLEGE OF HORTICULTURE
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DECLARATION

I, hereby declare that this thesis entitled **“Chemistry and transformation of boron in soils 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.

Vellanikkara

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(2009-21-108)

CERTIFICATE

Certified that this thesis, entitled **"Chemistry and transformation of boron in soils of Kerala"** is a record of research work done independently by **Mr. Santhosh, C.** under my guidance and supervision and that it has not previously formed the basis for the award of any degree, diploma, fellowship or associate ship to him.

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We, the undersigned members of the Advisory Committee of **Mr. Santhosh C.** (**2009-21-108)**, a candidate for the degree of **Doctor of Philosophy in Agriculture** with major in **Soil Science and Agricultural Chemistry,** agree that the thesis entitled **"Chemistry and transformation of boron in soils of Kerala"** may be submitted by Mr. Santhosh C. in partial fulfilment of the requirements for the degree.

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Santhosh, C.

DEDICATED TO MY FAMILY

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Introduction

1. Introduction

The element boron is unique among the essential mineral elements because it is the only element normally present in soil solution as non ionized molecule (H_3BO_3). Its quantitative requirement is very small to the tune of 10-20 mg kg^{-1} depending on the crop species. However the range between deficiency and toxicity being very narrow, hence boron needs judicious fertility management. Boron (B) is essential for normal growth of plants because it promotes proper cell division, cell elongation, cell wall strength, flowering, pollination, seed set and sugar translocation (Sims and Johnson, 1991). Boron is critical for the process of cell differentiation at all growing tips of plants (meristems) where cell division is active. Plants deficient in boron continue to undergo cell division in growing tips without differentiation of cells which would otherwise result in cells becoming stems, leaves, flowers, etc. Over the years, researchers have observed a close relationship between the primary cell walls and boron nutrition. Up to 90 per cent of the cellular boron has been localized in the cell wall fraction (Hanson and Breen, 1985; Hanson, 1991). The first symptoms of boron deprivation include abnormalities in cell wall and middle lamella organization (Hu and Brown, 1994 and 1996; Bell *et al.*, 1990).

However, it has been observed that in most plant species the boron requirement for reproductive growth is much higher than for vegetative growth (Matoh *et al.*, 1992) This is especially true for gramineaceous plants, which have the lowest cell wall pectin content and the lowest boron requirement to maintain normal vegetative growth, but need as much boron as other species at the reproductive stage. The major functions of B in growth and development of plants are based on its ability to form complexes with the compounds having *cis-diol* configurations. Loomis and Durst (1992) cited over 70 references that reported the effects of boron on pollen germination, or on flowering and fruiting of plants. Boron deficiency caused sterility in maize and flower malformations in a wide variety of both monocots and dicots. Boron deficiency causes many anatomical, physiological, and biochemical changes, most of which represent secondary effects. Because of the rapidity and the wide variety of symptoms that follow boron deficiency, determining the primary function of boron in plants has been one of the greatest challenges in plant nutrition.

Since boron is non-mobile in plants, a continuous supply from soil or planting media is required for meeting the requirements in all plant meristems. In mineral soils, release of boron is usually quite slow. Much of the available soil boron is held rather tightly by soil organic material. Boron deficiencies are generally related to high rainfall areas with acidic soil environment. Under acid soil conditions, boron is more water-soluble and can therefore be leached below the root-zones of plants by rainfall or irrigations particularly accentuated by light textured soils. It has also been shown that symptoms of boron deficiency are associated with high soil pH values (alkaline conditions). Reduced boron solubility under alkaline soil conditions can result in less plant uptake and increased potential for boron deficiencies. Its deficiency in plants is most widespread in coarse textured, low organic matter, high pH, and calcareous soils as well as in coarse textured, low organic matter, low pH tropical soils. This makes boron fertility management very challenging in most of the arable soils.

Experimental evidence suggests that B uptake is the result of passive assimilation of undissociated boric acid and some ionic forms. Boron uptake by a particular species should, therefore, be primarily determined by the B concentration in the soil solution and the rate of uptake of water by the plants. Soil factors affecting availability of B to plants are: pH, texture, moisture, temperature, organic matter, and the nature of clay minerals (Berger and Troug, 1945; Dyal and Hendericks, 1950; Datta *et al*., 1992). Boron adsorbing surfaces in soil include aluminium and iron oxides, magnesium hydroxide, oxy hydroxides dominated amorphous minerals, calcium carbonate, and organic matter. Plants respond directly to the activity of boron in soil solution and only indirectly to B adsorbed on soil constituents. Keren and Bingham (1985) concluded that maintaining B in the soil solution is important for plant nutrition and it is controlled by the pools of B in different soil fractions and their equilibration with the soil solutions. Although B exists in soil in different fractions as readily soluble, specifically adsorbed, oxide bound, organically bound and residual bound, readily soluble boron which include water soluble and nonspecifically adsorbed boron are immediately available for plant absorption. Hence, fertility management involves making the soil conditions favourable for shifting the equilibrium between these fractions towards maintenance of sufficient levels of boron in readily soluble pool.

Kerala, occupying the extreme end of west coast enjoys a tropical humid climate with an annual rainfall of 3000 mm. The tropical climate itself is responsible for the leaching of cations from soils, accumulation of iron and aluminium oxides in surface soils and rendering it acidic in reaction. The acidity in soil leads to the solubilisation of different forms of boron and its leaching losses in considerable quantities. The tropical soils of Kerala with high rainfall, low pH, low organic matter, higher content of sesquioxide and amorphous hydrous oxide minerals are expected to adversely affect retention and availability of boron. Hence a study on pattern of availability, dynamics and fertility management is to be undertaken at the agro ecological level in the state. The deficiency is nowadays widely reported in important crops such as rice, coconut, arecanut, banana and nutmeg from different parts of the state. Data on neither the status of boron in soils of the state nor its nutritional requirement for important crops is available. Moreover the knowledge on kinetics of transformation of boron, pattern of adsorption in soil and related thermodynamic parameters in these soils are lacking. Even though there are reports on the occurrence of boron deficiency in rice, at present there is no clear management strategy. On these back ground a study was undertaken with the following objectives of:

- Collection and characterisation of soil samples of 23 agro ecological units of the Kerala
- Quantification of boron existing in different forms and their contribution to available pool
- Understanding pattern of boron adsorption and related thermodynamic parameters
- Influence of organic matter on dynamics of boron in lateritic soils
- Optimisation of boron for rice nutrition.

Review of literature

2. REVIEW OF LITERATURE

The chemistry of boron in soils is very simple when compared to other nutrient elements (Goldberg, 1993). Boron does not undergo oxidation-reduction reactions or volatilization reactions in soils. Its acid (boric acid) is very weak, monobasic, and acts as a Lewis acid by accepting a hydroxyl ion to form the borate ion. The boron bearing minerals such as axulite, ulexite and tourmaline are stable to weathering and their contribution to plant available boron is insignificant and is mainly derived from the adsorbed and precipitated B on soil particles particularly in soils rich in oxides (Hingston, 1964; Bingham *et al*., 1970). Boron containing minerals are either very insoluble (tourmaline) or very soluble (hydrated boron minerals) and generally do not control the solubility of boron in soil solution.

Goldberg (1997) conducted a comprehensive study on B reactions in soils. According to her, B is a vital plant microelement. The chemistry of B is an exception compared to other macro and microelements, for the reason that the deficient and toxic B concentration ranges are very narrow. A large amount of B in soil solution directly influence plant growth than B adsorbed on different soil components. Several soil factors including texture, moisture, pH, temperature, clay mineralogy and organic matter influence plant B availability (Adriano, 1986). Diverse B adsorbing surfaces in soils comprise of clay mineral, organic matter, Iron (Fe) and Aluminium (Al) oxides, calcium carbonate and magnesium hydroxide.

Different B adsorption reactions were also reported by using the Freundlich and Langmuir adsorption isotherm equations and the phenomenological Keren model. Micronutrients, especially boron has diverse kind of reactions in soils. The biology and chemistry of B in soil is entirely different from other micronutrients (Loomis and Durst, 1992).

Boron has an imperative relationship with soil salinity, higher salts concentrations along with B significantly lowered the plant growth. Yermiyahu *et al.* (2008) revealed that both boron and salinity concomitantly affected plant growth either through soil or through irrigation water.

The most pertinent literature in respect of boron has been reviewed hereunder.

2.1. Essentiality of Boron

Warington (1923) proved with acknowledged results for the very first time that B was an essential plant nutrient. She conducted experiments on field bean *(Vicia faba)* and concluded that plants mostly died due to nonexistence of boron in the solution culture. Consequently, she suggested that for the renaissance of these plants, B was an indispensable element (Anon., 1935, 1936). Prior to the results of Warington, Agulhon (1910) and Maze (1915), in France established the beneficial effects of B on plant growth. Agulhon (1910), for the very first time, presented the acknowledged facts about prevalence of B deficit in field and sand culture trials, by suggesting that B encouraged the growth of oilseed rape *(Brassica napus* var. *oleifera),* turnip *(B. rapa),*maize *(Zea mays),* oat *(Avena sativa),* radish *(Raphanus sativus)* and wheat *(Triticum aestivum).* In contrast, he did not authenticate that the natural plant growth is unattainable in B deficit or absence. The results of Maze (1915) revealed that B (like aluminium, fluorine and iodine) was needed for growth of maize in solution culture. There again, he did not certify their essentiality but a few ancient studies showed its essential roles in crop nutrition (Arnon and Stout, 1939). After that era, a few other studies also showed its importance in many crops (Dregne and Powers, 1942).

2.2. B status in soils

2.2.1. World scenario

In different Russian states (like Latvia, Belarus, Estonia and Russia), most of the soils had lowest B levels. Pieve (1959) quoted water soluble B values of 0.08–0.38 mg kg^{-1} in Podzoluvisols, 0.30–0.90 mg kg^{-1} in Kastanozems and 0.38–1.58 mg kg^{-1} in Chernozems, while, > 50 % of the central and eastern Poland soils in 11 countries were acknowledged as extremely low in B (characteristically Podzols). In Latvia, almost 40 % of soils were B deficient and these soils were typically Podzoluvisols (Anspoks and Liepins, 1987). Likewise, a few researchers reported that the majority of southern Finland is prone to hold < 0.50 mg B L^{-1} hot water soluble boron. Moreover they also observed that soil B contents were more in soils with elevated pH and enhanced base exchange capacity (Kurki, 1982; Kiviniemi, 1946; Veijalainen, 1983). Wikner (1983) recognized that several B responsive soils in the Sao Paulo district of Brazil are recognized as latosols (Ferralsols), podzolic soil, Luvisols and Acrisols where water soluble B levels are normally < 0.50 mg kg^{-1}.

Sillanpaa (1982) performed an esteemed intercontinental estimation regarding micronutrient levels on the basis of soil chemical analysis in nearly 30 countries. Later, he also worked on boron status in wheat-sown areas of Finland and tropical and Mediterranean regions of the world (Sillanpaa and Vlek, 1985; Veijalainen, 1983). After eight years of research, Sillanpaa (1982) conducted field investigation in 14 participating nations to endorse the demand for micronutrients on the main cereal crops like wheat (*Triticum aestivum*), rice (*Oryza sativa*) and maize (*Zea mays*) and reported that the soils and crops of eleven countries showed good responses to B application.

Zheng *et al.* (1980; 1982; 1989) reported that cultivated soils in east and south China assemble the distinct foremost B scarce area of the planet. The soil maps of China demonstrate vast areas of soils keeping really low hot water soluble B levels (< 0.25 mg kg^{-1}). In north of the Yangtze, soils developed from calcareous and loess alluvium originated from Yellow river, therefore B deficiency is commonly intrinsic (Chang *et al.,* 1983 ; Chang, 1993). Conversely, the arid regions soils of western China are B loaded and typically categorized as *Lithic Yermosols* and *Lithic Kastanozems* (Zheng *et al.,* 1983). In Egypt and Syria, widespread B deficiencies were reported by many researchers (Elseewi and Elmalky, 1979 ; Xue *et al*., 1998) and it varied spatially (Ryan *et al.,* 1977; 1998).Will (1971) reported that B deficiency occurred in soils of New Zealand especially in the forests of pine. In Canada, B deficiency is most prevalent especially in the province of British Columbia on different soils which include *Luvisols, Podzols, Kastanozems* and *Okanagan valley* (Gupta, 1983, 1984). Similarly, B adsorption caused by ashed soils from volcanic activity in Southern Chile was also reported by some scientists (Schalscha *et al.,* 1973).

2.2.2. Indian scenario

In India, investigations on soil B status and crop responses to B application illustrated outstanding B deficit in various states. Sakal and Singh (1995) identified Bihar, Orissa, Meghalaya, Karnataka, West Bengal, Assam and Gujarat as predominantly B deficient areas in India. They further reported that in Maharashtra, most of the soils rarely had B deficiency as these soils were created from the basalts of the *Deccan Trap*. Likewise, other researchers also reported B deficiency in soils of India and responses of different crops to B application (Sarkar, 2006; Sarkar *et al.*, 2006; Prasad, 1978; Singh *et al.*, 1976).

Katyal and Agarwala (1982) reported that total average B content in Indian soils ranged from 3.80-630 mg B kg^{-1} and this total B content had no significance on plant availability. They analyzed 36825 soil samples, and reported that 33 % were deficient in available B. According to them, many crops responded to B application in different agroecological provinces of India (Sarkar, 2006). Available B content of Indian soils ranges from traces to 12.2 mg kg^{-1} (Das, 2000).

In Punjab, available B content of the surface soils has been reported to vary from 0.40 to as high as 7.49 mg kg^{-1} (Katyal and Agarwala, 1982) and in many areas typical B deficiency and toxicity symptoms was observed in many crops. Deficiency of B in alluvium-derived arid and semi arid soils of Punjab had been reported by Bansal *et al*. (1991) and Singh and Nayyar (1999). Boron toxicity has also been reported in soils of Punjab (Mandal *et al*., 1956; Singh and Kanwar, J.S., 1963; Sharma *et al.*, 1989; Arora and Chahal, 2005). Sastry and Viswanath (1946) reported that the total B content of the soils of Punjab, Sindh and Bihar ranged from 16 to 86 ppm and the total B was depended on the quality of irrigation water and the amounts of fertilizers used.

In an attempt to evaluate the B status of soils of some agro-eco zones in India, Ramamoorthy and Viswanath (1946) concluded that the total B content of arid regions varied from 7 to 80 ppm, semi arid regions 36 ppm, humid regions 34.5 ppm, and pre-humid regions 38.5 ppm on an average. Agarwala (1963) reported that the total boron content of alluvial soils, Bhabher soils, Bundelkhand and Vindhyan soils in Uttar Pradesh ranged from 49 to 340, 201 to 586 ppm, 201 to 630 and 58 to 467 ppm respectively.

When thirty major soils of Mewar regions of Rajasthan were analysed, Baser and Saxena (1967) reported that, most of these soils are adequate in soluble boron content and it was highly correlated with the uptake of B by gram plants.

Balasundaram *et al*. (1972), while studying on cold water and hot water soluble B of Tamil Nadu soils, have revealed that the cold water soluble B ranged from 1.6 to 8.0 mg kg^{-1}, while the hot water soluble B ranged from 0.6 to 2.51 mg kg^{-1}. On an average the hot water soluble B of alluvaial, black, lateritic and red soil was 0.64, 1.03, 0.50 and 0.61 mg kg^{-1} respectively.

Datta *et al*. (1994) reported that available B in the soils of Chotanagpur varied from 0.11 to 1.89 mg kg^{-1}. Soil pH, organic carbon and texture did not influence the available B content of these soils.

2.3. Boron availability in soil

Young soils and marine sediments are generally rich in B. Boron may also get accumulated 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.

$$B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+ \quad (pK=9.0)$$

The anion is adsorbed by Al/Fe oxides and clay minerals and the adsorption is stronger with higher 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 Linder, 1973).

2.3.1. Factors affecting B availability in soil

Plants obtain all the essential nutrients from soil medium through their roots, consequently all the soil properties are directly associated with the availability of influential nutrients particularly B. The availability of B is influenced by dynamic soil properties including organic matter, texture, cultivation, drought, and microbial activity (Mengel and Kirkby, 2001). Similarly, the results of other researchers revealed that there was an appreciable relationship amongst SAR, salinity and B on the rice seedling and their germination (Gandhi and Mehta, 1958). B moves in all directions in the soil by mass flow of water. Boron availability decreased with increasing pH and most of the total soil B is unavailable to plants (Borax, 1998).

In diverse soils, a small quantity of B is gradually complexed within organic matter (Yermiyaho *et al.,* 1995; Gu and Lowe, 1990) adsorbed on clays (Bingham 1982; Keren *et al.,* 1981; Hingston, 1964) and to some extent it is precipitated with $CaCO_3$ and is quite unavailable for plant growth (Shorrocks, 1997). Sandy soil (coarse texture) that is well drained is most likely to be B deficient because of leaching (Ouellette, 1958; Rashid, 1995; 1996 b).

2.3.1.1. Effect of calcium carbonate

Retention of B on calcium carbonate occurs via an adsorption mechanism (Ichikuni and Kikuchi, 1972; Scott *et al.,* 1975). The mechanism could be exchange with carbonate groups. The magnitudes of the B adsorption maxima for soil samples treated to remove calcium carbonate were statistically and significantly lower than those for untreated soil samples indicating that calcium carbonate acts as an important sink for B adsorption in calcareous soils (Goldberg and Forster, 1991; Tanaka, 1967). Boron adsorption on reference calcites increased with increasing solution pH from 6 to 9, exhibited a maximum at pH 9.5, and decreased with increasing solution pH from 10 to 11 (Goldberg and Forster, 1991; Communar *et al.,* 2004).

Application of lime increases B fixation by soils because it raises the soil solution pH (Elseewi, 1974, Elseewi and Elmalky 1979; Lehto and Malkonen, 1994; Mandal *et al.,* 1993). In addition to its effect on soil pH, calcium carbonate also acts as an important B adsorbing surface in calcareous soils (Elseewi, 1974; Elseewi and Elmalky, 1979; Goldberg and Forster, 1991). Boron adsorption was greater on soils having higher calcium carbonate content (Elrashidi and O'Connor, 1982; Elseewi, 1974).

Acid soluble B was significantly correlated with calcium carbonate content of soils (Elseewi and Elmalky, 1979). Magnitude of B adsorption on clay minerals is affected by the exchangeable cation (Keren and Gast, 1981, Keren and Mezuman, 1981and Keren and O'Connor, 1982; Evans, 1987). Calcium clays adsorbed more B than sodium and potassium clays (Keren and Gast, 1981; Keren and O'Connor, 1982; Mattigod *et al* ., 1985). An explanation for this result is that calcium 2:1 clays occur as tactoids consisting of several clay particles while the sodium forms exist in solution as single particles (Keren and Gast, 1981). In tactoids, the diffuse double layer and negative electric field from the planar surfaces is less extensive, making the edge sites of calcium clays more accessible to adsorbing borate anions than those of sodium clays (Keren and Gast, 1981). An alternative explanation for increased B adsorption in the presence of calcium is the formation and adsorption of the calcium borate ion pair (Mattigod *et al.,*1985).

According to some studies, B sorption heightens due to elevated levels of calcite in soil and liming diminishes the water-soluble B content of soils (Goldberg and Forster,1991; Lehto and Malkonen, 1994). $CaCO_3$ also acts as B adsorbing medium in calcareous soils because it raises the soil solution pH (Elseewi and Elmalky, 1979). B adsorption was greater on soils having higher $CaCO_3$ (Elrashidi and O'Connor, 1982), this B adsorption is due to the bonding of B with $CaCO_3$ which results in precipitation as Ca-borate or substitution of Carbon by B in $CaCO_3$ or simple surface adsorption of B on $CaCO_3$ (Goldberg and Forster, 1991; Cox and Reid, 1964). Tiwari e*t al.* (1988) reported that the available B content in the surface as well as the sub surface soils of Madhya Pradesh was negatively correlated with $CaCO_3$ but positively with pH

However there are also several reports to show that there was no significant relationship between $CaCO_3$ and water soluble B in soils (Bhattacharjee, 1956; Gandhi and Mehta, 1958 and Mathur *et al.* ,1964)

2.3.1.2. Influence of pH

Soil pH affects plant nutrient availability and thereby plant growth. B at high pH is less available to plants, specially cotton and wheat (Rashid, 2005; Communar and Keren, 2006). Boron availability decreased with increasing pH and most of the total soil B is unavailable to plants (Borax, 1998). Soluble B content in soils was significantly correlated with solution pH (Elrashidi and O'Connor, 1982). Some studies showed that pyrophyllitic soils and different ions played a significant role in B adsorption in relation to pH (Keren and Sparks, 1994; Communar and Keren, 2006). Keren *et al.* (1981) revealed that pH had a specific role in adsorption of B in sodium montmorillonitic clay soils.

In a recent study, a few researchers revealed that calcite which is used to raise soil pH however it maximized B fixation. They further found that adsorption of B straightforwardly amplified with increae in pH and soil pH had certain impacts on adsorption and desorption hysteresis of soils. Rodriguez *et al.* (2001) revealed that pH had certain impacts on B removal in de-salination and reverse-osmosis reactions or processes. Some researchers revealed that B retention by hydroxy Al and Fe was absolutely pH reliant and greatest retention occurred at alkaline pH (Sims and Bingham, 1968). It was accomplished that the hydroxyl ions in these solutions encouraged hydrolysis of the precipitates of hydroxy-Al and -Fe, consequentially B (as borate ions) was released from the precipitates.

Bingham *et al.* (1985) concluded that enhancement in pH > 7 resulted in abrupt decline in B absorption by plants. At pH 6.0, modifications in substrate temperature, addition of 2, 4- DNP and KCN failed to wield any consequences on B absorption. These results clearly signified that B absorption is non-metabolic, physical process in response to concentration gradient of B. Bingham *et al.* (1970) studied quantities of B adsorbed by the soil from a 4.80 mM B solution at pH 6 and 8.5 that included SO_4 or PO_4 ions in variable concentrations up to 0.1M. Soil pretreatment by repetitive saturation with 1.42 mM silica (Si) solution resulted in an insignificant reduction in the magnitude of B adsorbed consequently from the 4.8 mM B solution.

Several reports showed that pH directly controlled B availability to higher plants and B adsorption on primary soil particles (sand, silt or clay) enhances with pH (particularly at pH 5 - 9). Necessarily this means that the greater the pH, the more firmly is B adsorbed to soil and hence reduced availability

Soil pH has specific impacts on B availability more in terms of sorption reactions than by formation of fewer soluble compounds. Mortvedt *et al.* (1999) reported that at pH range of 5.5 – 7.50, the stability of B is highest. Boron is sorbed to Fe and Al oxides in soils and its availability is lowest at pH range 6-9. Numerous studies explained that there were relationships among the existence of Ca ions and B availability and higher Ca levels at elevated pH lessen the B uptake in plants. This is the reason that high B levels in calcareous soils do not produce B toxicity in crops which otherwise might be toxic in conditions other than calcareous.

Kanwar and Singh (1961) reported that water soluble B increases with pH in saline alkali soils of Punjab. In soils of Rajasthan, Mathur *et al.* (1964) observed a similar relationship. Kanwar and Singh (1961) also reported a significant positive correlation between SAR and water soluble B in soils. Bhattacharjee (1956) reported that the availability of of B was comparatively more when the pH is between 6.0 and 8.0. Sharma and Shukla (1972) observed that available B correlated with pH, ESP, clay and organic matter. But Ghani and Haque (1945) and Gandhi and Mehta (1958) reported that there was no relationship between water soluble B and pH

2.3.1.3. Effect of organic matter

Organic matter is an important soil constituent affecting the availability of B. This is considered as the leading source of reserve B because it complexes with B to remove it from the soil solution when the levels are high after B fertilization (Borax, 1998). It then replenishes the soil solution with B to sustain ample levels when B is removed by crops or by leaching. Soil organic matter adsorbs more B than mineral soil constituents on a weight basis (Gu and Lowe, 1990; Gupta, 1979). Boron adsorption on an organic soil (Mengel and Kirkby, 2001) and composted organic matter increased with increasing pH (Yermiyahu *et al.*, 1995). Adsorption of B on soil humic acid increased with increasing pH up to a maximum near pH 9, and decreased with increasing pH above 9 (Gu and Lowe, 1990).

Communar and Keren (2008) studied different impacts of dissolved organic matter (DOM) and treated sewage effluents on B adsorption in soil. They revealed that concentrations of micro and macro elements with organic matter amplified in treated sewage waste-matter via their complexation at pH of 7.70. The influences of humus on adsorption of B were more than that of DOM. Moreover, DOM formed various complexes with free soil solution-B. Consequently, soil B concentration significantly reduced as the total DOM concentration increased.

Many researchers conducted experiments on organic matter (OM) in relation to available B fraction and they concluded that organic matter straightforwardly bestow an imperative responsibility in controlling the soil solution B concentration and there was a significant role of OM in de-sorption or adsorption of B in soils with respect to solution concentration (Marzadori *et al.,* 1991).

Yermiyaho *et al.* (1988) conducted an experiment on B sorption on composted organic matter and results showed that at pH 8.0, the extent of sorbed B enhanced by almost 57 %. They also determined the sorption isotherms of B on organic matter at three pH levels of soil 7.0, 7.90, and 8.90. The sorption improved with high pH and increasing B concentration in solution. The compost restrained 158 g kg^{-1} and 56 g kg^{-1} of humic acid and fulvic acid, respectively, adding together 21.40 % of the OM. They further concluded that at pH 8, the amount of sorbed B increased by about 57 %. The sorption of B enhanced with increasing concentration in solution and pH. They also studied the influence of soil OM content on B uptake by bell pepper along with soil solution B concentration. He revealed that OM significantly affected B uptake by bell pepper plants. Moreover he reported that uptake of B by plant is controlled by soil solution B levels than total soil B content. On the commencement of the trial, B concentration in the soil solution diminished with improving rates of compost and ultimately increasing levels of compost guided to smaller amount of B in the leaf tissues. This decline in B concentration was more at elevated levels of B application. Similarly, the consequences of compost levels on plant B concentration were too enormous at highest B application levels. Adjusted soil solution B concentration was positively correlated with the leaf B concentration.

In the arid regions of western Rajasthan, Satyanarayana (1958) found a significant positive correlation between available B and organic matter content of these soils while the semi arid regions of central parts of Rajasthan the correlation was not significant. Mandal *et al.* (1993) studied the influence of organic matter and lime application on the recovery of added B by different extractants in two B deficient acid alluvial soils and concluded that the effect is well pronounced in the finer textured soils than the coarse textured soils.

The available B status of the major soil groups of Madhya Pradesh showed a positive correlation with organic matter content (Saha *et al*., 1998). Ghosh and Sarkar (1994) showed that available B content of the soils of Sinhbhum and Debatoli soil series had significantly and positively correlated with organic matter content (0.6647**) and negatively correlated with clay.

Ghani and Haque (1945) reported that they could not observe any correlation between organic matter and water soluble B in the soils of Bengal, but they presented evidences that much of the available boron was in the organic combination in these soils. Gandhi and Mehta (1958) also reported that there was no significant correlation between organic matter and water soluble B in the soils of Gujarat.

2.3.1.4. Effect of soil texture

Though not much work has been done on the relation between available B and soil texture, usually in the humid regions the light textured soils contain less available B in the plough layer than do slightly acidic silt and clay loam soils. But the soil texture seemed to have secondary importance in increasing B availability.

Kanwar and Singh (1961) reported a significant positive correlation between saturation water percentage and water soluble B, since the saturation percentage is dependent on the clay content, a relation between the texture and water soluble B could be expected. However Mathur *et al.* (1964) revealed that there was a negative significant correlation between the finer fraction of soil and water soluble B content in the irrigated and non irrigated soils of Rajasthan.

2.3.1.5. Macronutrients

Nitrogen is of utmost importance in affecting B uptake by plants (Chapman and Vanselow, 1955; Lehto, 1995). It is reported that application of N is helpful in alleviating B toxicity on soils low in available N content (Gupta *et al.,* 1985). 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.

2.3.1.6. Methods of application of boron fertilizers

Two principal methods of applying B are soil application and foliar spraying. Soil applications of B made alone or in mixed fertilizers are common, and most data reported on the B uptake have been obtained when fertilizers containing B were added through broadcasting or in bands. Touchton and Boswell (1975) reported that band-or foliar-applied B in corn resulted in greater B uptake in plants than B applied by broadcast. Early foliar application results in greater absorption of B than when applied at later stages of growth (Gupta and Cutcliffe, 1972; 1978). Mortvedt (1991) stated that early-morning foliar applications of nutrients may result in increased absorption, as the relative humidity is high, the stomata are open, and photosynthesis is taking place.

2.3.1.7. Quality of irrigation water

In the arid areas of Rajasthan, Mathur *et al.* (1964) found that the use of well waters containing 2.8 to 4.1 ppm boron for irrigation increased water soluble B of surface soil from 0.35 to 2.03 ppm and that of sub soil from 0.36 to 4.87 ppm. Their findings reveal that waters containing more than 2.0 ppm boron can build up a higher boron status in soil which might be toxic to the crop growth. Kanwar and Singh (1961) reported that liberal use of irrigation water containing B above the safe limits may build up high B concentration in soil.

2.3.1.8. Salt concentration

In arid soils the available B exists as sodium or potassium borates. Under conditions of saline and sodic soil formation boron moves along with other salts and get deposited at the surface. Kanwar and Singh (1961) reported that there was highly significant positive correlation between water soluble B and electrical conductivity of saturation extract of soil. Gandhi and

Mehta (1958) also reported that saline soils of Gujarat and Maharashtra contains much higher water soluble B than non saline soils of the area.

2.3.1.9 Climate

The B deficiency is normally found in the tropical humid climate where the soil is acidic compared to the soils of the low rainfall areas. Kanwar and Singh (1961) determined the B content of soils of different agro climatic regions of Punjab with rainfall varying from 25 to 178 ppm and concluded that water soluble B of the soils of the zone with annual rainfall of 50 to 76 cm, 76 to 102 cm, 102 to 178 cm were 0.38, 0.19, 0.34 ppm respectively. Mandal *et al.* (1993) reported that the fixation of B in six soils under study varied from 6.5 to 11.1 mg kg^{-1} as the texture varied from sandy loam to clay loam. Gandhi and Mehta (1958) reported that leaching of B was high in uncultivated soils than in cultivated soils.

2.4. Boron fractions present in soils

Many soil scientists conducted experiments on fractionation schemes to evolve the B distribution in soil (Hou *et al.,* 1994, 1996; Jin *et al.,* 1987). Fractionation of soil B provides an insight into its diverse forms in which B exists in soil, B dynamics, bioavailability and other environment hazardous implications (Scott *et al.,* 1975). In soil, B is distributed in various soil components like soil solution, organic matter and clay minerals. Readily soluble B in soil solution is known as plant available B, nevertheless this B hardly represent < 3% of entire soil B (Tsadilas *et al*, 1994; Jin *et al.,* 1987; Russell, 1973). Recent studies also clearly indicated that residual B constituted the most important fraction of 78.75% (Zheng *et al.,* 1989). Datta (1996) reported various procedures for extraction and determination of soil boron. Plants vary in their B requirement, but the range between deficient and toxic soil solution concentrations for B is lesser in comparison with all other plant nutrient elements.

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.

Datta *et al.* (2002) evaluated the existing sequential fractionation scheme for boron involving the use of chemicals, the extraction scheme proposed here partitioned B in to five pools as readily soluble, specifically adsorbed, oxide bound and residual B. Relationships of individual B fractions with physico chemical properties of the experimental soils confirmed the validity of the proposed fractionation scheme. The relationships of different B fractions with extractable B in soils suggest that hot $CaCl_2$ and salicylic acid may be better extractants for available boron in soils.

Rashid *et al.* (2007) conducted field and greenhouse experiments to assess the importance of B distribution in calcareous soils as it influenced the bioavailability and discharge for plant utilization. Out of nine soils employed in this investigation, eight soils were medium textured and exceptionally low in organic matter content. Except the *Shahdara* series (tested at 0.30 mg kg^{-1}), hot water soluble B passed its critical boundary of 0.50 mg kg^{-1} in all soils. Total B content ranged from 31- 41 mg kg^{-1} while non-specifically adsorbed B (extracted by $CaCl_2$), specifically adsorbed B (extracted by mannitol), B occluded in Mn hydroxides (extracted by HCl-NH_2OH) and B occluded in non-crystalline Al and Fe oxy hydroxides (extracted by NH_2-oxalate) were 1.20 %, 17.40, 55.90 % and 10.50 to 23.80 % of total soil B, respectively.

Hot water soluble boron (HWSB) content was less in ignored soil than finely supervised soils. They also revealed that soil OM and HWSB were significantly correlated (at $P < 0.01$) with total B. Elevated soil B quantities were fixed during 8 to 12 weeks than after 2 to 4 weeks of incubation periods. An elevated proportion of boron was fixed or adsorbed in the sandy clay loam (*O'leary*) followed by sandy loam soil (*dunstaffnage*) with each practice of incubation. Above a twelve-week period, altering the soil moisture content from 50 to 100 % of the field capacity had no influence on fixed B. The maximum HWSB amounts were recorded in *Caribou* silt loam, *Acadia* silty clay loam and silt loam to *Interval* loam to soil series while it was relatively minimum in *Permo-carboniferous* rocks derived soils (Gupta, 1969; Hou and Houng, 1991). Similarly, Gupta (1969) could get an important correlation between hot water extractable B and total soil B together with fixation of supplemental B. He also reported that hot-water soluble and total B content of soils respectively fluctuated from 0.38-4.67 and 45-124 mg kg^{-1}. Usually the B content was uppermost in heavy textured and lowest in light textured sandy soils. HWSB fraction changed from 0.44 to 4.69 % of total soil B, with negligible proportion in the coarser soils and greatest in the finer soils. Likewise, some other researchers also reported HWSB content in Taiwanese soils (Hou and Houng. 1991; Lee, 1995; Yang, 1960).

In soil mass, B is distributed in various soil components like soil solution, organic matter and clay minerals. Xu *et al.* (2001) in a detailed study about B-fractions of 13-chinese soils and concluded that non-specifically and specifically adsorbed B comprised <1% of total B while residual B was dominant in all soils. Readily available B in soil solution was known as plant available B however; this B form only constitutes <3% of total soil B (Tsadilas *et al*, 1994; Jin *et al.*, 1987).

Hot water extractable B had been regarded as a suitable index of plant available B (Bingham, 1982). But in some studies, levels of hot water extractable B had 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 *et al.* (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. Tsadilas (1997) showed that B content in olive tree leaves correlated well with amorphous Fe-Al oxyhydroxide-occluded B, specifically adsorbed B and Mn-oxyhydroxide-occluded B besides water soluble B.

Jin *et al.* (1987) studied B fractionations in relation to its availability to corn in 14 soils and reported that only 0.34, 0.23 and 0.05 to 0.30 percent of the total soil B was in water-soluble, non-specifically adsorbed, exchangeable, and specifically adsorbed forms respectively. According to Hou *et al.*, (1994 ; 1996) specifically adsorbed and readily soluble B accounted for only < 2% of the total soil B while organically bound B and oxide bound B contained 8.6% and

2.3 %, respectively. Most soil B was found in residual or occluded forms (Hou *et al.,* 1994; 1996; Jin *et al.,* 1987). Zheng *et al.* (1989) also reported that residual B constituted the most important fraction accounting an average content of 78.75% of total boron in soil. Datta (1996) reported various extraction procedures to determine B fractions in soil.

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) is 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).

2.5. Boron adsorption on soils

When B is released by minerals or by organic matter during its weathering, or when it is added to soil through fertilizers, a large part of it remains in solution, while another part is adsorbed by soil particles (Gupta *et al*., 1985). Boron can be adsorbed by iron and aluminum oxides and their hydroxides or by several clay minerals (Keren and Gast, 1983; Goldberg and Glaubig, 1985). Bingham *et al*. (1971) found a positive correlation between the content of Al_2O_3 and the adsorption of B in four Mexican soils and six Hawaiian soils.

Soil organic constituents also play an important role in soil B adsorption. Available B is found associated mainly with organic matter and this explains the high available B contents in surface horizons (Evans and Sparks, 1983). Boron adsorption on soil is affected by many factors.

2.5.1. Factors affecting B adsorption on soil

2.5.1. 1. *Effect of pH*

Boron adsorption is highly influenced by pH, increases as the pH increases, attaining a maximum in the alkaline range and diminishes abruptly at high pH (Keren and Gast, 1983; Goldberg and Glaubig, 1985). The maximum development of adsorption sites occurs at a pH equivalent to the pK of boric acid, approximately 9.1 (Schalcha *et al*., 1973). The agricultural practice that is most often used to raise pH is liming. It is expected that after liming, there will be an increase in B adsorption, especially in soils that contain high amounts of iron and aluminum oxides. Hatcher *et al*. (1967) showed that the adsorption of B increased two to five times after liming in various acidic North American soils, accompanied by a pH increase. In a Brazilian medium-textured O*xisol* (Cruz *et al*., 1987), lime application to increase the pH from 4.2 to 5.6 significantly increased (around 14%) the amount of adsorbed boron.

2.5.1. 2. *Oxide minerals*

The adsorption behaviour of B on Al and Fe oxide minerals (McPhail *et al*., 1972; Choi and Chen, 1979; Goldberg and Glaubig, 1985) as well as on layer silicate clay minerals (Sims and Bingham, 1967; Keren and Mezuman, 1981; Mattigod *et al*., 1985; Goldberg and Glaubig, 1986) has been investigated previously. Boron adsorption on both types of minerals exhibited strong pH dependence. Adsorption peaks for the oxide minerals occurred in the pH range 7 to 9 (Goldberg and Glaubig, 1985). For the clay minerals the range for the adsorption peaks was shifted upward to pH 8 to 10 (Beyrouty *et al*., 1984; Goldberg and Glaubig, 1986).

Boron adsorption on both crystalline and amorphous aluminum and iron oxides increased with increasing pH up to an adsorption maximum at pH 6 to 8 for aluminum oxides and pH 7 to 9 for iron oxide (Bloesch *et al*., 1987; Choi and Chen, 1979; Goldberg and Glaubig, 1985; McPhail *et al*., 1972; Metwally *et al*., 1974; Scharrer *et al*., 1956; Su and Suarez, 1995). Above the maximum, B adsorption decreased with increasing pH. Boron adsorption was greatest on freshly precipitated solids and decreased with aging due to increasing crystallinity (Hatcher *et al*., 1967).

Boron adsorption per gram was greater for aluminium than iron oxides (Goldberg and Glaubig, 1985; Scharrer *et al.*, 1956). This is likely due to the higher surface area of aluminum oxides, since adsorption per square meter was similar in magnitude for aluminum and iron oxides (Goldberg and Glaubig, 1985). Boron adsorption on oxide minerals occurred rapidly, being virtually complete after one day of reaction time (Choi and Chen, 1979; Scharrer *et al*., 1956).

Mechanism of B adsorption on aluminium and iron oxide minerals is considered to be ligand exchange with reactive surface hydroxyl groups (Goldberg, 1993; McPhail *et al* 1972). Ligand exchange with surface hydroxyl groups is a mechanism whereby anions become specifically adsorbed on mineral surfaces. This specific adsorption produces a shift in the zero point charge (ZPC) of the mineral to a more acid pH value. Boron adsorption occurs specifically since it produces a shift in ZPC of aluminum and iron oxides (Alwitt, 1972; Fricke and Leonhardt, 1950; Goldberg, 1993; Su and Suarez, 1995). Specifically adsorbed ions are held in inner-sphere surface complexes that contain no water between the adsorbing ion and the surface functional group. Kinetic experiments using pressure jump relaxation indicated that B got adsorbed as an inner-sphere surface complex on aluminum oxide via ligand exchange of borate with surface hydroxyl groups (Toner and Sparks, 1995).

Fourier transform infrared spectroscopic analyses have shown that B is adsorbed via ligand exchange as both $B(OH)_3$ and $B(OH)_4$ species on amorphous aluminum and iron oxide (Su and Suarez, 1995).

2.5.1.3. *Soil texture*

Adsorbed B is dependent on soil texture, and increased with increasing clay content (Bhatnager *et al*., 1979; Elrashidi and O'Connor, 1982; Mezuman and Keren, 1981; Wild and Mazaheri, 1979). Boron adsorption maxima increased with increasing clay content (Biggar and Fireman, 1960; Goldberg and Glaubig, 1986; Nicholaichuk *et al*., 1988; Singh, 1964). A highly significant correlation was found between content of the clay minerals kaolinite, montmorillonite, and chlorite and the B adsorption maximum. Hingston (1964), Keren *et al.* (1981) and Scharrer *et al.* (1956) showed that the rate of B adsorption on clay minerals consisted of a fast adsorption reaction and a slow fixation reaction. Short term experiments have shown that B adsorption reaches equilibrium in less than one day.

Long term experiments indicated that fixation of B increased even after six months of reaction time (Harder, 1961; Jasmund and Lindner, 1973). Boron adsorption by clay minerals is considered to be a two step process. Initially, B adsorbs onto the particle edges, subsequently migrates, and incorporates structurally into tetrahedral sites replacing structural silicon and aluminum (Couch and Grim, 1968; Fleet, 1965; Harder, 1961). The mechanism of the B adsorption step is considered to be ligand exchange with surface hydroxyl groups on the clay particle edges (Couch and Grim, 1968; Goldberg *et al*., 1993; Keren and Sparks, 1994; Keren and Talpaz, 1984; Keren *et al*., 1994).

2.5.1.4. Soil moisture

Adsorbed B was independent of variations in soil moisture content from 50 to 100 percent of field capacity (Gupta 1968) and increased with decreasing soil water content in another experiments (Mezuman and Keren, 1981). Wetting and drying cycles increased the amount of B fixation. The effect of drying became more pronounced with increasing additions of B (Biggar and Fireman, 1960).

2. 5.1.5. ***Soil temperature***

Boron adsorption increases with increasing soil temperature (Fleming, 1980). However, this may be due to an interactive effect of soil temperature with soil moisture since B deficiency is associated with dry summer conditions. Boron adsorption decreased as a function of temperature in the range of 10 – 40°C on soils dominant in crystalline minerals (Biggar and Fireman, 1960; Goldberg *et al.,* 1993). In contrast, B adsorption increased slightly as the temperature of an amorphous soil increased from 10 to 40°C (Bingham *et al*., 1971). The effect of temperature on B adsorption by clays has been investigated (Couch and Grim, 1968; Goldberg *et al*., 1993; Harder, 1961; Jasmund and Lindner, 1973; Singh, 1971). In crystalline clay minerals, for a very short reaction time of two hours, B adsorption in the pH range of 5.5 – 9.5 decreased with increasing temperature (Goldberg *et al*., 1993). Also in clays B adsorption for longer reaction times of twelve hours to sixty days increased with increasing temperature (Couch and Grim, 1968; Jasmund and Lindner, 1973; Singh, 1971). These results suggest that initial adsorption of B on crystalline clay minerals is exothermic while the subsequent B fixation reaction is endothermic.

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 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).

2.5.1.6. *Presence of competing ions*

Competing ions such as silicate, sulfate, phosphate, and oxalate decreased the magnitude of B adsorption on oxides (Bloesch *et al*., 1987; Choi and Chen, 1979). The effect of competing ions on B adsorption can be slight, in the case of sulfate, or substantial in the case of phosphate (Bloesch *et al*., 1987; Metwally *et al*., 1974). The ability of competing anions to leach adsorbed B from oxides increased in the order: chloride < sulfate = arsenate < phosphate (Metwally *et al*., 1974). Significant silicate adsorption produced only a slight decrease in B adsorption by aluminum oxide suggesting that some B sorption sites show B preference (Goldberg and Glaubig, 1988).

2.5.1.7. *Calcium carbonate*

Application of lime increases B fixation by soils because it raises the soil solution pH (Elseewi, 1974; Elseewi and Elmalky, 1979). In addition to its effect on soil pH, calcium carbonate also acts as an important B adsorbing surface in calcareous soils (Elseewi, 1974; Elseewi and Elmalky, 1979; Goldberg and Forster, 1991). Boron adsorption was greater on soils having higher calcium carbonate content (Elrashidi and O’Connor, 1982). Acid soluble B was highly significantly correlated with calcium carbonate content of soils (Elseewi and Elmalky, 1979). Retention of B on calcium carbonate occurs via an adsorption mechanism (Ichikuni and Kikuchi, 1972). The mechanism could be the exchange with carbonate groups. The magnitudes of the B adsorption maxima for soil samples treated to remove calcium carbonate were statistically significantly lower than those for untreated soil samples indicating that calcium carbonate acts as an important sink for B adsorption in calcareous soils (Goldberg and Forster, 1991). Boron adsorption on reference calcites increased with increasing solution pH from 6 to 9, exhibited a maximum at pH 9.5, and decreased with increasing solution pH from 10 to 11 (Goldberg and Forster, 1991).

Magnitude of B adsorption on clay minerals is affected by the exchangeable cations (Keren and Gast, 1981; Keren and Mezuman ,1981; Keren and O'Connor ,1982). Calcium clays adsorbed more B than sodium and potassium clays (Keren and Gast, 1981; Keren and O'Connor, 1982; Mattigod *et al.,* 1985). An explanation for this result is that calcium 2:1 clays occur as tactoids consisting of several clay particles while the sodium forms exist in solution as single particles (Keren and Gast, 1981). In tactoids, the diffuse double layer and negative electric field from the planar surfaces is less extensive, making the edge sites of calcium clays more accessible to adsorbing borate anions than those of sodium clays (Keren and Gast, 1981). An alternative explanation for increased B adsorption in the presence of calcium is the formation and adsorption of the calcium borate ion pair (Mattigod *et al*., 1985).

2.5.1.8. *Humus*

Humus extracted from a soil retained significant amounts of B and was considered to play an important role in B adsorption (Parks and White, 1952). Soil organic matter adsorbs more B than mineral soil constituents on a weight basis (Gu and Lowe, 1990; Yermiyaho *et al*., 1988)). Boron adsorption on a mineral soil increased with increasing additions of composted organic matter (Yermiyahu *et al*., 1995). The presence of organic material can also occlude B reactive adsorption sites on clays (Gu and Lowe, 1992) and soils (Harada and Tamai, 1968). Boron adsorption on an organic soil (Huettl, 1976; Lehto, 1995) and composted organic matter increased with increasing pH (Yermiyaho *et al*., 1988).

Adsorption of B on a soil humic acid increased with increasing pH up to a maximum near pH 9, and decreased with increasing pH above 9 (Gu and Lowe, 1990). Boron adsorption on composted organic matter occurred rapidly, reaching equilibrium after three hours and increased with increasing solution ionic strength (Yermiyaho *et al*., 1988).

2.5.2. Adsorption pattern of B in soil

Sorption isotherm describes the relation between the amount of substance that is adsorbed by the solid phase of the soil and its equilibrium amount in soil solution. Sorption is one of the most important chemical processes in soil, which affects the fate and mobility of nutrients in the soil. Sorption studies are practical for some of the essential elements such as P, K, S, Cu, Zn, Mn, and B (Huettl, 1976). However, these studies are conducted to determine whether any of the applied plant nutrients will react, fix or complex with the soil. In the systematic approach of evolving fertilizer optima for enhancing crop productivity, understanding the nutrient sorption characteristics of the soil of the experimental site is inevitable. This approach also envisages the safe level of any one of the nutrients in the soil because it should be adjusted in the available pool of the soil at a level in which it is neither deficient nor toxic to the crops (Huettl, 1976). It is observed, in general, that the adsorption of boron increases as the boron in balance is increased by added fertilizer.

Empirical models provide descriptions of experimental adsorption data without a theoretical basis. Boron adsorption reactions on oxides, clay minerals, and soil materials have historically been described using adsorption isotherm equations (Choi and Chen, 1979; Elrashidi and O'Connor, 1982; Evans, 1987; Goldberg and Forster, 1991; Mondal *et al.*, 1993; Nicholaichuk *et al.*, 1988; Singh, 1971). The most popular are the Langmuir and Freundlich adsorption isotherm\ equations but Tempkin and Brunauer–Emmett–Teller (BET) adsorption isotherm equations have also been used (Mondal *et al.*, 1993). Krishnasamy *et al.* (2005) studied the kinetics of B adsorption in soils. Adsorption reaction is important for retention and release of B for plant growth. The adsorption by the soil is calculated as the boric acid in 0.01 M $CaCl_2$ initially added and quantity remaining in solution after equilibrium. Results show that finer the texture, concentration of B in the equilibrium solution is lower. Texture and CEC of the soils influenced the B concentration in the equilibrium solution. Equilibrium period of 24 hours was sufficient to study B adsorption characteristics of soils (Gu and Lowe, 1990).

2.5.2.1. 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 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; Keren *et al.*, 1985).

Harter and Smith (1981) investigated that although the adsorption isotherm equations are often excellent at describing B adsorption, they are simply numerical relationships used to describe data. Independent experimental evidence for adsorption must be present before any chemical meaning can be assigned to adsorption isotherm equation parameters (Veith and Sposito, 1977). The adherence of experimental sorption data to the Langmuir or Freundlich equations provides no information about the chemical mechanism of reaction (Sposito, 1982).

Barrow (1978) observed that in linearising adsorption isotherm equations, all data points are not given equal weighting and the variances of some of the values are disproportionately increased during the transformation. Direct fitting of adsorption data using non-linear least squares methods avoids the difficulties of changes in error distributions and biased parameters associated with linear transformations (Singh, 1971). Nonlinear least squares fits of B adsorption data were much improved over linear transformations as measured by the coefficient of determination, R^2 (Goldberg and Forster, 1991).

2.5.2.2. The Langmuir adsorption isotherm equation

The Langmuir adsorption isotherm equation was developed to describe gas adsorption onto clean solids, but has often been used to describe B adsorption by soil materials. Strictly, the Langmuir adsorption isotherm equation is obeyed only for a uniform adsorbent surface without lateral interactions, implying a constant free energy of adsorption (Brunauer *et al*., 1967). The Langmuir adsorption isotherm has been used to describe B adsorption on aluminum and iron oxide (McPhail *et al*., 1972), clay minerals (Gu and Lowe, 1992; Hingston, 1964; Singh, 1971; Goldberg and Glauibig, 1986; Gupta, 1979; Gupta, 1984; Sanjay and Chahal, 2009) calcite (Goldberg and Forster, 1991), humic acids (Gu and Lowe, 1990), and soils (Bhatnagar *et al*., 1979;Biggar and Fireman, 1960;Bingham *et al*., 1970; Elrashidi and O'Connor, 1982; Evans, 1987; Marzadori *et al*., 1991; Mondal *et al*., 1993; Nicholaichuk *et al*., 1988; Okazaki and Chao, 1968; Schalscha *et al*., 1973; Singh, 1971). For many studies, the Langmuir adsorption isotherm equation was able to describe B adsorption only under conditions of low solution B concentration (Bhatnagar *et al*., 1979; Biggar and Fireman, 1960; Elrashidi and O'Connor, 1982; Goldberg and Forster, 1991; Hingston, 1964; McPhail *et al*., 1972).

2.5.2.3. The Freundlich adsorption isotherm equation

The Freundlich adsorption isotherm equation has often been used to describe B adsorption by soil materials. The equation and its linear form are provided elsewhere (Goldberg, 1993). In the Freundlich adsorption isotherm equation, the affinity terms are distributed approximately log normally implying heterogeneity of B adsorbing sites (Sposito, 1984). The Freundlich adsorption isotherm equation is strictly valid only for adsorption data at low concentrations (Sposito, 1984), but has often been used to describe B adsorption by soils over the entire concentration range studied. The Freundlich adsorption isotherm has been used to describe B adsorption on aluminium oxide (Choi and Chen, 1979), clay minerals (Couch and Grim, 1968; Fleet, 1965; Jasmund and Lindner, 1973; Singh, 1971), calcite (Goldberg and Forster, 1991), and soils (Bhatnagar *et al*., 1979; Elrashidi and O'Connor, 1982; Evans, 1987; Goldberg and Forster, 1991; Lehto, 1995; Nikolaichuk *et al*., 1988).

Bhatnagar *et al.* (1979) studied B adsorption in five different textured calcareous soils of Punjab. Sorption was fitted to Freundlich and Langmuir adsorption models. Freundlich model showed better fit of sorption data than Langmuir model as was evident from higher values. B adsorption isotherm are to be constructed for site specific B fertilizer application. High clay contents ranging from 70 – 320 g kg^{-1} and more $CaCO_3$ (35 to 128 g kg^{-1}) increased the amounts of adsorption of B in these soils. On an average maximum adsorption was observed in Bhalwal soil(108.4 mg kg^{-1}) followed by Sultanpur (78 mg kg^{-1}), Shahpur (63.4 mg kg^{-1}), Pindorian (52.0 mg kg^{-1}) and Shahdra soils (47.0 mg kg^{-1}).

2.6. Crop responses to boron

Bell (1997) reported B deficiency in diversity of flora by means of different techniques alone or in combinations comprised plant deficiency symptoms, soil and plant analysis along with B fertilizer effects on various plant species. Indigenous information of crops, soils and other characteristics known to emphasize B deficit bestow imperative background for its prognosis and identification. Nevertheless, precise prognosis and diagnosis of boron deficit relies on soil and plant analysis calibrated standards. For B deficit identification, the plant portion sampled required to expose existing B supply. Plant and soil analysis are perhaps more valuable whilst utilize to forecast the probability of B insufficiency. Few studies showed that exemption of B from the nutrient culture is pursued by abrupt negative alterations in membrane transportation and enlargement approaches of plant cells (Atwell *et al.,* 1999; Rerkasem, 1996) and subsequently collapse of membrane integrity, which eventually ensued the maximum solute leak into the cell protoplasm (Singh *et al*., 1976; Cakmak *et al.* 1995; Tiwari, 1996; Hanson and Breen 1985; Singh, 2004; Dordas and Brown, 2005).

Mortvedt and Woodruff (1993) reviewed the usage and chemistry of B via its speciation in plants. In biological perspective, the chemistry of the exceptional B element is controlled by B-oxygen complex. They briefly depicted distribution, chemistry and occurrence of these compounds. They elucidated B associations with cell wall membranes, sugar transport, enzymes and certain polyols. The magnitude of B indispensability in plants has been identified for more than 75 years. Although numerous functions have been attributed, yet the interactions amongst its biomolecules and compulsory tasks remained unrevealed. Latest explorations on the partial characterization, complexation and isolation of B compounds of diols, hydroxyacids and polysaccharides were summarized (Bruaner *et al*., 1967; Bell *et al*., 1990; Cakmark and Romheld, 1997; Dordas and Brown, 2005).

Hu and Brown (1997) and Bingham *et al.* (1971) conducted a study regarding different mechanisms of B absorption by plant roots. Their experimental verification advocated that B uptake is the outcome of the passive absorption of undissociated H_3BO_3. This obvious elucidation of B uptake, yet, does not successfully clarify field interpretations where amplified deviation in B concentrations is examined between various species, even after these species are grown-up in identical ecological conditions. The visible negation between field observations and investigational results, advocates, that plant B uptake is estimated by dynamic attributes, which are unrevealed so far. A few other scientists reported significant effects of B on vegetable crops (Yuh, 1956; Tanaka, 1967; Muller and McSweeney, 1976; Chang *et al*., 1992; Cheng and Rerkasem, 1993; Ayars *et al*., 1994).

Ross *et al.* (2006) reported that B deficiency was a serious problem in soybean crop in Arkansas, USA. They conducted field experiments on alkaline soils to assess the response of soybean growth, yield and tissue B content to B application rate and time. They applied B fertilizer at levels of 0, 0.28, 0.56, 1.12, and 2.24 kg B ha^{-1}. Although, B application had no considerable impact on yield at one location, however it significantly improved yields from 4 to 130 % at other three sites. Leaf and seed B content enhanced with B application. The optimum yields produced with B application at 0.28 to 1.12 kg ha^{-1} levels.

2.6.1. Boron and rice growth

In rice, positive crop responses to B application were initially observed by Chaudhry *et al.* (1977) in cvs. Basmati-370 and IR-6, grown in major rice growing areas of Punjab, with a mean paddy yield increase of 14%. Yield increases with B accrued because of reduced panicle sterility (on lower portion of the ear) and increased productive tillers per hill. Post-harvest grain shedding reduced with improved B nutrition. Also, B deficiency in rice caused an uneven crop maturity. Optimum B dose for effective management of B deficiency in rice is 0.75 kg ha^{-1}(Rashid *et al*., 2004).

On an average of five years (1998-2002), B application @1kg ha^{-1} produced the highest paddy yield of 4285 kg ha^{-1}, which is significantly higher than NPK+Zn, NPK and control and at par with all other doses of B (Rashid, 2004)). These paddy yield results are in agreement with those of Rashid *et al*. (2002), Ali *et al*. (1996), Tandon (1999) and PARC (2002). Contrary to the perception that B deficiency hampers grain set more than vegetative growth the mean yield reduction with B deficiency was slightly greater in straw (20%) than paddy (18%).

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, 1996a; 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*. (2005) 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 kharif (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%) (Sakar and Singh, 2003). 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; Yermiyahu *et al.*, 2001). 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).

Boron fertilization in soil deficient situations not only enhances yield of crops but, in many instances, the quality of grains is improved. This implies, apart from causing yield reductions; inadequate B supply to plants may also deteriorate the quality of the crop produce, and, hence, will lower the price of grain produced in B deficient situations (Rashid *et al*., 2004).

Increasing rice grain yield and grain zinc contents has become important measures to supply food and to improve human Zn nutrition to people whose staple food is rice grain. Effective fertilizer management such as B at late stage of rice growth may efficiently increase rice yield as well as grain Zn content (Yermiyahu *et al*., 1988; Aslam *et al*., 2002; Yu *et al*., 2002). A field experiment was conducted to examine the effect of B spray on late growth of rice. Two contrasting types of rice cultivars, namely the hybrid (cv, Shanyou 63) and conventional (cv. Erjiufeng) rice were compared. The hybrid rice had longer growth life and higher yield potential than the conventional one. Boron was sprayed at heading stage. Senescence of flag leaf was greatly delayed by B spray, as was also reflected in significant increase of photosynthetic rate and grain filling rate, and decrease of respiration rates.

The effects of B spray on these plant growth parameters were much greater for hybrid than the conventional rice cultivar, although the length of grain filling period was not affected by B application in both cultivars. At maturity, the single grain weight and grain yield of Sanyou 63 were increased but not that of Erjiufeng. Moreover, Zn content in the polished rice was increased by B spray in both types of rice. In conclusion, B spray in combination with Zn and other nutrient management at the late stage of rice growth are recommended in the field practice to increase grain yield and improve grain Zn content, especially to the rice cultivars with characters of high yield potential and longer grain filling period. As fertilizer boron dosage for correcting the deficiency is very small (0.75kg B ha^{-1}) and crop yield increases with B applications are appreciable, its use is highly cost-effective. Wheat yield increased by 13% over control with the application of one kg B ha^{-1} (Hussain & Yasin, 2004). Similarly 16% yield increase of paddy over control was observed with the same level of boron. Rashid *et al.* (2002) reported an increase of 5 to 26% in rice yield with B application. Ali *et al.* (1996) reported an increase in paddy grain yield due to B application to the tune of 34.6 and 19% at 2.0kg B ha^{-1}on Miranpur and Satgara soils, respectively.

Hussain & Yasin (2004) conducted field experiments to study the residual effect of Zn and B in rice-wheat system. Wheat grain yield ranged from 3.45 to 3.53 t ha^{-1}. Highest yield was produced from 5kg Zn+2kg B ha^{-1} whereas lowest yield was produced from control. Cumulative application of boron gave an increase of 10% over control; direct application gave an increase of 9% over control. However, residual effect of B increased paddy by 4% over control.

Materials and methods

3. MATERIALS AND METHODS

The present investigation entitled "Chemistry and transformation of boron in soils of Kerala" was carried out in the Radiotracer laboratory, College of Horticulture, Kerala Agricultural University during 2010-2012. This project included both laboratory research and field experiments. The laboratory studies were conducted to assess the boron supplying power and adsorption capacity of soils of all agro ecological units in the state of Kerala. The field experiment was conducted in farmer’s field at Elavampadam in Palakkad district to investigate the response of rice to different levels boron. The materials used and the methods adopted to achieve the objectives mentioned in the introduction are summarised below.

Experiment 1. Collection and characterization of soil samples

3.1.1 Collection

Representative soil samples were collected from 23 agro ecological units. The details of sample location are presented in table 1. The agro ecological zones and agro ecological units of Kerala is presented in plate 1 and 2.

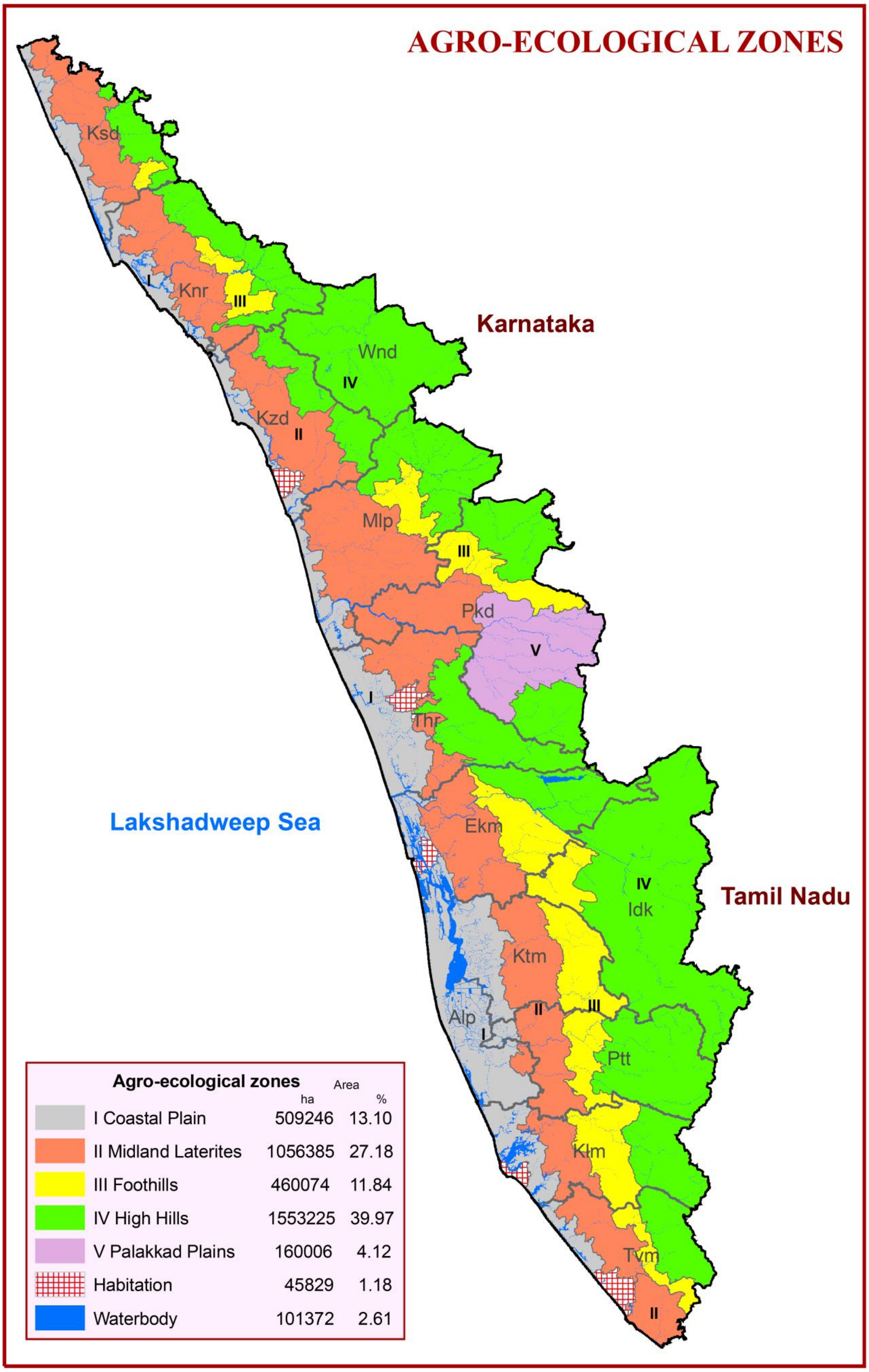
3.1.2. Characterisation of soil samples

The soil samples were air dried under shade, ground and sieved through 2 mm sieve and used for characterization. The samples were characterized with respect to texture, pH, EC, AEC, CEC, exchangeable cations, organic carbon available nutrient status (P, K, Ca, Mg, Fe, Cu, Mn, Zn) with special reference to available B. The procedures adopted for the characterisation of soil samples are detailed hereunder.

3.1.2.1. Soil pH

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

PLATE 1. AGRO-ECOLOGICAL ZONES IN KERALA



Agro-ecological zones	Area ha	%
I Coastal Plain	509246	13.10
II Midland Laterites	1056385	27.18
III Foothills	460074	11.84
IV High Hills	1553225	39.97
V Palakkad Plains	160006	4.12
▦ Habitation	45829	1.18
Waterbody	101372	2.61

PLATE 2. AGRO-ECOLOGICAL UNITS IN KERALA

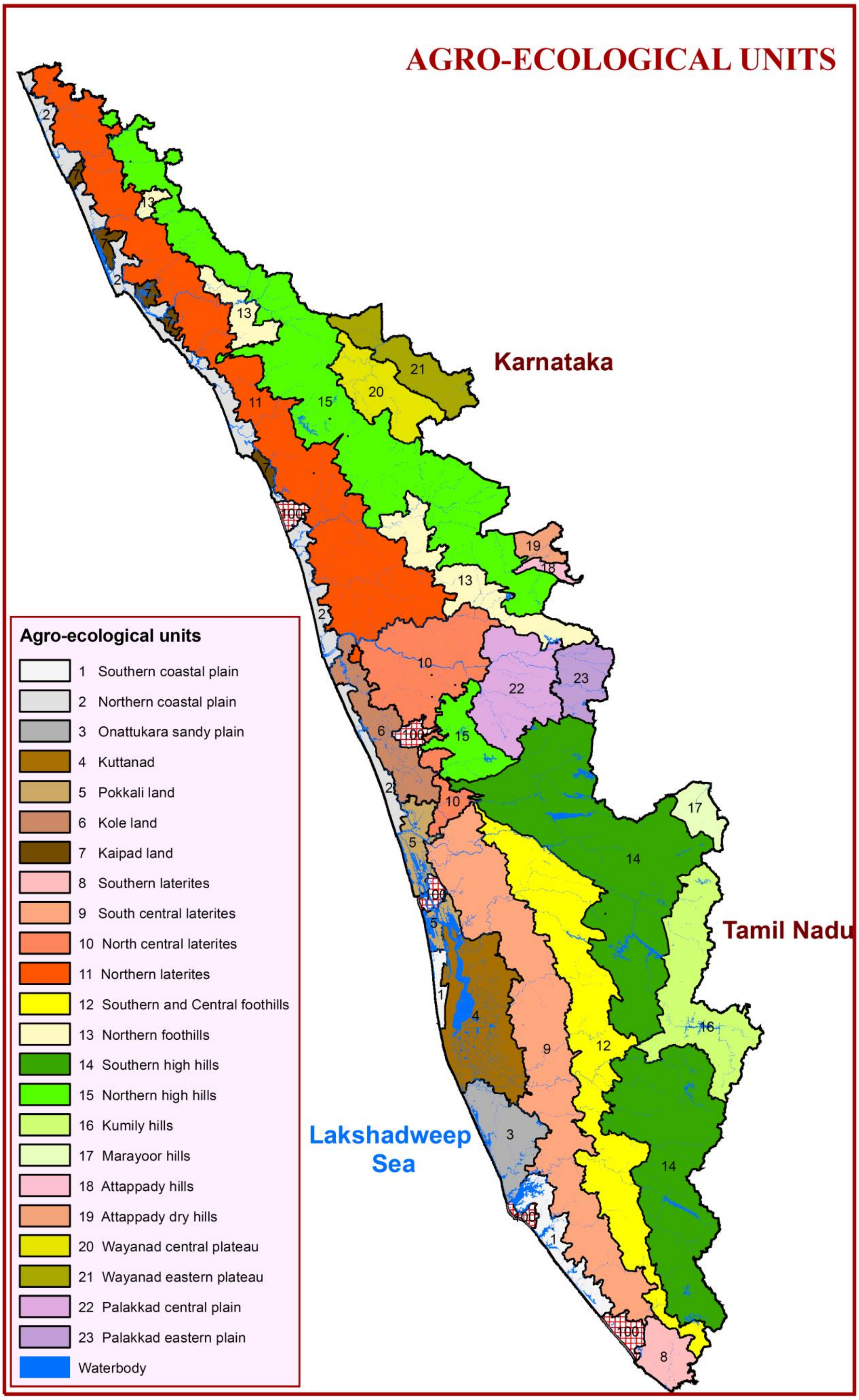


Table 1. locations of sampling

AEU. No.	Agro ecological unit (AEU)	Soil taxonomy- subgroup	Sample number	location	
AEZ -1 COASTAL PLANE					
AEU1	Sothern coastal plain	Typic Ustipsamments)	1.	Cherthala -1	
			2	Cherthala-2	
AEU2	Northern coastal plain	(Typic Ustipsamments)	3	Edavilangu -1	
			4	Edavilangu -2	
AEU3	Onattukara sandy plain	Aquic Ustipsamments	5	Kayamkulam -1	
			6	Kayamkulam-2	
AEU4	Kuttanad	Typic Tropaquepts	7	Thiruvarpu	Karappadam -1
			8		Karappadam-2
		Aquic Tropaquepts	9	Thiruvarpu	Kayal -1
			10		Kayal-2
AEU-5	Pokkali lands	Aquic Ustipsamments	11	Vyttila - 1	
			12	Vyttila - 2	
			13	Vyttila - 3	
			14	Vyttila - 4	
AEU-6	Kole lands	Aquic Tropaquepts	15	Vengidangu	Thekkekonchira
			16		Vadakkekonchira
AEU7	Kaipad lands	Aquic Tropaquepts	17	Kannapuram-1	
			18	Kannapuram-2	
AEZ2 - MID LAND LATERITE					
AEU8	Southern laterites	Typic Kandiustults	19	Kalliyoor - 1	
			20	Kalliyoor - 2	
AEU9	South central laterite	Ustic Kanhaplohumults	21	Mavelikkara - 1	
			22	Madappally - 1	

AEU10	North central laterite	Ustic Kanhaplohumults	23	Pattambi	Upland-1
			24		Upland - 2
		Oxic Tropaquepts	25		Lowland - 1
			26		Lowland - 2
AEU11	Northern laterite	Ustoxic Humitropepts	27	Panniyoor - 1	
			28	Panniyoor - 2	
AEZ3 - FOOT HILLS					
AEU12	Southern and Central foot hills	Ustic Humitropepts	29	Neriamangalam -1	
			30	Neriamangalam - 2	
			31	Kavalangad - 1	
			32	Kavalangad – 2	
AEU13	Northern foot hills	Ustic Kandihumults	33	Wandoor-1	
			34	Wandoor – 2	
AEZ-4 HIGH HILLS					
AEU14	Southern high hills	Ustic Haplohumults	35	Adimali - 1	
			36	Adimali – 2	
AEU15	Northern high hills	Ustic Humitropepts	37	Vythiri - 1	
			38	Vythiri - 2	
		Typic Haplostalfs	39	Agali - 1	
			40	Agali - 2	
AEU16	Kumily dry hills	Ustic palehumults	41	Pampadumpara - 1	
			42	Puliyanmala - 2	
AEU17	Marayoor dry hills	Typic Ustitropepts	43	Marayoor - 1	
			44	Marayoor -2	
AEU18	Attappady dry hills	Typic Haplustalfs	45	Sholayoor - 1	
			46	Sholayoor - 2	
AEU19	Attappady extremely	Lithic Rhodustalfs	47	Pudoor - 1	

	dry hills		48	Pudoor - 2	
AEU20	Wayanad central plateau	Kanhaphic Haplustalfs	49	Ambalavayal	Upland - 1
			50		Upland - 2
		Aeric Tropaquepts	51		Lowland - 1
			52		Lowland - 2
AEU21	Wayanad eastern plateau	Ustic Haplohumult	53	Sulthan Bathery - 1	
			54	Sulthan Bathery - 2	
AEZ5 - PALAKKAD PLAINS					
AEU22	Palakkad central plain	Aquic Ustropepts	55	Anchumoorthy - 1	
			56	Anchumoorthy - 2	
			57	Vadakkenchery lowland - 1	
			58	Vadakkenchery lowland - 2	
AEU23	Palakkad eastern plain	Typic Haplustulfs	59	Nalleppilly	Upland - 1
			60		Upland - 2
		Udic Haplustept	61		Lowland - 1
			62		Lowland - 2
		Typic Haplustert	63	Chittoor	Black soil
			64		Upland - 1
		Vertic Epiaquept	65		Lowland - 1

3.1.2.2. 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).

3.1.2.3. Organic carbon

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

3.1.2.4. 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 colour method (Watanabe and Olsen, 1965) using a spectrophotometer (Model: Specrtaquant Pharo M)

3.1.2.5. Available potassium

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

3.1.2.6. Available calcium and magnesium

Available calcium and magnesium in the soil samples were extracted using neutral normal ammonium acetate and its content in the extract was estimated using Perkin Elmer Atomic Absorption Spectrophotometer (Model: AAnalyst 400).

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

Available micronutrients in soil samples were extracted using 0.1M HCl (Sims and Johnson, 1991). Four grams soil was shaken for 5 minutes with 40 ml of 0.1M HCl. It was filtered through Whatmann No.1 filter paper and the filtrate was collected and analysed for Fe, Cu, Mn and Zn using Perkin Elmer Atomic Absorption Spectrophotometer (Model: AAnalyst 400).

3.1.2.6. Available boron

Available boron in soil samples were extracted with hot water (Berger and Truog, 1939; Gupta, 1972) and estimated colorimetrically by Azomethine – H using spectrophotometer (Model: Specrtaquant Pharo M)

3.1.2.7. Exchangeable cations and cation exchange capacity

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 $BaCl_2$ solution and cations in the extract were estimated. Four grams of soil samples were taken in a centrifuge tube and 40 ml of 0.1M $BaCl_2$ 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: AAnalyst 400) for the determination of exchangeable Ca, Mg, Fe, Al, Mn, Cu and Zn. Exchangeable Na and K were estimated with the help of flame photometer (Model: Elico CL361). The sum of exchangeable cations expressed in cmol(+) kg^{-1} was recorded as the CEC of the soils.

3.1.2.8. Anion exchange capacity

Ten gram of the soil samples were taken and leached with 100 ml $BaCl_2$ - TEA. The soil samples were again leached with 100 ml $CaCl_2.2H_2O$ solution. The Ca saturated soil was dried at 45°C. Afterwards 20 ml 0.01M phosphoric acid was added and shaken for 30 minutes and was allowed to stand for 24 hours and again shaken for 30 minutes. The suspension was centrifuged and the supernatant solutions were decanted. 1 ml of aliquot was pipetted out and P was estimated using ascorbic acid blue colour method. AEC was recorded as cmol(-) kg^{-1} (Baruah and Borthakur, 1997).

3.1.2.9. Soil texture

Texture of the soils was determined by International pipette method (Robinson, 1922). Twenty grams soil samples were taken in 500 ml beaker, 10 ml portion of 30 per cent H_2O_2 was added and warmed on a hot plate. This was continued till large bubbles cease to form, to ensure that all organic matter had been destroyed. 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 20 ml of suspension was 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.

3.1.2.10. Total sesquioxides in soil

Twenty gram of soil samples were digested initially by using 8N HCl and extract was taken and made up to 500 ml. Fifty ml of the extract was boiled with ammonium chloride, after cooling it was again boiled with excess ammonium hydroxide and set aside to settle the precipitate. 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).

EXPERIMENT 2

3.2. Fractionation of soil boron

Thirty soil samples were selected from 65 samples characterised and one sample collected from experimental field were subjected to fractionation of soil B. Samples were selected to represent all agro ecological units ensuring the variations in their physico-chemical properties. The selected samples are listed in table 2.

Table 2. Samples selected for fractionation

Sample number	Agro ecological unit	Location	
1	Southern coastal plain	Cherthala-2	
2	Northern coastal plain	Edavilangu -2	
3	*Onattukara* sandy plain	Kayamkulam -1	
4	*Kuttanad*	Thiruvarpu	*Karappadam* -1
5			*Kayal*-2
6	*Pokkali* lands	Vyttila-1	
7		Vyttila - 2	
8	*Kole* lands	Vengidangu	Vadakkekonchira
9	*Kaipad* lands	Kannapuram-1	
10	Southern laterite	Kalliyoor -1	
11	South central laterite	Madappilly – 1	
12	North central laterite	Pattambi	Upland -1
13			Lowland – 1
14	Northern laterite	Panniyoor – 1	

15	Southern and central foot hills	Neriamangalam 2	
16		Kavalangad – 1	
17	Northern foot hiills	Wandoor - 2	
18	Southern high hills	Adimali – 2	
19	Northern high hills	Vythiri – 2	
20	Kumily dry hills	Pampadumpara - 1	
21	Marayoor dry hills	Marayoor - 1	
22	Attappady dry hills	Sholayoor - 1	
23	Attappady extremely dry hills	Pudoor - 1	
24	Wayanad central plateau	Ambalavayal	Upland-2
25			Lowland -1
26	Wayanad eastern plateau	Sulthan Bathery -2	
27	Palakkad central plain	Anchumoorthy upland-2	
28		Elavampadm lowland	
29	Palakkad eastern plain	Nallepilly	Upland -2
30			Lowland -1
31		Chittoor black soil	

The procedure for the extraction and determination of soil B fractions as given by Datta *et al*. (2002) is presented below.

3.2.1. Readily soluble B (RS - B)

Five grams of soil in duplicate were weighed into 50 ml polythene centrifuge tubes to which 10 ml of 0.01M $CaCl_2$ were added and shaken for 16 hours (Hou *et al*., 1994, 1996). After centrifuging at 10000 rpm for 30 minutes the supernatant solution was filtered through whatman No.42 filter paper. Boron was determined in clear extracts using azomethine-H (Bingham, 1982).

3.2.2. Specifically adsorbed B (SA- B)

The residue from 3.2.1 was then extracted with 10 ml of 0.05 M KH_2PO_4 by shaking for one hour (Hou *et al*., 1994, 1996). After Centrifuging at 10000 rpm for 30 minutes, the supernatant solution was filtered through whatman No.42 filter paper. Boron was determined in the clear extracts using azomethine-H (Bingham, 1982).

3.2.3. Oxide bound B (OX- B)

The residue from 3.2.2 was extracted with 20 ml of 0.175M ammonium oxalate, pH 3.25 (Jin *et al*., 1987; McLaren and Crawford, 1973) by shaking for 4 hours (Hou *et al*., 1991, 1994). The yellow to reddish colour of the extracts due to the dissolution of Fe and organic matter was eliminated by treating with NaOH and $HClO_4$.

3.2.3.1. Elimination of colour of the extracts

To remove the colour, a 14 ml aliquot of the extracts was taken in a 50 ml Teflon beaker and 2 ml of 5 N NaOH solution was added and weighed and then warmed on a hot plate to completely precipitate the dissolved Fe as $Fe(OH)_3$ (Jackson, 1973). The beaker with the aliquot was weighed again and the loss in weight was made up with distilled water. The suspension was filtered through Whatman no.42 to separate the Fe. Nine ml aliquot of the filtrate was taken in a 50 ml teflon beaker and 4 ml concentrated H_2SO_4 and 1 ml $HClO_4$ (60%) were added and heated on a hot plate at 135^0C to destroy the organic matter. When the volume was reduced to about 6 ml, $HClO_4$ was added in an increment of 0.5 ml until the solution became colourless and the volume reduced to 4 or 5 ml. The content was transferred to a 15 ml graduated polyethylene centrifuge tube and the final volume was made up to 6 ml. After centrifuging at 10,000 rpm for 15 min., B in the clear extracts was determined by the carmine method (Bingham, 1982).

3.2.4. Organically bound B (OR- B)

A subsample of two grams of the residue from the ammonium oxalate extraction was treated with 20 ml of 0.5 M NaOH (Choudhari and Stevenson, 1957) by shaking for 24 h followed by filtration through Whatman no. 42. All the extracts were dark red in colour due to the dissolution of organic matter which was eliminated by the same procedure detailed in 3.2.3.1. The final volume was made up to 7 ml. After centrifuging the samples at 10,000 rpm for 15 minutes B in the supernatant was determined with carmine.

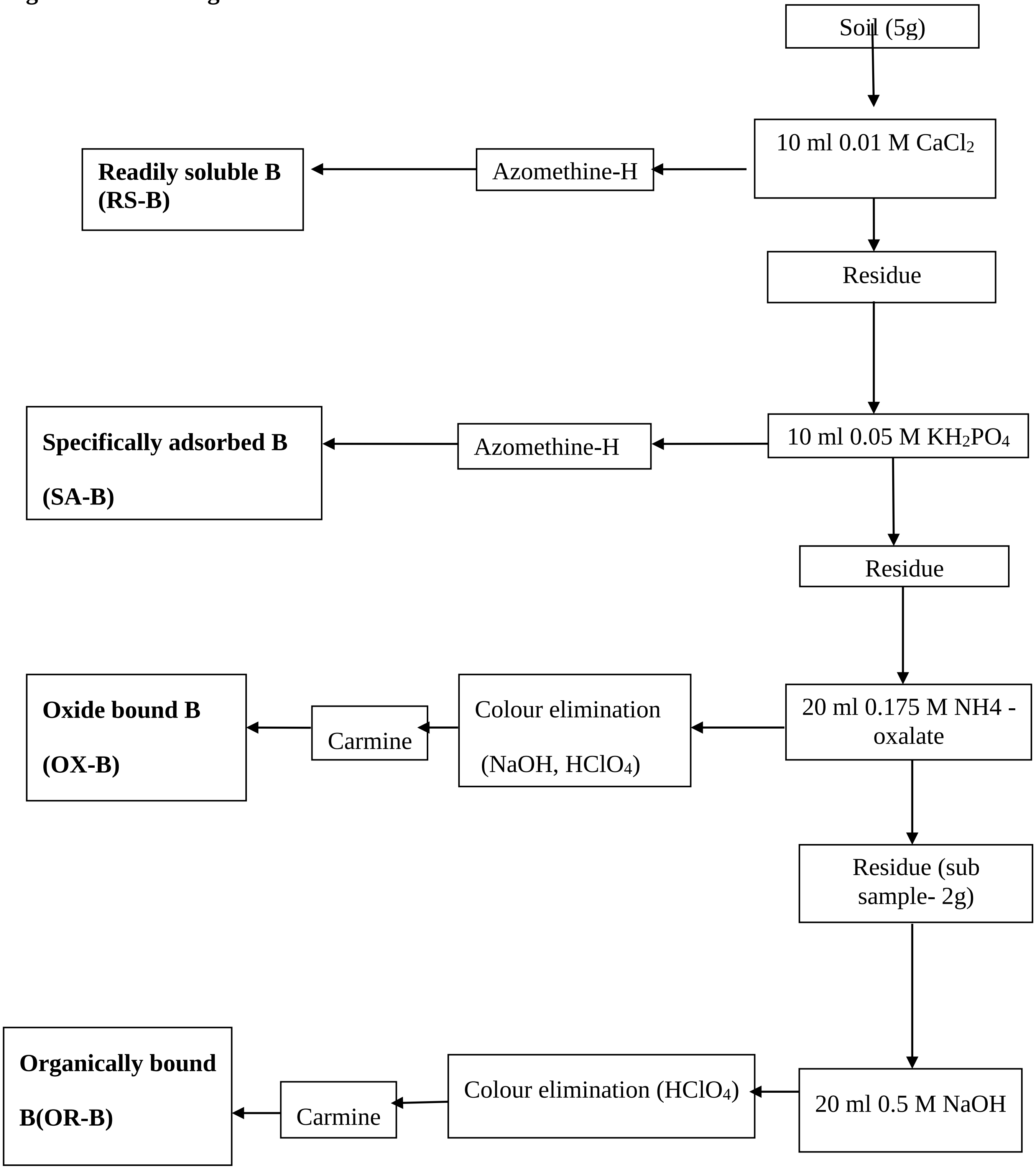
3.2.5. Total B (TB)

Exactly 0.2 gram of the soil sample was taken in 50 ml teflon beaker and 3 ml aqua regia (Datta *et al.*, 2002) was added and kept overnight for wet digestion and digested at 135^0C for 2 hr and filtered through Whatman no. 42 and diluted with distilled water and B was estimated with carmine.

3.2.6. Residual B (RES-B)

The residual boron was estimated by subtracting the sum of RS-B, SA -B, OX- B, OR- B from total boron.

Figure. 1. Flow diagram of fractionation of B in soil



Residual B (RES-B) = TOTAL B – (RS-B + SA-B + OX-B + OR-B)

Experiment 3

3.3. Adsorption study

Six soil types were selected for adsorption studies representing unique soil environments from the 31 soil samples selected for the fractionation. Pattambi (upland-1) soil (S_1) in order to represent the mid land laterite belt of Kerala, Elavampadam low land soil (S_2) being the soil from experimental field representing central Palakkad plains, *Onattukkara* (Kayamkulam-1) soil (S_3) in order to represent coastal sandy soils of the state, Chittoor black soil (S_4) being a near neutral black soil, Vengidangu (Vadakkekonchira) *Kole* land soil (S_5) being rich in organic matter, high in iron and aluminium, *Kuttanad (Kayal*-2) soil (S_6) being clayey, rich in organic matter and acid sulphate in origin were selected for the study. For adsorption study, 2.50 g soil samples were equilibrated with different B concentration levels (0, 0.5, 1.0, 2.0, 4.0, 8.0, 12, 16, 20 and 24 mg L^{-1}) as boric acid in 25 ml solution of 0.01 M $CaCl_2$ at 25 and 40^0C. Soil samples were shaken for 24 hours to achieve steady state condition (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 (Q) and equilibrium B concentration (I) were drawn for each soil. Best fit curves were obtained using regression equations. Slopes of these curves were considered as buffer power with respect to each soil. Further, by using the data on adsorption the following two adsorption isotherms were fitted for each soil.

a) Langmuir adsorption isotherm

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

where

C= concentration

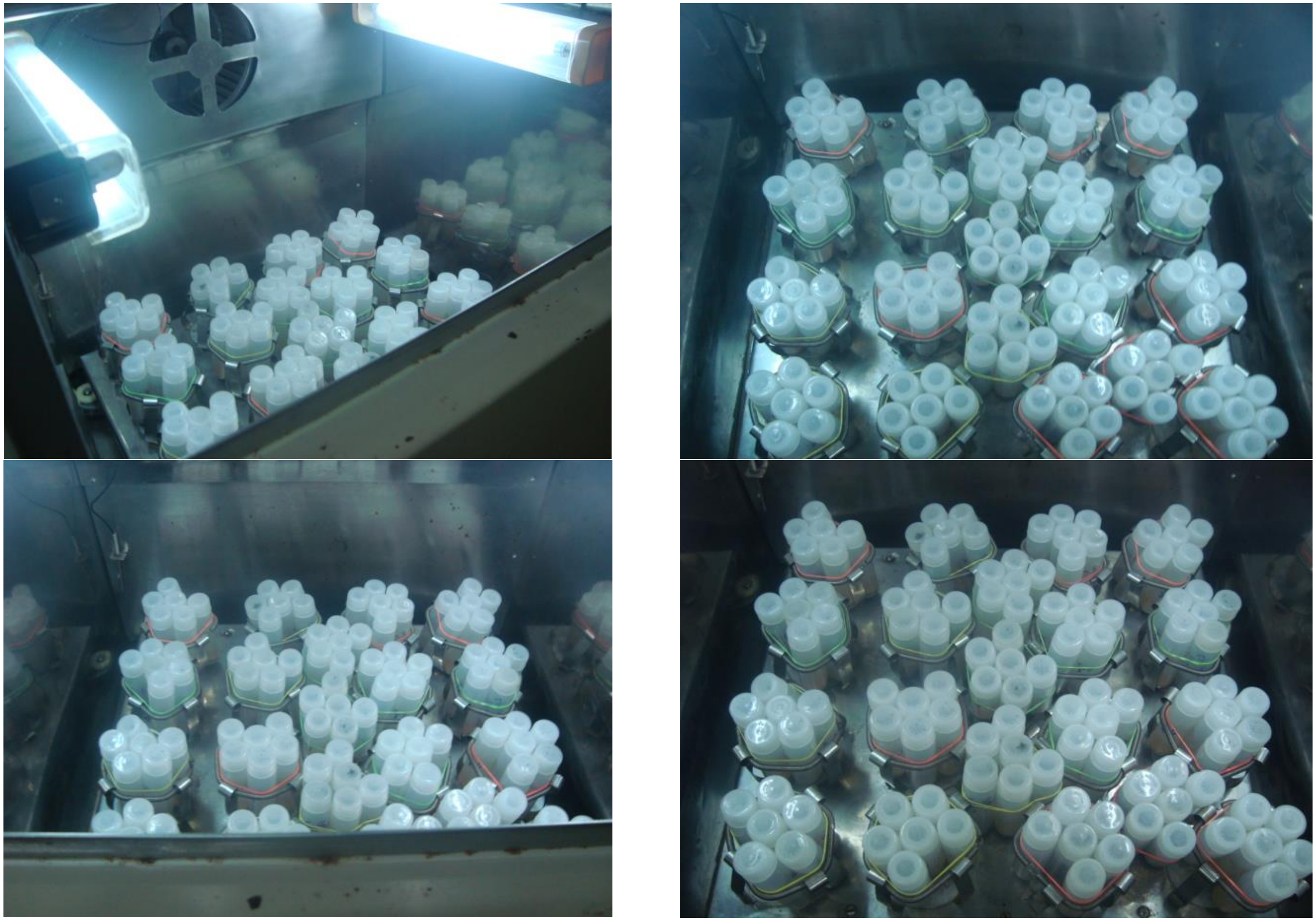
x/m=amount adsorbed per unit weight of soil

K= bonding energy coefficient

M=adsorption maximum.

PLATE 3. Orbital incubator shaker

PLATE 4. Samples in orbital incubator shaker for adsorption study



b) Freundlich adsorption isotherm

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

Thermodynamic parameters

Thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constant, K^0 following the procedure of Biggar and Cheung (1973).

$$K^0 = a_s/a_e = \gamma_s Cs / \gamma_e Ce \qquad (2.1)$$

Where:

a_s = activity of adsorbed solute

a_e = activity of solute in equilibrium

Cs = µg of solute adsorbed per millilitre of solvent in contact with the adsorbed surface

Ce = µg of solute adsorbed per millilitre of solvent in equilibrium

γ_s = activity coefficient of adsorbed solute

γ_e = activity coefficient of solute in equilibrium solution

Cs was calculated according to the following equation (Fu *et al.*, 1948)

$$Cs = (\rho_1/ M_1)\, A_1 / S/N\, (x/m) – A_2/M_2 \times 10^6 \qquad (2.2)$$

ρ_1 = density of solvent (density of water g cc^{-1})

M_1 and M_2 molecular weights of solvent and solute respectively (g mol^{-1})

A_1 and A_2 = respective cross sectional areas of solvent and solute molecule (cm^2 molecule^{-1})

N = Avogadro’s number (6.023 x 10^{23} molecules mol^{-1})

S = surface area of adsorbent (cm^2 g^{-1})

x/m = specific adsorption ($\mu g\ g^{-1}$)

The cross sectional area (cm^2) of the solvent and solute molecules were estimated from the following equation (Kodera and Osuoshi, 1959)

$$A = 1.091 \times 10^{-6} \left[(M \times 10^{24}) / (N \times P)\right]^{2/3} \qquad (2.3)$$

where M & P are molecular weight and density respectively

Surface area of the adsorbent (soil) was determined by following the procedure of Carter *et al.* (1965). About 1.1g of calcium saturated soil samples were placed in shallow small weighing cans and dried to a constant weight over P_2O_5 in an evacuated desiccators. Approximately 3 ml of ethylene glycol monoethyl ether (EGME) was added to each dried sample to form mineral absorbate slurry. The slurry was allowed to equilibrate for at least one hour. The samples were kept in evacuated desiccators. The samples were first weighed one hour after the evacuation, then at successfully at longer time intervals until a constant weight was attained. Carter *et al* (1965) calculated that 2.86×10^{-4} g of EGME was required to form a monolayer of 1 m^2. The surface area of the soil was calculated based on the amount of EGME retained using the following equation:

Surface area

$$S\ (m^2 g^{-1}) = 1\ m^2 / 2.86 \times 10^{-4}\ X \text{ amount of EGME retained (g) / weight of soil taken (g)} \qquad (2.4)$$

In equation (2.2) since $S/N\ (x/m) >> A_2/M_2 \times 10^6$, the equation is reduced to

$$Cs = (\rho_1 / M_1)\ A_1 \ /\ S/N\ (x/m) \qquad (2.5)$$

This can be used to calculate Cs in $g\ ml^{-1}$

At lower concentration, activity coefficient approaches unity and hence $Cs/Ce = K_0$

Values of K_0 were obtained by plotting (Cs/Ce) vs Cs and extrapolating to zero.

The standard free energy (ΔG^0) was calculated from

$$\Delta G^0 = -RT \ln K_0 \qquad (2.6)$$

The standard enthalpy (ΔH^0) was obtained from the integrated form of the Vant Hoff equation,

$$\ln K_o / K_1 = -\Delta H/R \left[(1/T_2) - (1/T_1)\right] \qquad (2.7)$$

The standard entropy (ΔS^0) was calculated from

$$\Delta S^0 = (\Delta H^0 - \Delta G^0) / T \qquad (2.8)$$

Experiment 4.

Effect of organic matter on adsorption of boron

3.4. Incubation experiment

An incubation experiment was conducted in three soils *viz. Onattukara* (Kayamkulam -1) sandy soil (S_1), lateritic soil (upland-2) from Pattambi (S_2), lowland soil from Elavampadam (S_3) to study the effect of organic matter on adsorption of boron in soil. The selection was made so as to represent coastal sandy soil with low organic matter content (*Onattukara*), and lateritic soil with low organic matter (Pattambi upland soil). Low land soil of Elavampadam being experimental field soil was also included in the study. The study involved the addition of different levels organic matter and borax to soil. Available boron in samples drawn after incubation for definite period *ie*. 1, 2 and 3 months were analysed. In the experiment vermicompost was added to 1 kg soil so as receive organic matter at the following doses shown below

O_0 : 0 t ha^{-1}
O_1 : 5 t ha^{-1}
O_2 : 10 t ha^{-1}
O_3 : 15 t ha^{-1}

After the addition of organic matter it was kept for incubation in plastic jars for one month. During this period the soil is subjected to alternate wetting and drying. After one month borax solution was applied so as to receive an application of borax at the following levels:

B_0: 0 kg ha^{-1}
B_1 : 3 kg ha^{-1}
B_2 : 6 kg ha^{-1}
B_3 : 12 kg ha^{-1}
Number of treatments in each soil: 16

Replication: 2

Design: CRD

Available boron in the soil was analysed by drawing samples at 1, 2 and 3 months after the application of borax by hot water extraction method (Gupta, 1972) and then colorimetrically by Azomethine-H (Bingham, 1982).

Table 3. Treatment combinations in the incubation experiment

Sl.No.	Treatment combinations		
1	$S_1 O_0 B_0$	$S_2 O_0 B_0$	$S_3 O_0 B_0$
2	$S_1 O_0 B_1$	$S_2 O_0 B_1$	$S_3 O_0 B_1$
3	$S_1 O_0 B_2$	$S_2 O_0 B_2$	$S_3 O_0 B_2$
4	$S_1 O_0 B_3$	$S_2 O_0 B_3$	$S_3 O_0 B_3$
5	$S_1 O_1 B_0$	$S_2 O_1 B_0$	$S_3 O_1 B_0$
6	$S_1 O_1 B_1$	$S_2 O_1 B_1$	$S_3 O_1 B_1$
7	$S_1 O_1 B_2$	$S_2 O_1 B_2$	$S_3 O_1 B_2$
8	$S_1 O_1 B_3$	$S_2 O_1 B_3$	$S_3 O_1 B_3$
9	$S_1 O_2 B_0$	$S_2 O_2 B_0$	$S_3 O_2 B_0$
10	$S_1 O_2 B_1$	$S_2 O_2 B_1$	$S_3 O_2 B_1$
11	$S_1 O_2 B_2$	$S_2 O_2 B_2$	$S_3 O_2 B_2$
12	$S_1 O_2 B_3$	$S_2 O_2 B_3$	$S_3 O_2 B_3$
13	$S_1 O_3 B_0$	$S_2 O_3 B_0$	$S_3 O_3 B_0$
14	$S_1 O_3 B_1$	$S_2 O_3 B_1$	$S_3 O_3 B_1$
15	$S_1 O_3 B_2$	$S_2 O_3 B_2$	$S_3 O_3 B_2$
16	$S_1 O_3 B_3$	$S_2 O_3 B_3$	$S_3 O_3 B_3$

PLATE 5. Incubation experiment with organic matter

PLATE 6. Incubation experiment with organic matter

Experiment 5. Boron fertilization for rice

3.5. Field experiment

The field experiment to investigate the response of rice to boron was conducted in the field of Mr. Manoj, Aandiman Mandiram, Elavampadam in Palakkad district, in the mundakan season of 2011. The field is located at N10^0 57.75 latitude, E076^0 48.75 longitude and at an altitude of 220 ft. above MSL.

The climate is tropical sub humid to humid monsoon type (mean annual temperature 27.6 °C; rainfall 1966 mm) with a dry period of around five months. The soil of the area is sandy loam in texture with pH 4.5. The physico- chemical properties of the experimental soil is given in the table 4.

Table 4. Physico-chemical properties of experimental soil

Parameter	Value
pH (1:2.5)	4.5
EC (dS m^{-1})	0.046
Sand (%)	48.5
Silt (%)	39.0
Clay (%)	12.5
Sesquioxide content (%)	11.0
Anion exchange capacity (cmol(-) kg^{-1})	2.65

Cation exchange capacity (cmol(+) kg^{-1})	6.12
Organic carbon (%)	0.8
Available phosphorus (kg ha^{-1})	26.0
Available potassium (kg ha^{-1})	107.0
Available calcium (mg kg^{-1})	165
Available magnesium (mg kg^{-1})	14.50
Available sulphur (mg kg^{-1})	5.25
Available manganese (mg kg^{-1})	23.0
Available iron (mg kg^{-1})	160.0
Available copper (mg kg^{-1})	3.58
Available zinc (mg kg^{-1})	1.37
Available boron (mg kg^{-1})	0.40

The experiment was laid out in randomised block design (fig. 2) with seven doses of borax *viz*. 0 kg ha^{-1} (T_1), 2 kg ha^{-1} (T_2), 4 kg ha^{-1} (T_3), 6 kg ha^{-1} (T_4), 8 kg ha^{-1} (T_5),10 kg ha^{-1} (T_6), 12 kg ha^{-1} (T_7) in three replications.

Variety

Jyothi, a short duration variety of 110-120 days duration was used for the study. Jyothi is tolerant to Brown plant hopper, rice blast.

Fig. 2. Layout of experimental field

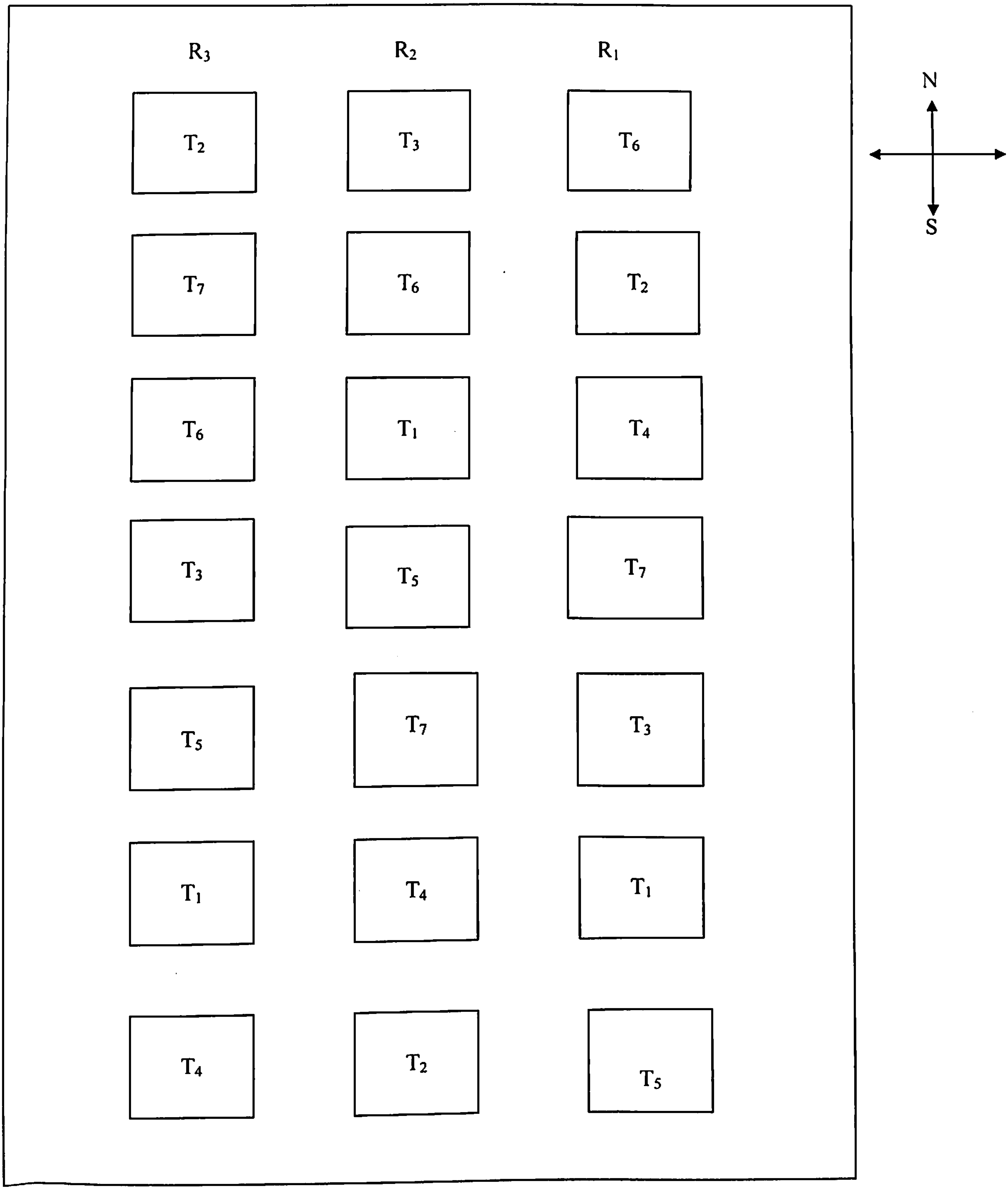


PLATE 7. Field preparation for rice cultivation

PLATE 8. Field prepared for rice cultivation

PLATE 9. Transplanting of rice seedlings

PLATE 10. Overview of field

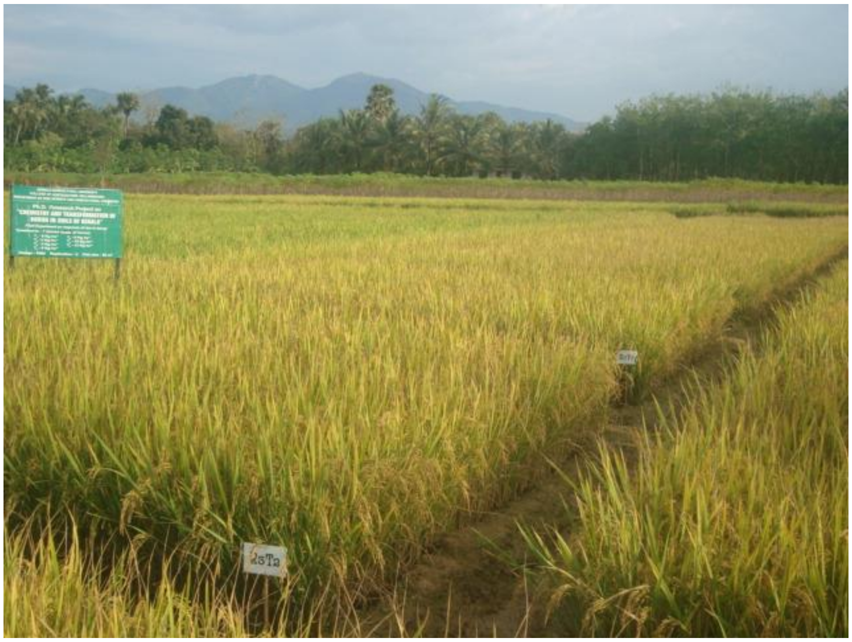
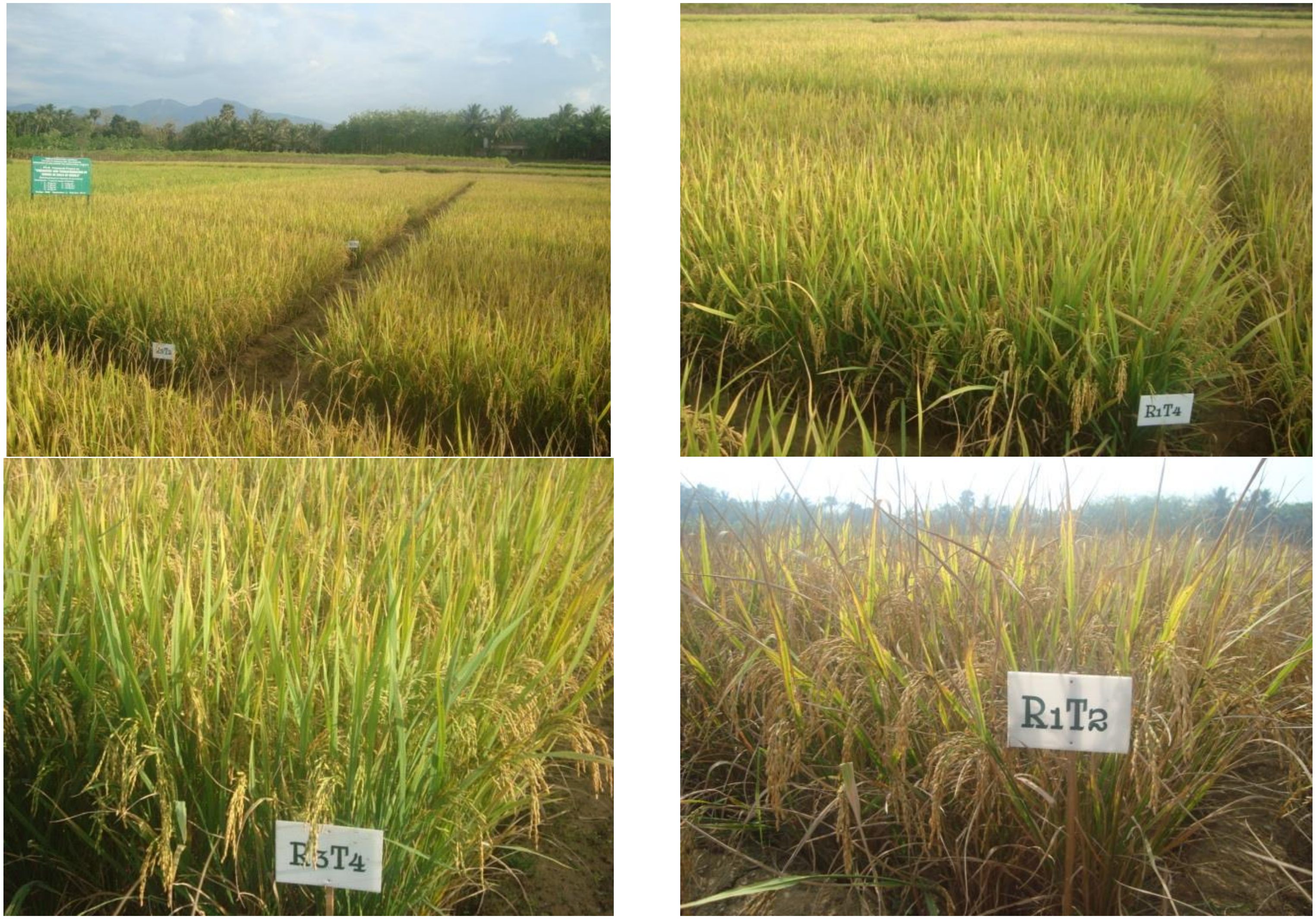


PLATE 11. Overview of field



Land preparation

The experimental area was ploughed well and plots of 5m x 4m were prepared by constructing bunds of 30 cm width and height. Irrigation and drainage channels were provided between each plot.

3.5.1. Crop culture

Seedlings, 18 day old were transplanted at a spacing of 15 cm x 10 cm. Fertilizer application and plant protection measures were done as per the package of practices recommendations of KAU (KAU, 2007). The magnesium deficiency was anticipated as is revealed by the initial soil test data. Magnesium sulphate was applied @ 80 kg ha^{-1} to correct the deficiency appeared in the field after the maximum tillering stage.

3.5.1.1. Biometric observations

The following observations were made in the field experiment.

3.5.1.1.1. Tiller production

The number of tillers per hill at weekly interval was recorded up to maximum tillering stage.

3.5.1.1.2. Productive tillers

The number of productive tillers per hill was recorded at harvest stage.

3.5.1.1.3. Thousand grain weight

One thousand grains were counted from the produce of each plot and their weight was recorded and expressed in grams.

3.5.1.1.4. Filled grains per panicle

The number of filled grains per panicle was counted and recorded.

3.5.1.15. Grain and straw weight

The crop harvested from each plot was threshed, winnowed and the weight of straw and grain was recorded separately and expressed as Mg ha^{-1}

3.5.2. Analysis of soil and plant samples

Soil and plant samples were drawn at panicle initiation (PI) and harvest stage and analysed for nutrient content.

3.5.2.1. Soil analysis

Soil samples drawn from each plot was dried under shade, sieved through 2 mm sieve and analysed for pH, EC,OC, and available nutrients as P, K, Ca, Mg, S and micronutrients Fe, Mn, Zn, Cu and available boron as per the procedures detailed in 3.1.2.

3.5.2.2. Fractionation of boron

Fractionation of boron in soil samples drawn from each plot were also done at both stages as panicle initiation and harvest. The procedures adopted are detailed in 3.2.

3.5.2.3. Plant analysis

Plant samples were collected from each plot at panicle initiation and harvest stage. Shoot and root samples at panicle initiation and root, straw and grain samples at harvest stage were drawn. The collected samples were powdered in stainless steel grinder and used for the analysis.

Table 5. Methods of plant analysis

Sl. No.	Element	Method
1	Nitrogen	Modified Kjeldhal's digestion method (Jackson, 1973)
2	Phosphorus	Diacid digestion of leaf sample followed by filtration. Vanabdomolybdate phosphoric yellow colour in nitric acid system (Piper, 1966)
3	Potassium	Diacid digestion of leaf sample followed by filtration. Flame photometry determination (Jackson, 1973)
4	Calcium and magnesium	Diacid digestion of leaf sample followed by filtration. The filtrate was collected, analysed for Ca and Mg using Perkin-Elmer AAS (Piper, 1966)
5	Iron, manganese,zinc and copper	Diacid digestion of leaf sample followed by filtration. The filtrate was collected, analysed for Fe, Mn,Zn and Cu using Perkin-Elmer AAS (Piper, 1966)

Estimation of boron in plant samples

Boron in plant samples was determined by dry ashing (Gaines and Mitchell, 1979) and then colorimetrically by Azomethine-H (Bingham, 1982). For dry ashing, 1g dried and ground plant samples (straw/grain) were taken in silica crucibles. Crucibles were placed in the muffle furnace and the temperature was slowly raised to 550^0C. Ashing was continued for 6 hours after attaining 550^0C. The ash was extracted in 10 ml of 0.36 N H_2SO_4 for one hour at room temperature and filtered through Whatman No.42 filter paper and used for B determination by colorimetric procedure using azomethine-H.

3.6. Statistical analysis

Correlation studies of data were carried out by the method suggested by Panse and Sukatme (1978). Correlation and regression analysis of data generated in various experiments were carried out based on the method suggested by Cox (1987) using SPSS package. Path coefficient analysis was carried out in SPAR1 package. Analysis of variance in CRD and RBD was made in MSTATC package. Adsorption isotherm equations were fitted using STATISTICA package.

Results

4. Results

The data generated from the various experiments conducted to realise the objectives of the study are presented in this chapter

Experiment 1

Characterisation of soil samples

Representative soil samples (65 Nos.) collected from 23 agro ecological units of Kerala (Table 1) were analysed to study the nutrient status of the soils. The data are presented in the table 6.

4.1 Electrochemical properties and available nutrient status

4.1.1 Soil pH

The pH of the soils ranged from 2.95 to 6.28. The lowest pH was recorded in the *Pokkali* soils (AEU 5, sample No. 12) and highest in the upland soils of Nalleppilly (AEU 23, sample No. 62). The *Karappadam* soils of *Kuttanad* recorded a pH of 4.1 and black cotton soils of Chittoor recorded a pH of 6.11

4.1.2 Electrical conductivity

The lowest EC of 0.01dSm^{-1} was recorded in the soils of Sulthan Bathery (AEU 21, sample No. 53) and the highest of 15.2 dSm^{-1} was recorded in Vyttila 2 soils of AEU 5 (sample No. 12). Electrical conductivity of 8.944 and 9.523 dSm^{-1} were recorded respectively in Kannapuram-1 and Kannapuram-2 (sample Nos. 17 and 18) soils of AEU 7 (*Kaipad* lands).

4.1.3 Organic Carbon

The organic carbon status of the soils varied from 0.255 to 5.53 per cent. Soils from Edavilangu (AEU 2, sample No. 3) recorded the lowest and soils from Panniyoor (AEU 11, sample No. 27) recorded the highest value. Samples from Adimali, Agali, Vythiri, *Kole*, Vyttila, Pampadumpara, soils of *Kuttanad* and Panniyoor were with organic carbon content above 2 per cent.

Table 6. Electro chemical properties and nutrient status of soils of different AEUs of Kerala

Sample No.	pH	EC (dSm^{-1})	OC (%)	(kg ha^{-1})		(mg kg^{-1})								
				P	**K**	**Na**	**Ca**	**Mg**	**S**	**Fe**	**Mn**	**Zn**	**Cu**	**B**
1	5.01	0.081	0.449	69.20	51.7	9.5	74.50	24.00	5.56	15.86	8.21	3.51	0.96	0.44
2	4.87	0.087	0.546	77.56	42.9	7.0	35.15	22.15	21.53	10.02	12.24	4.92	0.33	0.48
3	4.88	0.043	0.255	300.16	68.2	8.5	108.90	13.60	9.72	39.62	4.06	5.86	1.33	0.15
4	5.06	0.035	0.472	215.60	50.6	10.0	43.00	23.15	2.43	39.99	3.67	3.14	0.30	0.50
5	5.30	0.034	0.285	37.29	80.3	5.0	51.60	24.10	6.94	2.62	4.10	1.91	1.34	0.89
6	5.38	0.040	0.352	48.44	94.6	6.5	75.40	18.55	6.94	8.29	6.88	3.33	3.27	0.98
7	3.60	0.011	3.82	9.20	238.7	213.5	86.40	12.25	114.24	115.60	20.82	3.68	5.15	2.03
8	3.69	0.316	3.82	5.60	190.3	186.0	40.55	21.30	62.50	103.40	16.87	2.63	2.29	1.67
9	4.00	0.145	3.82	7.28	184.8	151.0	126.70	22.80	34.03	108.00	23.09	4.17	5.97	0.93
10	4.10	0.268	3.82	5.60	211.2	227.0	91.85	22.95	38.01	92.00	17.70	4.54	4.38	1.39
11	4.74	1.230	1.86	78.40	539.0	566.5	75.30	22.90	308.33	156.20	3.83	3.99	4.10	4.71
12	2.95	15.20	1.108	46.48	405.9	579.5	59.10	21.45	320.43	151.00	2.84	2.15	3.62	2.02
13	4.04	3.591	2.89	68.60	375.1	113.8	193.85	21.40	386.11	154.10	12.27	5.57	3.22	1.47
14	4.01	2.980	2.504	78.40	477.4	1195	146.50	21.45	402.65	151.00	13.80	5.84	3.31	4.00
15	4.06	0.618	1.707	32.76	104.5	130.0	76.60	24.03	125.00	117.20	19.11	3.54	3.21	2.87
16	3.96	0.545	2.87	17.64	232.1	175.5	141.90	23.25	52.78	109.60	25.00	3.10	0.73	0.64
17	3.45	8.944	1.107	31.92	479.6	869.0	52.45	18.30	593.75	145.50	2.35	12.78	1.69	7.96
18	3.67	9.523	0.835	30.52	476.3	809.5	61.75	22.15	478.12	136.40	4.01	5.63	1.46	5.96
19	5.10	0.182	1.535	173.60	462.0	43.5	188.50	12.30	31.25	23.53	21.38	9.01	1.81	0.69
20	4.75	0.062	1.438	110.32	403.7	19.0	97.12	23.30	31.25	23.93	13.24	8.01	3.20	0.42
21	5.77	0.110	1.97	88.55	167.2	15.5	288.30	25.40	3.47	31.13	37.50	20.86	2.12	0.52
22	5.16	0.055	3.047	56.00	339.9	9.0	86.95	24.40	13.54	24.85	38.23	3.48	3.09	0.56
23	4.90	0.032	1.161	31.36	137.5	10.5	17.70	23.29	3.82	5.92	23.25	1.56	1.84	1.70
24	5.48	0.178	1.361	26.32	171.6	12.0	41.90	23.20	3.82	18.02	25.40	2.75	1.72	0.96
25	4.75	0.076	1.283	19.60	121.0	9.0	31.15	79.30	6.60	26.80	9.46	2.88	3.43	0.38
26	4.69	0.078	0.667	9.63	57.12	27.0	28.90	21.85	20.40	79.30	10.10	2.30	2.90	0.50
27	4.64	0.037	5.53	6.87	189.2	13.0	136.80	20.20	25.83	75.40	10.31	0.95	3.05	1.30

Sample No.	**pH**	**EC (dSm^{-1})**	**OC (%)**	**(kg ha^{-1})**		**(mg kg^{-1})**								
				P	**K**	**Na**	**Ca**	**Mg**	**S**	**Fe**	**Mn**	**Zn**	**Cu**	**B**
28	5.50	0.047	5.47	7.82	279.4	15.5	140.90	23.25	16.32	78.00	28.46	5.53	1.84	1.43
29	4.71	0.031	1.53	38.90	148.5	7.5	24.05	24.70	5.21	4.05	6.52	4.44	3.83	0.05
30	5.55	0.041	1.07	25.20	123.2	11.5	28.90	9.22	8.59	7.75	9.22	0.73	0.37	0.94
31	4.80	0.055	1.77	13.72	113.3	8.0	31.35	18.45	3.47	41.61	9.33	1.84	4.90	0.96
32	4.52	0.029	2.00	12.56	176.0	12.5	57.00	22.40	6.25	28.74	17.62	2.91	3.51	0.54
33	4.68	0.033	1.46	5.04	100.1	14.5	40.35	20.70	17.01	27.29	28.23	1.79	0.49	1.12
34	4.65	0.080	0.85	80.08	189.2	10.0	125.65	25.00	2.43	13.23	13.30	3.87	0.94	0.54
35	4.30	0.044	2.13	96.60	115.5	10.5	23.60	23.90	9.37	16.87	11.35	2.76	8.53	0.50
36	4.83	0.027	2.00	83.70	111.1	8.5	24.70	20.75	5.21	14.68	7.37	2.48	4.50	0.80
37	5.06	0.095	1.91	23.02	385.0	15.5	142.10	20.30	4.51	48.90	20.62	2.01	6.72	1.21
38	4.41	0.077	2.60	50.12	196.9	13.0	122.95	24.75	9.72	74.20	15.82	2.54	5.53	0.33
39	5.38	0.053	1.72	12.60	166.1	10.5	384.90	23.60	4.17	9.27	12.32	2.49	2.79	1.14
40	4.83	0.026	2.23	14.80	290.4	14.0	181.70	25.35	14.58	3.61	30.48	3.19	5.44	0.48
41	4.56	0.318	3.08	110.00	1106.6	24.5	220.50	22.30	87.15	21.33	39.37	8.47	12.10	2.72
42	4.98	0.076	1.84	77.30	688.6	11.0	360.60	23.20	19.11	14.39	24.06	5.77	1.55	1.16
43	5.28	0.086	1.18	10.28	345.4	15.0	392.10	20.30	9.17	23.37	17.90	7.44	2.61	1.18
44	5.50	0.192	1.05	80.90	401.5	14.0	410.60	21.05	3.82	43.34	34.30	17.25	2.83	1.94
45	5.18	0.051	0.87	3.640	211.2	17.0	369.65	23.15	49.65	8.84	40.36	1.66	2.22	0.40
46	5.15	0.035	0.63	34.16	305.8	16.5	84.25	24.70	6.94	23.82	26.93	1.50	0.09	0.89
47	5.58	0.106	0.50	49.89	293.7	11.5	204.30	22.10	24.61	7.67	38.76	5.56	2.31	2.67
48	5.96	0.144	1.10	33.85	415.8	12.1	220.24	21.68	39.06	8.90	25.18	3.98	1.35	1.10
49	5.35	0.053	1.37	18.76	206.8	7.0	105.60	18.75	2.08	21.83	30.76	1.79	1.59	1.27
50	4.62	0.024	1.25	9.15	75.9	8.0	98.30	15.40	12.91	19.24	10.10	1.18	2.91	0.71
51	5.15	0.092	1.56	7.84	95.7	23.5	143.45	21.00	9.38	57.95	40.52	37.30	3.94	0.75
52	5.65	0.035	0.79	21.73	101.9	40.0	150.20	21.80	3.40	59.30	38.50	35.40	3.21	0.89
53	5.11	0.010	1.90	10.66	223.3	13.0	148.10	20.10	40.42	13.60	16.80	4.98	2.51	1.20

Sample No.	**pH**	**EC (dSm^{-1})**	**OC (%)**	**(kg ha^{-1})**		**(mg kg^{-1})**								
				P	**K**	**Na**	**Ca**	**Mg**	**S**	**Fe**	**Mn**	**Zn**	**Cu**	**B**
54	6.05	0.074	1.27	51.67	337.7	11.0	160.3	25.02	31.25	25.19	24.43	9.68	3.05	1.76
55	5.13	0.159	1.01	103.60	489.5	30.5	319.5	24.15	10.76	78.01	37.68	18.22	5.82	1.47
56	5.29	0.023	1.16	32.20	466.4	10.0	60.45	24.75	11.81	4.17	16.69	1.40	5.62	0.89
57	4.68	0.358	0.992	33.60	254.1	97.5	292.5	24.00	33.00	110.90	35.17	9.71	33.2	2.19
58	5.14	0.292	1.234	30.52	301.4	66.0	269.6	22.70	51.04	133.80	38.90	11.07	9.44	0.94
59	5.60	0.090	0.795	178.69	363.0	55.5	289.2	21.30	31.25	7.58	34.17	6.60	2.59	1.36
60	5.13	0.296	0.922	70.00	227.7	125.0	577.0	23.50	48.61	140.20	39.99	5.13	6.56	2.10
61	5.35	0.226	1.125	23.24	77.0	123.5	393.5	26.30	9.56	142.10	40.08	37.91	6.39	0.89
62	6.28	0.114	0.722	30.24	77.0	54.0	420.2	26.80	25.69	145.20	36.30	35.60	6.10	1.29
63	6.11	0.128	0.744	28.00	407.0	75.5	657.0	23.25	2.78	22.20	54.91	2.18	0.48	1.23
64	5.02	0.114	1.270	27.70	303.6	8.5	377.7	27.20	9.03	82.62	41.86	37.40	4.30	1.30
65	5.02	0.115	0.966	13.88	71.6	162.5	386.9	25.30	29.37	81.40	40.10	35.90	4.00	0.90
Range	2.95-6.28	0.01-15.2	0.255 -5.53	3.64 - 300.16	42.9-1106.6	5 - 1195	17.7 - 657	9.22 – 79.3	2.08 – 593.75	2.62 – 156.2	2.35 – 54.91	0.73 – 37.91	0.09 – 33.2	0.05 – 7.96

The *Karapadam* and *Kayal* soils (sample Nos. 7, 8, 9 and 10) of *Kuttanad* recorded organic carbon status of 3.82 per cent.

4.1.4. Available phosphorus

The available phosphorus ranged from 3.634 to 300.16 kg ha^{-1}. Very low P status was observed in soil-1 from Sholayoor (sample No. 45) and highest in Edavilangu-1 soils (AEU 2, sample No. 3)). Very low P content of 5.6 and 7.28 was recorded in *Karapadam*-2 and *Kayal*-1 soils of *Kuttanad* respectively. Out of 65 samples, 11 samples were with P deficiency (< 10 kg ha^{-1}).

4.1.5. Available potassium

Available potassium was observed to range from 42.9 to 1106.6 kg ha^{-1}. The lowest available K was recorded in Cherthala-2 soils of AEU 1 (sample No.2) and the highest in Pampadumpara-1 (sample No. 41) soils. Potassium deficiency (<110 kg ha^{-1}) was reported in 23 per cent of soil samples under study.

4.1.6. Available sodium

The highest available sodium content of 1195 mg kg^{-1} was recorded in sample from Vyttila (sample No. 14) and the lowest of 5.0 mg kg^{-1} in soil from Kayamkulam-1 of Onattukara sandy plain (AEU 3, sample No. 5). Soils of *Kaipad* (sample Nos. 17 and 18) recorded 809.5 and 860 mg kg^{-1} respectively, soils of Vyttila, *Kole*, *Kuttanad* also recorded very high values.

4.1.7. Available calcium

Available calcium content of soils found to range from 17.7 to 657 mg kg^{-1}. Out of 65 samples, 54 were deficient (< 300 mg kg^{-1}) in calcium. The lowest calcium status was observed in upland soils of Pattambi (sample No. 23). Black cotton soils from Palakkad eastern plain recorded the highest calcium status of 657 mg kg^{-1} (sample No. 63) and the low land soil from Chittoor recorded 577 mg kg^{-1} (sample No. 60). Soils from Adimali, Neriamangalam, Kavalangad, Cherthala, *Kuttanad*, Kayamkulam recorded very low values.

4.1.8 Available magnesium

The available magnesium ranged from 9.22 to 79.3 mg kg^{-1}. All the samples under study were deficient (<120 mg kg^{-1}) in magnesium.

4.1.9 Available sulphur

The lowest sulphur content of 2.08 mg kg^{-1} was recorded in the upland-1 soils of Ambalavayal (AEU 20, sample No. 49) and the highest of 573.75 mg kg^{-1} was found in Kannapuram-1 soils of *Kaipad* (sample No. 17) lands. Soils of *Pokkali* recorded very high values of sulphur. Out of 65 samples, 12 were deficient in sulphur (< 5 mg kg^{-1}).

4.1.10. Available micronutrient

The data on available (0.1 N HCl extractable) micronutrient (Fe, Mn, Zn and Cu) are presented in table 6.

4.1.10.1 Available iron

The available Fe content of soils ranged from 2.62 to 156.2 mg kg^{-1}. Out of 65 samples, only 4 were deficient with Fe content less than 1 mg kg^{-1}. Very high value of Fe was observed in Vyttila-1 soils, Vyttila-2, Vyttila-3 and Vyttila-4 soils of *Pokkali* lands (AEU 5) and they were 156.2, 151.0, 154.1 and 151.0 mg kg^{-1} respectively.

4.1.10.2 Available Manganese

Available Mn was found to range from 2.35 to 54.91 mg kg^{-1}. None of the samples were deficient in available Mn. Kannapuram-1 (sample No. 17) soils of AEU 7 recorded the lowest and black soils (AEU 23, sample No.63) of Chittoor recorded the highest value.

4.1.10.3 Available Zn

The lowest available Zn (0.73 mg kg^{-1}) was recorded in Neriamangalam-2 soils of AEU 12 (sample No. 30) and the highest (37.91 mg kg^{-1}) in low land soil-1 Nalleppilly from the Eastern Palakkad plains (sample No. 64). Zinc deficiency was reported in only two samples.

4.1.10.4 Available Copper

The lowest available copper was recorded in Sholayoor-2 soils (sample No. 46) and highest in low land-2 soils (sample No. 58) from Vadakkenchery in the Palakkad central plains. nine samples out of 65, were deficient in Cu with a value of < 1.0 mg kg^{-1}

4.1.11 Available boron

The hot water extractable boron was found to vary from 0.05 to 7.96 mg kg^{-1}. Ten samples out of 65 were deficient with a boron status <0.5 mg kg^{-1}. Out of 65 samples, 25 samples were having boron content between 0.5 and 1.0 mg kg^{-1}. Available boron content between 1.0 and 2.0 mg kg^{-1} was recorded in 22 samples.

The lowest boron content of 0.05 mg kg^{-1} was recorded in Neriamangalam-2 soils (AEU 12, sample No. 30). The soils of northern costal sandy plain (Edavilangu-1) recorded a boron content of 0.15 mg kg^{-1} while the soils of southern coastal sandy plain (Cherthala-1 and Cherthala-2) recorded 0.44 and 0.48 mg kg^{-1} respectively. Vyttila-1 and 4 soils of *Pokkali* lands recorded 4.71 and 4.0 mg of B kg^{-1} respectively. Soils of *Karappadam* land of *Kuttanad* recorded higher boron status than *Kayal* land soils. Low land soils from northern central laterite (AEU10) were deficient in boron. The highest boron (7.96 mg kg^{-1}) content was recorded in Kannapuram-1 soils (sample No. 17) of *Kaipad* lands. Soils of dry hills (sholayoor-1, sample No. 45) were sufficient in boron.

4.1.12 Exchangeable cations, cation exchange capacity and percentage base saturation

The 0.01M $BaCl_2$ extractable exchangeable cations of the soils under study are presented in table 7 and 8. The exchangeable potassium ranged from 110 (0.28 cmol(+) kg^{-1}) to 465 mg kg^{-1} (1.18 cmol(+) kg^{-1}). The highest exchangeable K was found in Pampadumpara-1 (sample No. 41) soils followed by Pampadumpara-2 (sample No. 42) soils. The amount of exchangeable Na was found to vary from 63 (0.27 cmol(+) kg^{-1}) to 1857 mg kg^{-1}(8.10 cmol(+) kg^{-1}) with a mean value of 229.8 mg kg^{-1}(0.9 cmol(+) kg^{-1}) . Exceptionally high values of Na were found in *Pokkali* and *Kaipad* lands because of direct sea water inundation.

Table 7. Exchangeable cations and CEC of soils of AEUs in Kerala

Sample No.	Exchangeable cations (mg kg^{-1})									CEC (cmol(+) kg^{-1})
	K	**Na**	**Ca**	**Mg**	**Al**	**Fe**	**Mn**	**Zn**	**Cu**	
1	113	66	278.4	3.29	0.12	0.67	10.84	1.63	0.05	2.04
2	110	64	250.2	4.31	4.74	0.30	8.91	1.84	0.35	1.94
3	121	70	220.0	4.02	0.07	9.25	2.14	1.10	0.06	1.79
4	111	63	335.8	2.64	0.03	2.88	3.61	1.97	0.13	2.29
5	128	69	387.4	6.69	7.35	1.09	2.81	0.81	0.60	2.72
6	133	568	308.8	2.75	6.35	3.87	1.91	1.15	0.11	4.47
7	158	193	1180.2	71.06	116.70	10.27	30.72	2.02	4.48	9.20
8	164	289	778.8	90.71	205.50	0.72	30.26	2.14	0.79	8.73
9	169	271	943.0	132.1	180.50	3.04	27.36	2.34	0.78	9.55
10	169	242	1231.0	77.24	481.20	0.88	26.71	1.91	0.71	13.74
11	293	913	233.0	54.20	16.06	43.74	6.54	1.92	0.54	6.70
12	247	888	693.4	137.90	71.04	149.60	6.42	1.33	0.83	10.46
13	209	1857	710.0	91.93	163.80	27.96	19.20	4.42	0.73	14.93
14	255	1789	652.6	90.70	109.20	55.75	18.53	3.89	0.92	13.94
15	146	196	1145.8	8.06	109.90	2.96	26.19	2.18	0.40	8.36
16	173	245	971.2	88.38	164.50	11.25	36.71	2.16	0.56	9.11
17	243	1401	348.2	90.33	123.50	92.02	6.59	2.27	0.40	10.94
18	236	1276	450.6	71.31	67.91	58.80	6.75	4.73	0.37	10.00
19	295	89	1167.0	15.44	12.26	1.67	22.77	2.66	0.87	7.34
20	246	98	1147.4	16.46	13.19	1.76	2.95	0.94	0.31	7.10
21	158	77	1224.6	9.32	5.20	1.84	2.14	0.38	0.31	7.01
22	217	66	437.6	6.90	7.36	1.84	38.99	1.18	0.09	3.32
23	145	70	386.6	7.29	20.32	6.14	29.69	0.98	0.38	3.03
24	163	65	357.2	7.21	19.32	2.31	27.43	1.00	0.25	2.87
25	133	106	293.8	13.98	23.02	6.10	13.05	1.20	0.35	2.72
26	130	101	290.2	12.90	24.10	5.70	12.30	1.00	0.30	2.67
27	140	80	246.0	19.91	71.00	4.22	10.62	0.44	0.45	2.95
28	177	73	699.8	10.65	39.33	1.52	28.90	0.50	0.03	4.91
29	159	75	473.6	4.43	29.58	0.23	7.23	2.16	0.27	3.50
30	134	69	167.8	5.88	2.81	12.74	12.61	0.53	0.52	1.66
31	134	65	290.6	2.88	66.02	2.45	13.34	1.10	0.19	2.90
32	146	65	366.0	3.35	43.98	4.68	15.97	2.01	0.21	3.08
33	125	167	315.8	6.03	57.35	2.96	23.78	0.80	0.19	3.41

Sample No.	Exchangeable cations (mg kg^{-1})									CEC (cmol(+) kg^{-1})
	K	Na	Ca	Mg	Al	Fe	Mn	Zn	Cu	
34	168	65	565.2	4.97	50.32	3.15	13.77	0.79	0.23	4.20
35	211	66	1148.0	9.47	72.30	2.66	9.45	1.42	0.22	7.50
36	137	67	256.2	1.99	84.21	4.74	12.32	1.05	0.19	2.94
37	241	73	260.0	16.31	23.63	15.05	26.70	0.87	0.60	2.79
38	157	72	1148.8	34.00	19.04	0.63	16.22	1.13	0.23	7.02
39	155	86	1230.4	129.50	3.60	2.16	5.02	0.63	0.27	8.07
40	205	73	1215.0	341.10	4.25	0.20	13.09	0.50	0.27	9.86
41	465	82	1191.0	48.13	10.20	8.76	33.67	1.60	0.38	8.18
42	374	78	1214.8	118.80	2.67	0.18	11.73	1.04	0.29	8.44
43	246	78	426.0	19.47	2.04	298.00	12.28	1.92	0.44	4.40
44	245	74	1226.0	9.08	2.93	2.11	0.92	0.53	0.26	7.20
45	150	80	1277.2	11.64	5.72	0.16	6.45	0.52	0.23	7.30
46	209	65	497.0	8.46	0.20	5.98	23.09	0.67	0.25	3.48
47	217	69	712.6	13.90	0.10	2.29	25.51	0.32	0.37	4.64
48	244	88	1225.2	70.46	0.40	1.69	1.26	0.19	0.44	7.74
49	156	64	595.2	5.69	29.40	2.78	31.09	0.65	0.78	4.15
50	127	63	682.0	5.82	113.30	4.14	18.26	0.87	0.80	5.40
51	148	96	629.4	5.30	12.30	4.03	16.52	3.22	0.16	4.21
52	146	90	602.3	4.70	15.20	4.80	15.20	3.10	0.15	4.07
53	188	68	1230.0	15.15	2.20	1.95	13.75	1.82	0.55	7.14
54	228	68	1178.0	7.83	3.10	2.06	15.62	2.15	0.32	6.94
55	275	86	1228.4	14.47	12.30	10.78	2.76	0.67	0.26	7.53
56	281	67	459.2	15.24	13.09	2.39	10.03	0.67	0.33	3.63
57	182	179	731.8	67.82	0.20	0.96	26.72	1.12	0.08	5.57
58	204	148	615.2	47.40	0.20	1.92	45.30	3.52	0.23	4.82
59	243	117	1227.4	59.03	0.01	29.38	4.42	0.31	0.49	7.88
60	172	181	1225.8	71.68	0.04	1.50	17.54	0.52	0.14	8.02
61	121	201	1223.2	132.70	0.11	3.30	29.59	18.13	0.20	8.58
62	120	189	1205.0	110.20	0.21	3.10	28.90	17.69	0.30	8.25
63	239	212	1235.0	51.160	0.03	18.14	1.28	0.33	0.21	8.21
64	204	98	1202.8	95.04	0.10	2.64	17.00	16.65	0.09	7.88
65	220	168	1185.0	90.20	0.30	2.70	20.00	15.65	0.40	8.10
Range	110 - 465	63 - 1857	167.8 – 1277.20	1.99- 341.1	0.01 – 481.2	0.16 – 298.0	0.92 – 45.30	0.19 – 18.13	0.03 – 4.48	1.66 – 14.93
Mean	190	229.80	754.83	43.18	42.26	15.0	16.24	2.41	0.42	6.20

Table 8. Exchangeable cations and percentage base saturation of soils of AEUs in Kerala

Sample No.	cmol(+) kg^{-1}					PBS
	K	Na	Ca	Mg	Al	
1	0.29	0.29	1.39	0.03	0.001	97.81
2	0.28	0.28	1.25	0.04	0.053	95.18
3	0.31	0.3	1.1	0.03	0.001	97.62
4	0.28	0.27	1.68	0.02	0.015	98.64
5	0.33	0.3	1.94	0.06	0.082	96.33
6	0.34	2.47	1.54	0.02	0.071	97.91
7	0.4	0.84	5.9	0.59	1.297	84.09
8	0.42	1.26	3.89	0.76	2.283	72.46
9	0.43	1.18	4.72	1.1	2.006	77.76
10	0.43	1.05	6.16	0.64	5.347	60.28
11	0.75	3.97	1.17	0.45	0.178	94.56
12	0.63	3.86	3.47	1.15	0.789	87.08
13	0.53	8.07	3.55	0.77	1.82	86.57
14	0.65	7.78	3.26	0.76	1.213	89.31
15	0.37	0.85	5.73	0.07	1.221	83.99
16	0.44	1.07	4.86	0.74	1.828	77.94
17	0.62	6.09	1.74	0.75	1.372	84.15
18	0.6	5.55	2.25	0.59	0.755	89.99
19	0.75	0.39	5.84	0.13	0.136	96.80
20	0.63	0.43	5.74	0.14	0.147	97.60
21	0.4	0.33	6.12	0.08	0.058	98.99
22	0.55	0.29	2.19	0.06	0.082	93.00
23	0.37	0.3	1.93	0.06	0.226	88.08
24	0.42	0.28	1.79	0.06	0.215	88.70
25	0.34	0.46	1.47	0.12	0.256	87.74
26	0.33	0.44	1.45	0.11	0.268	87.27
27	0.36	0.35	1.23	0.17	0.789	71.25
28	0.45	0.32	3.5	0.09	0.437	88.75
29	0.41	0.33	2.37	0.04	0.329	89.65
30	0.34	0.3	0.84	0.05	0.031	92.21
31	0.34	0.28	1.45	0.02	0.734	72.49
32	0.37	0.28	1.83	0.03	0.489	81.62
33	0.32	0.73	1.58	0.05	0.637	78.45
34	0.43	0.28	2.83	0.04	0.559	85.23
35	0.54	0.29	5.74	0.08	0.803	88.61

Sample No.	cmol(+) kg^{-1}					
	K	**Na**	**Ca**	**Mg**	**Al**	**PBS**
36	0.35	0.29	1.28	0.02	0.936	65.96
37	0.62	0.32	1.3	0.14	0.263	84.93
38	0.4	0.31	5.74	0.28	0.212	96.04
39	0.4	0.37	6.15	1.08	0.04	99.15
40	0.52	0.32	6.08	2.84	0.047	98.98
41	1.19	0.36	5.96	0.4	0.113	96.60
42	0.96	0.34	6.07	0.99	0.03	99.05
43	0.63	0.34	2.13	0.16	0.023	74.10
44	0.63	0.32	6.13	0.08	0.033	99.36
45	0.38	0.35	6.39	0.1	0.064	98.83
46	0.53	0.28	2.49	0.07	0.002	96.91
47	0.55	0.3	3.56	0.12	0.001	97.71
48	0.62	0.38	6.13	0.59	0.004	99.74
49	0.4	0.28	2.98	0.05	0.327	89.17
50	0.32	0.27	3.41	0.05	1.259	75.13
51	0.38	0.42	3.15	0.04	0.137	94.70
52	0.37	0.39	3.01	0.04	0.169	93.74
53	0.48	0.3	6.15	0.13	0.024	98.78
54	0.58	0.3	5.89	0.07	0.034	98.47
55	0.7	0.37	6.14	0.12	0.137	97.47
56	0.72	0.29	2.3	0.13	0.145	94.57
57	0.47	0.78	3.66	0.57	0.002	98.17
58	0.52	0.64	3.08	0.4	0.002	96.19
59	0.62	0.51	6.14	0.49	0.005	98.47
60	0.44	0.79	6.13	0.6	0.001	99.17
61	0.31	0.87	6.12	1.11	0.001	97.96
62	0.31	0.82	6.03	0.92	0.002	97.84
63	0.61	0.92	6.18	0.43	0.001	99.08
64	0.52	0.43	6.01	0.79	0.001	98.40
65	0.56	0.73	5.93	0.75	0.003	98.39

Exchangeable Ca varied from 167.8 (0.80 cmol(+) kg^{-1}) to 1277.2 mg kg^{-1} (6.30 cmol(+) kg^{-1}) with a mean of 754.83 mg kg^{-1} (3.70 cmol(+) kg^{-1}). Highest exchangeable Ca was recorded in Sholayoor-2 (sample No 46) soils of AEU 19. Very high exchangeable Ca status was recorded in soils of eastern palakkad plains. Exchangeable Mg was found to vary from 1.99 (0.16 cmol(+) kg^{-1}) to 341.1 mg kg^{-1} (2.84 cmol(+) kg^{-1}) with a mean status of 43.18 mg kg^{-1} (0.35 cmol(+) kg^{-1}).

Exchangeable Al varied from 0.01 (0 cmol(+) kg^{-1}) to 481.2 mg kg^{-1} (5.84 cmol(+) kg^{-1}) with a mean of 42.26 mg kg^{-1} (0.47 cmol(+) kg^{-1}). The highest was recorded in *Kayal*-2 soils of *Kuttanad*. High values of exchangeable Al was found in soils of *Kuttanad, Pokkali, Kole, Kaipad* where high acidity persists due to direct sea water inundation. The amount of exchangeable Fe varied from 0.16 (0.05 cmol(+) kg^{-1}) to 298.0 mg kg^{-1} (1.06 cmol(+) kg^{-1}) and the exchangeable Mn was found to range from 0.92 (0.003 cmol(+) kg^{-1}) to 45.3 mg kg^{-1}(0.016 cmol(+) kg^{-1}). The exchangeable Zn ranged from 0.19 (0.005 cmol(+) kg^{-1}) to 18.13 mg kg^{-1} (0.05 cmol(+) kg^{-1}) and the exchangeable Cu was found to range from 0.03 (0.001 cmol(+) kg^{-1}) to 4.48 mg kg^{-1}0.013 cmol(+) kg^{-1}).

Cation exchange capacity of soils under study ranged from 1.66 to 14.93 with a mean of 6.28 cmol(+) kg^{-1}. The lowest CEC was noticed in Neriamangalam-2 soils and highest in Vyttila-3 soils of *Pokkali* lands. The CEC of southern coastal sandy, northern coastal sandy plain and northern central laterites were very low (< 2 cmol(+) kg^{-1}) indicating low fertility status of the soils. Percentage base saturation varied from 60.28 to 99.70 per cent.

Out of the 65 samples, thirty one soil samples characterised were selected for fractionation of soil B. The samples were selected to represent all agro ecological units ensuring the inclusion of the variations in their physico-chemical properties. The selected samples are listed in table 2.

4.1.13. Analysis of texture, sesqui oxide and AEC

The data on the analysis of texture, sesqui oxide and AEC of the soils of the 23 AEUs are presented in the table 9. Sand fraction in soils ranged from 15 to 94.2 per cent. The maximum sand was estimated in Kayamkulam -1 soils and the minimum in *kayal*-2 soils of Kuttanad. Silt fraction ranged from as low as 2.5 per cent in Cherthala soils to as high as 70 per cent in *Kole* land soils. The lowest clay content of 2.7 per cent was recorded in Kayamkulam 1 soils and the highest in kayal 2 soils kuttand. Soils of northern coastal plain were sandy where as the Edavilangu soil of southern coastal plain was loamy sand in texture. Fifty per cent of the soils under study were sandy loam in texture. The *Kayal* and *Karappadam* soils of *Kuttand* were clayey where as the *Pokkali* soils were loamy in texture. A wide variety of texture was exhibited by the soils of different AEUs.

Sesqui oxide was found to range from 0.5 (Cherthala–2) to 22.5 per cent (Adimali-2). The sandy soils of Edavilangu, Kayamkulam and *Kaipad* soils of Kannapuram recorded low values as 2, 2.1 and 3 per cent of sesqui oxide respectively while the lateritic soils from low and uplands of Pattambi and Panniyoor recorded 21.75, 18.0 and 17 per cent sesqui oxide respectively.

Anion exchange capacity ranged from 1.54 to 5.26 cmol(-) kg^{-1}. The highest AEC was recorded in Pampadumpara soils and the lowest in Cherthala soils.

4.1.14. Correlation coefficient between electrochemical properties and nutrient status of soils

The correlation coefficient for available boron with electrochemical properties and other nutrient elements are given in the table 10. Hot water extractable boron had significant negative correlation with pH. Electrical conductivity, available K, Na, S, Fe exchangeable K, Na, Fe, CEC had significant positive correlation with available B.

Exchangeable Al had high significant negative correlation with pH and positive correlation with OC. The basic cations (Na and K), available S and Fe had significant effect on EC. Organic carbon had significant positive correlation with CEC, available Fe and Na.

Table 9. Textural class, sesquioxide and AEC of soils of AEUs in Kerala

Sl.No.	Location	Textural class	Sand (%)	Silt (%)	Clay (%)	Sesquioxide (%)	AEC (cmol(-) kg^{-1})
1	Cherthala 2	Sandy	92.5	2.5	5	0.5	1.54
2	Edavilangu 2	Loamy sand	82.5	10	7.5	2	1.8
3	Kayamkulam 1	Sandy	94.2	3.1	2.7	2.1	2.25
4	Karappadam 1	Clayey	20	38	42	21.25	3.84
5	Kayal 2	Clayey	15	34.5	50.5	20.75	3.51
6	Vyttila 1	Loam	43.35	46.65	10	8.5	4.45
7	Vyttila 2	Loam	42	47	11	9.75	3.92
8	Venkidangu (Vadakkekonchira)	Silt loam	15.7	70	14.3	18.75	3.74
9	Kannapuram 1	Sandy loam	76.5	10	13.5	3	1.62
10	Kalliyoor 1	Sandy clay loam	62	14	24	7.5	4.59
11	Madappally 1	Sandy clay loam	59	19	22	14.55	3.23
12	Pattambi upland 1	Sandy loam	52	35.5	12.5	18.5	3.78
13	Pattambi lowland 1	Sandy clay loam	57.5	15	27.5	21.75	2.9
14	Panniyur upland 1	Sandy loam	61.4	25.7	12.9	17	3.6

Sl.No.	Location	Textural class	Sand (%)	Silt (%)	Clay (%)	Sesquioxide (%)	AEC (cmol(-) kg^{-1})
15	Neriamangalam 1	Sandy loam	61	21	18	14.25	4.01
16	Kavalangad 1	Sandy loam	68.5	16.5	15	17.75	3.09
17	Wandoor 2	Loamy sand	79.5	13	7.5	3	3.04
18	Adimali 2	Sandy clay loam	58	22	20	22.5	4.16
19	Vythiri 2	Sandy loam	70.5	14.7	14.8	20	3.03
20	Pampadumpara 1	Sandy loam	65	19	16	18	5.26
21	Marayoor 1	Sandy loam	75.2	12.5	12.3	7.5	4.44
22	Sholayoor 1	Sandy loam	56	30.5	13.5	13.25	2.64
23	Pudur 1	Loamy sand	78	12.5	9.5	8.75	1.97
24	Ambalavayal upland 1	Sandy loam	64.7	17.8	17.5	10	2.73
25	Ambalavayal lowland 1	Sandy clay loam	64.5	12.5	23	4.5	3.04

Sl.No.	**Location**	**Textural class**	**Sand (%)**	**Silt (%)**	**Clay (%)**	**Sesquioxide (%)**	**AEC (cmol(-) kg^{-1})**
26	Sulthan Bathery 2	Sandy loam	70	22.5	7.5	5	1.62
27	Anchumoorthy 2	Sandy loam	75.5	10	14.5	10	3.88
28	Elavampadam	Sandy loam	52	28.5	19.5	11	2.65
29	Nalleppilly upland 1	Sandy loam	69.3	17.8	12.9	8.2	3.01
30	Nalleppilly lowland1	Sandy loam	58	27.5	14.5	9	2.89
31	Chittoor black soil	Sandy loam	68	22	10	7	4.22

Table 10. Correlation between different soil parameters and nutrient contents in soils

	Av. B	**pH**	**EC**	**K**	**Na**	**S**	**Fe**	**Ex.K**	**Ex.Na**	**Ex.Fe**	**CEC**	**OC**	**Ex.Al**
Av. B	1												
pH	-0.387**	1											
EC	0.601**	-0.578**	1										
K	0.458**	-0.111	0.275*	1									
Na	0.795**	0.562**	0.702**	0.313*	1								
S	0.842**	-0.594**	0.792**	0.391**	0.882**	1							
Fe	0.531**	-0.498**	0.489**	0.104	0.642**	0.631**	1						
Ex.K	0.372**	-0.058	0.213	0.954**	0.248*	0.299*	0.035	1					
Ex.Na	0.680**	0.515**	0.672**	0.298*	0.832**	0.922**	0.625**	0.212	1				
Ex.Fe	0.319**	-0.229	0.490**	0.230	0.373**	0.388**	0.197	0.241	0.338**	1			
CEC	0.445**	-0.425**	0.412**	0.413**	0.077	0.583**	0.578**	0.397**	0.611**	0.156	1		
OC	0.026	-0.365**	-0.068	0.172	0.554**	0.068	0.251*	0.099	0.082	-0.081	0.302*	1	
Ex.Al	0.207	-0.644*	0.183	0.050	0.312*	0.304*	0.383*	-0.097	0.319**	0.023	0.502**	0.529**	1

Experiment 2

Fractionation of boron in soil

Thirty one soil samples, representing all agro ecological units ensuring the inclusion of the variations in their physico-chemical properties, mainly with respect to available B were subjected to fractionation of soil B. The selected samples are listed in table 2.

4.2.1. Fraction of boron in soil

The data on various fractions as well as total B in soils of the AEUs are given in the table 11. The readily soluble B (RS-B) ranged from 0.1 to 2.48 mg kg^{-1}. The lowest RS-B was recorded in the Cherthala soils of southern coastal sandy plain and the highest in *Kaipad* soils of Kannapuram. Vyttila -2 soils recorded the second highest value for RS-B. (2.21 mg kg^{-1}). The upland soils of Nalleppilly (AEU 23) also recoded low value for RS-B. Soils of foot hills except Kavalangad soils recorded low values for RS-B.

Specifically adsorbed B was found to range from 0.16 to 2.6 mg kg^{-1}, the highest being in Vyttila soils and the lowest in soil from Cherthala. *Kaipad* soils also recorded high values for SA-B.

Oxide bound B were in the range of 0.5 to 7.8 mg kg^{-1}. The *Karappadam* and *Kayal* soils of *Kuttanad* recorded 7.2 and 6.9 mg kg^{-1} of SA-B. Upland soils of southern central laterites, north central laterite and northern laterites recorded 5.9, 7.1 and 5.2 mg kg^{-1} for OX-B.

Organically bound B varied from 0.38 to 8.1 mg kg^{-1}. The highest value was recorded in the *Karappadam* soils of *Kuttanad* and the lowest in *Onattukara* sandy soils. Soils of southern and northern coastal sandy plains recorded 0.96 and 0.80 mg kg^{-1} of OR-B respectively. Soils from Wandoor and extremely dry hills of Attappady recorded very low values for OR-B.

Among the five fractions of soil B, the dominant fraction was RES-B which varied from 25.78 to 317.51 mg kg^{-1} in soils of Cherthala and Vythiri respectively. Soils from Sulthan Bathery, low land of Ambalavayal and uplands of Wandoor recorded 57.67, 77.54 and 93.5 mg kg^{-1} of RES-B respectively.

Table 11. Fractions of boron in soils of different AEUs in Kerala

Sample No.	Sample Location	(mg kg^{-1})					
		RS-B	SA-B	OX.-B	OR-B	RES-B	Total-B
1	Cherthala 2	0.10	0.16	0.50	0.96	25.78	27.5
2	Edavilangu 2	0.47	0.95	1.40	0.80	161.38	165.0
3	Kayamkulam 1	0.66	1.12	1.50	0.38	121.34	125.0
4	*Karppadam* 1	1.22	1.36	7.20	8.10	214.62	232.5
5	*Kayal* 2	1.29	1.53	6.90	7.90	262.38	280.0
6	Vyttila 1	2.21	2.33	3.20	4.20	145.56	157.5
7	Vyttila 2	1.05	2.60	3.50	3.90	146.45	157.5
8	*Kole* 1	1.72	1.50	6.10	4.10	136.58	150.0
9	Kannapuram 1	2.48	2.53	1.60	2.30	111.09	120.0
10	Kalliyoor 1	1.12	1.21	3.10	2.80	224.27	232.5
11	Madappally 1	0.86	1.16	5.90	5.90	198.68	212.5
12	Pattambi upland 1	0.91	1.29	6.20	2.10	262.00	272.5
13	Pattambi lowland 1	1.24	1.30	7.10	2.00	263.36	275.0
14	Panniyur upland 1	1.20	1.10	5.20	2.80	257.01	267.3
15	Neraimangalam 2	0.52	1.19	5.60	2.14	160.55	170.0
16	Kavalangad 1	1.07	1.17	6.20	2.20	236.86	247.5
17	Wandoor 2	0.71	0.69	1.80	0.80	93.50	97.5
18	Adimali 2	0.47	0.78	7.80	3.20	177.75	190.0
19	Vythiri 2	0.45	1.84	6.70	3.50	317.51	330.0
20	Pampadumpara 1	1.14	2.05	6.50	4.98	212.83	227.5
21	Marayoor 1	1.03	1.17	3.20	1.80	217.80	225.0
22	Sholayoor 1	0.76	1.55	4.60	2.10	203.49	212.5
23	Pudur 1	0.84	1.74	3.10	1.00	233.32	240.0
24	Ambalavayal upland1	0.45	1.28	4.30	3.24	145.73	155.0
25	Ambalavayal Lowland 1	0.93	1.38	1.90	3.25	77.54	85.0
26	Sulthan Bathery 2	1.07	2.00	2.91	3.85	57.67	67.5
27	Anchumoorthy upland 2	0.86	1.14	4.40	3.20	190.40	200.0
28	Elavampadam	0.78	0.83	4.40	1.70	122.29	130.0
29	Nalleppilly upland 2	0.33	1.81	3.10	2.20	192.56	200.0
30	Nallepilly lowland 1	1.03	1.10	3.20	3.90	183.27	192.5
31	Chittoor black cotton	0.67	1.40	3.0	1.30	143.63	150.0

Table 12. Percentage distribution of fractions of boron in soils of different AEUs in Kerala

Sample No.	Sample Location	RS-B	SA-B	OX.-B	OR-B	RES-B	Total-B
1	Cherthala 2	0.36	0.58	1.82	3.49	93.75	27.5
2	Edavilangu 2	0.28	0.58	0.85	0.48	97.81	165.0
3	Kayamkulam 1	0.53	0.90	1.20	0.30	97.07	125.0
4	*Karppadam* 1	0.52	0.58	3.10	3.48	92.31	232.5
5	*Kayal* 2	0.46	0.55	2.46	2.82	93.71	280.0
6	Vyttila 1	1.40	1.48	2.03	2.67	92.42	157.5
7	Vyttila 2	0.67	1.65	2.22	2.48	92.98	157.5
8	*Kole* 1	1.15	1.00	4.07	2.73	91.05	150.0
9	Kannapuram 1	2.07	2.11	1.33	1.92	92.58	120.0
10	Kalliyoor 1	0.48	0.52	1.33	1.20	96.46	232.5
11	Madappally 1	0.40	0.55	2.78	2.78	93.50	212.5
12	Pattambi upland 1	0.33	0.47	2.28	0.77	96.15	272.5
13	Pattambi lowland 1	0.45	0.47	2.58	0.73	95.77	275.0
14	Panniyur upland 1	0.45	0.41	1.95	1.05	96.15	267.3
15	Neriamangalam 2	0.31	0.70	3.29	1.26	94.44	170.0
16	Kavalangad 1	0.43	0.47	2.51	0.89	95.70	247.5
17	Wandoor 2	0.73	0.71	1.85	0.82	95.90	97.5
18	Adimali 2	0.25	0.41	4.11	1.68	93.55	190.0
19	Vythiri 2	0.14	0.56	2.03	1.06	96.22	330.0
20	Pampadumpara 1	0.50	0.90	2.86	2.19	93.55	227.5
21	Marayoor 1	0.46	0.52	1.42	0.80	96.80	225.0
22	Sholayoor 1	0.36	0.73	2.16	0.99	95.76	212.5
23	Pudur 1	0.35	0.73	1.29	0.42	97.22	240.0
24	Ambalavayal upland1	0.29	0.83	2.77	2.09	94.02	155.0
25	Ambalavayal Lowland 1	1.09	1.62	2.24	3.82	91.22	85.0
26	Sulthan Bathery 2	1.59	2.96	4.31	5.70	85.44	67.5
27	Anchumoorthy upland 2	0.43	0.57	2.20	1.60	95.20	200.0
28	Elavampadam (low land)	0.60	0.64	3.38	1.31	94.07	130.0
29	Nalleppilly upland 2	0.17	0.91	1.55	1.10	96.28	200.0
30	Nallepilly lowland 1	0.54	0.57	1.66	2.03	95.21	192.5
31	Chittoor black cotton	0.45	0.93	2.00	0.87	95.75	150.0

Soils from southern, south central, north and northern laterite recorded 224.22, 198.68, 257.01 and 263.36 mg kg^{-1} of RES-B.

The total boron was found to vary from 27.5 to 330.0 mg kg^{-1}.

4.2.2. Percentage distribution of fractions of B in soil

The data on percentage distribution of fractions of B in soil are presented in table 12. Readily soluble B constituted very low percentage of contribution to the total boron content of the soil. RS-B contribution was to the tune of 0.14 to 2.07 per cent with a mean of 0.59 per cent. *Kaipad* soils of Kannapuram recorded the highest per cent of RS-B. The dominant fraction, RES-B constituted 85.44 to 97.81 (mean 94.45) per cent of total B in soil. Remaining 2.19 to 14.56 per cent of total B was distributed in the rest of four fractions.

Specifically adsorbed B constituted 0.14 to 2.96 per cent with a mean of 0.86 per cent. Highest percentage of SA-B was recorded in the soils of S. Bathery in Wayand eastern plateu. OX-B constituted 0.85 to 4.31 per cent with a mean of 2.31. This is the second dominant fraction of soil B. Edavilangu soils of northern coastal sandy plain had very low content of oxide bound B. organically bond B varied from 0.3 to 5.7 (mean 1.79) per cent of total B in soils of Kayamkulam and Sulthan Bathery respectively. Soils of Edavilangu, Pudoor, Marayoor, black soils of Chittoor, Sholayoor also had very low amount of B bound to organic matter in soil.

4.2.3. Correlation between different fractions of soil boron

The correlation coefficients between the different fractions of B are given the table 13. The readily soluble B, the immediately available fraction of soil B had significant positive correlation with SA-B (0.588**) and organically bound B (0.348*). Oxide bound B had high significant correlation with OR-B (0.564**) and RES-B (0.688**).

Table 13. Correlation coefficients between different fractions of B in soil

Fractions of B	RS-B	SA-B	OX-B	OR-B	RES-B	TB
RS-B	1					
SA-B	0.588*	1				
OX-B	0.071	0.046	1			
OR-B	0.348*	0.309	0.564**	1		
RES-B	0.030	0.098	0.688**	0.255	1	
TB	0.052	0.117	0.714**	0.297	0.999**	1

Table 14. Correlation coefficients of fractions of B with electro chemical properties and nutrient contents of soil

Fractions of B	**pH**	**EC**	**OC**	**K**	**Na**	**S**	**Fe**	**Cu**
RS-B	-0.472**	0.365*	0.319	0.459**	0.737**	0.718**	0.510**	0.067
SA-B	-0.284*	0.602**	0.091	0.528**	0.696**	0.703**	0.511**	0.349*
OX-B	-0.259*	0.185	0.610**	0.049	0.185	0.227	0.011	0.444*
OR-B	-0.429*	0.067	0.712**	0.281	0.200	0.119	0.334*	0.422*
RES-B	0.101	0.183	0.432*	0.070	0.205	0.218	0.011	0.338*
Total-B	0.123	0.174	0.460**	0.084	0.189	0.204	0.028	0.356*

Table 15. Correlation coefficients of fractions of B with exchangeable cations and soil parameters

Fractions of B	Ex. K	Ex. Na	Ex. Mg	Ex.Al	Ex.Fe	Ex.Mn	Ex.Cu	CEC	Sand	Silt	Clay	Sesqui oxide	AEC
RS-B	0.409*	0.633**	0.413*	0.315	0.444*	0.077	0.106	0.478**	-0.424*	0.441*	0.180	0.105	0.168
SA-B	0.486**	0.531**	0.684**	0.122	0.640**	0.116	0.054	0.617**	-0.275	0.371*	0.003	0.057	0.129
OX-B	0.030	0.248*	0.071	0.355*	0.181	0.475**	0.043	0.076	-0.624**	0.386*	0.636**	0.986**	0.490**
OR-B	0.228	0.156	0.393*	0.584**	0.088	0.584**	0.359*	0.546**	-0.746**	0.495**	0.712**	0.547**	0.375*
RES-B	0.038	0.184	0.019	0.176	0.204	0.283	0.061	0.090	-0.295	0.061	0.471**	0.717**	0.379*
Total-B	0.050	0.173	0.039	0.201	0.193	0.306	0.070	0.113	-0.331	0.091	0.496**	0.742**	0.395*

4.2.4. Correlations of fractions of B with electrochemical properties and available nutrient contents in soil.

The correlation coefficients for fractions of B with electro chemical properties and nutrient contents of soil is presented in the table 14. Readily soluble B had significant negative correlation with soil pH (-0.472**), positive correlation with available K (0.459**), Na (0.737**), S (0.718**), Fe (0.510**), and Cu. Specifically adsorbed B also had negative correlation with pH, high positive correlation with EC, available K, Na, S and Fe. Both OX-B and OR-B also had significant negative correlation with soil pH. OX-B had significant positive correlation with OC (0.616**) and available Cu (0.444*). Content of B bound to soil organic matter had very high significant correlation with OC (0.712**) and available Fe (0.334**). Residual B was highly correlated with OC and available Cu.

4.2.5. Correlation of fractions of B with exchangeable cations and soil parameters

Data given in table 15 shows that there was significant correlation of exchangeable K (0.409*), Ex. Na (0.653**), Ex. Mg (0.413*) and CEC (0.478**) with RS-B. The sand fraction in soil is negatively correlated with RS-B. Specifically adsorbed B also had significant correlation with Ex. K (0.486**), Ex. Na (0.531**), Ex. Mg (0.684**) and CEC (0.617**). The silt fraction in soil is positively correlated (0.371*) with SA-B. It was also significantly correlated with exchangeable Fe (0.640**).

OX-B was correlated with exchangeable Na, Al (0.355*) and Mn (0.475**) positively. It also had significant positive correlation with silt (0.386*), clay (0.636**) but negative significant correlation with sand (-0.624**) fraction in soil. Unlike RS-B and SA-B, oxide bound B had very high positive correlation with sesquioxide (0.986**) and AEC (0.490**).

The amount of B bound with soil organic matter also had significant negative correlation with sand (-0.746**). Organically bound B, RES-B and total B had significant positive correlation with sesquioxide. Barring RS-B and SA-B, all other fractions of B had significant positive correlation with AEC and clay.

Experiment 3

Adsorption study

3.1. Q-I relationship

Quantity – intensity relationship with respect to the six soils varying in physico-chemical properties and representing different AEUs were studied at two temperatures *viz*. 25 and 40^0C. From the data obtained, Q-I curves were plotted with the amount of B adsorbed on Y axis and the equilibrium concentration of B in the solution on the X axis. The Q and I parameters were calculated from the adsorption experiments with increasing concentration of B added to a fixed weight of soil (2.5g) as detailed in chapter 2. The concentration of B in solution after equilibration for 24 hours was considered as intensity factor. The amount of B adsorbed on solid phase per unit weight was considered as the quantity factor. The Q/I curves were fitted with these data and intercepts and slopes were computed from the best fit curves using regression analysis. The slope of the curve is the parameter which explains the buffer power *ie*. B supplying power of soil. The simple linear equation $\Delta Q = bC + K$ was used to obtain the best curve, where b is the buffer power (slope of the curve) and K is the intercept.

The values both b and K were computed for six soils at two temperatures 25 and 40^0C are presented in table 16 and 17 respectively. At 25^0C, *Kole* land soils of Vadakkekonchira (Thrissur) recorded the highest buffer power of 0.64 L kg^{-1} and the minimum of 0.38 L kg^{-1}in Pattambi soils, whereas at 40^0C, the maximum buffer power of 0.69 L $kg^{-1}$was recorded in soils of Pattambi. *Onattukara* sandy soils exhibited desorption showing negative buffer power of -0.47 L kg^{-1}.

The buffer powers of the soils at two temperatures are presented in the table 16. The buffer power was found to be decreased at 40^0C than at 25^0C in the low land soils of Elavampadam, *Kole* land, *Kayal* lands of *Kuttanad*. In the upland soils of Pattambi and Chittoor buffer power was higher at 40^0C (0.69 and 0.59 L kg^{-1}) than at 25^0C (0.38 and 0.40 L kg^{-1}) respectively.

Table 16. Buffer power (b) and intercept of Q/I curve of the soils for boron adsorption at 25^0 C

Sl. No.	Soil	Intercept of the Q/I curve (K) (mg kg^{-1})	Buffer power (b) (L kg^{-1})
1	Pattambi (upland -1)	1.01	0.38
2	Elavampadam (low land)	0.37	0.44
3	*Onattukara* (Kayamkulam-1)	0.33	-0.47
4	Black (Chittoor)	1.32	0.40
5	*Kole* (Vadakkekonchira)	0.46	0.64
6	*Kuttanad (kayal* -2)	0.92	0.62

Table 17. Buffer power (b) and intercept of Q/I curve of the soils for boron adsorption at 40^0C

Sl. No.	Soil	Intercept of the Q/I curve (K) (mg kg^{-1})	Buffer power (b) (L kg^{-1})
1	Pattambi (upland -1)	-0.44	0.69
2	Elavampadam (low land)	-0.05	0.27
3	*Onattukara* (Kayamkulam-1)	-2.4	-0.25
4	Black (Chittoor)	-1.69	0.59
5	*Kole* (Vadakkekonchira)	-0.78	0.46
6	*Kuttanad (kayal* -2)	-0.66	0.49

3.2. Adsorption isotherms

The data obtained from the adsorption experiments were fitted into linear forms of Langmuir, Freundlich equations. Table 18 gives the equation for Langmuir isotherms at 25^0C. The data for only two soils *ie. Onattukara*, and *Kayal* lands could be fitted by the linear form of Langmuir. The adsorption maxima (M) was high for *Kayal* lands of *Kuttanad*. (17.0 mg kg^{-1}) and very low for *Onattukara* (0.05 mg kg^{-1}). The bonding energy coefficient (K) was high for *Onattukara* soils (1.535 mL g^{-1}), whereas the data generated at 40^0C for none of the soils could be explained by Langmuir adsorption isotherm.

Table 19 gives the equations for Freundlich isotherms at 25^0C. The data for all the soils could be described by the linear form of Freundlich equation with the sole exception of *Onattukara* soils. K is defined as the amount of B adsorbed at unit soil solution concentration of B. At 25^0C, the values of K ranged from 1.35to 2.585 mg kg^{-1}.

Equations for Freundlich isotherms at 40^0C are given in table 20. Similar to trend at 25^0C all the soil except *Onattukara* soil could be described with the data generated. The values for K ranged from 0.26 to 0.71 mg kg^{-1}.

3.3. Thermodynamics of boron adsorption

The surface area and values of thermodynamic equilibrium constant K_0(25) and K_0(40), free energy ΔG^0(25) and ΔG^0(40), enthalpy change ΔH, entropy ΔS^0(25) and ΔS^0(40) are given in table 21. The lowest surface area of 8.79 m^2 g^{-1} was recorded in the sandy soils of Onattukara and largest surface area of 114.43 was recorded in the clayey soils of *Kayal* lands of *Kuttanad*.

K_0(25) was maximum in the black soils from Chittoor (54.36) and minimum in the soils of *Kayal* lands (3.58). Soil from *Onattukara* recorded maximum value for K_0 (40) was 154.77 and the minimum in the soils of *Kayal* land was 2.9. Except in the soils from Chittoor and *Kayal*, K_0 increased with temperature.

Table. 18. Langmuir adsorption characteristics of *Kuttanad* and *Onattukara* soils for boron adsorption at 25^0C

Soil	Equation	M (mg kg^{-1})	K (mL g^{-1})	Variance (%)
Kuttanad Kayal (*Kayal* -2)	C/(x/m) = 0.6727+0.0588C	17.0	0.087	68.0
Onattukara sandy (Kayamkulam -1)	C/(x/m) = 1.296+1.99C	0.50	1.535	79.24

Table 19. Freundlich adsorption characteristics of the soils for boron adsorption at 25^0C

Sl No.	Soil	Freundlich equation	K (mg kg^{-1})	1/n	Variance (%)
1	Pattambi (upland -1)	log x/m=0.1322+0.5861 log C	1.3558	0.5861	79.80
2	Elavampadam (low land)	log x/m=0.1628+0.5527 log C	1.4580	0.5527	55.20
3	*Onattukara* (Kayamkulam-1)	NS			
4	Black (Chittoor)	log x/m=0.4126+0.7805 log C	2.8580	0.7805	79.00
5	*Kole* (Vadakkekonchira)	log x/m=0.3461+0.5134 log C	2.2178	0.5134	54.00
6	*Kuttanad (kayal* -2)	log x/m=0.22174+0.6436log C	1.6653	0.6436	94.80

Table. 20. Freundlich adsorption characteristics of the soils for boron adsorption at 40^0C

Sl No.	Soil	Freundlich equation	K (mg kg^{-1})	1/n	Variance (%)
1	Pattambi (upland -1)	log x/m = -0.2182+0.9456 log C	0.6050	0.9456	86.00
2	Elavampadam (low land)	log x/m = -0.1996 +0.3756 log C	0.6315	0.3756	60.00
3	*Onattukara* (Kayamkulam-1)	NS			
4	Black (Chittoor)	log x/m = -0.5840+1.0414 log C	0.2606	1.0414	52.50
5	*Kole* (Vadakkekonchira)	log x/m = - 0.1488+1.0042log C	0.7090	1.0042	79.80
6	*Kuttanad (kayal* -2)	log x/m = -0.1223+0.7869log C	0.7545	0.7896	82.20

Table 21. Thermodynamic parameters for boron adsorption

Sl.No.	Soil	Surface area ($m^2 g^{-1}$)	K_0		ΔG^0 (kcal mol^{-1})		ΔH (kcal mol^{-1})	ΔS (kcal $mol^{-1} K^{-1}$)	
			25^0C	40^0C	25^0C	40^0C		25^0C	40^0C
1	Pattambi (upland -1)	47.68	37.23	40.15	-2.13	-2.29	11.90	0.0471	0.0471
2	Elavampadam (low land)	73.11	13.53	40.67	-1.54	-2.30	173.53	0.587	0.587
3	*Onattukara* (Kayamkulam-1)	8.79	30.71	154.77	-2.02	-3.13	255.02	0.862	0.862
4	Black (Chittoor)	31.79	54.36	40.60	-2.36	-2.30	-46.00	-0.146	-0.146
5	*Kole* (Vadakkekonchira)	79.47	4.78	5.8	-0.92	-1.09	30.49	0.105	0.105
6	*Kuttanad (kayal* -2)	114.43	3.58	2.9	-0.75	-0.66	-33.21	-0.108	-0.108

Reverse was the trend for free energy of adsorption where the negative value increased with temperature or the absolute value decreased except in the soils of Chittoor and *Kayal* as it were for $K_{0.}$ The maximum of -0.75 kcal mol^{-1} was recorded for $\Delta G^0(25)$ in soils of Kayal and minimum of -2.36 kcal mol^{-1} in the black soils of Chittoor. On the other hand minimum $\Delta G^0(40)$ was recorded in the soils of *Onattukara* (-3.13 kcal mol^{-1}) and the maximum in the soils of *Kayal* lands of *Kuttanad* (-0.66 kcal mol^{-1}).

The change in enthalpy was negative only for the soils from *Onattukara* and *Kayal* lands. The maximum ΔH of 255.02 kcal mol^{-1} was recorded in the soils of *Onattukara* and the minimum in the black soils of Chittoor.

Entropy change $\Delta S^0(25)$ and $\Delta S^0(40)$ were negative for soils of Chittoor and *Kayal* lands. Except in these two soils, ΔS^0 decreased with increase temperature. The maximum value for $\Delta S^0(25)$ (0.86 kcal mol^{-1} K^{-1}) and $\Delta S^0(40)$ (0.82 kcal mol^{-1} K^{-1}) was recorded in the soils of *Onattukara* and the minimum in the soils of *Kayal* lands of *Kuttanad* .

Experiment 4

Effect of organic matter on boron adsorption

An incubation experiment in the laboratory was conducted in three soils viz. Onattukara sandy soil (S_1), lateritic upland soil from Pattambi (S_2), lowland soil from Elavampadam (S_3) to study the effect of organic matter on adsorption of boron in soil by adding different levels organic matter and borax to soil. The hot water extractable boron was estimated at three different stages *viz.* one month, two months and three months after incubation.

4.1. Effect of different levels of organic matter and borax on the availability of B in soils after one month of incubation.

The data on the available B estimated after one month of incubation are given in the table 22. In sandy soils of Onattukara, the highest available B of 1.60 mg kg^{-1} was recorded in the treatment where borax was applied @ 6 kg ha^{-1} and minimum in the treatment without borax. An increase in the dose of borax to 12 kg ha^{-1} resulted in a decrease in the content of available B to 1.53 mg kg^{-1}. Even though the available B had increased with the levels of borax, the treatment with 6 kg borax ha^{-1} was only significantly different from others.

In this soil, the lowest available B of 1.48 mg kg^{-1} was recorded at 15 t OM ha^{-1} and the highest of 1.53 mg kg^{-1} at 5 t OM ha^{-1}. The treatment without organic matter recorded an available B of 1.50 mg kg^{-1} which was higher than that recorded at O_3 (15 t OM ha^{-1}), but not significant.

The highest available B of 1.77 mg kg^{-1} was observed in the treatment combination with 12 kg borax and 0 t organic matter ha^{-1} (B_3O_0) and the lowest of 0.97 mg kg^{-1} in B_0O_0. Here the treatment combinations B_1O_0, B_2O_0, B_2O_1, B_2O_2, B_0O_2 and B_0O_3 were on par.

In the upland soils of Pattambi, the application of borax did not produce any significant change in the availability of boron though a slight decrease was noticed with the increasing levels of borax. Increase in the levels of organic matter reduced the status of available B from

Table 22. Effect of different levels of organic matter and borax on the availability of B in soils after one month of incubation

Soil	Organic matter / Borax	B_0	B_1	B_2	B_3	Mean
S_1	O_0	0.97	1.57	1.7	1.77	**1.50**
	O_1	1.51	1.46	1.63	1.52	**1.53**
	O_2	1.60	1.40	1.58	1.47	**1.51**
	O_3	1.67	1.35	1.51	1.39	**1.48**
	Mean	**1.43**	**1.44**	**1.60**	**1.53**	
S_2	O_0	1.56	1.74	1.79	1.87	**1.74**
	O_1	1.62	1.65	1.71	1.74	**1.68**
	O_2	1.76	1.52	1.64	1.49	**1.60**
	O_3	1.86	1.50	1.56	1.38	**1.57**
	Mean	**1.70**	**1.60**	**1.66**	**1.62**	
S_3	O_0	2.17	2.13	2.09	1.95	**2.08**
	O_1	2.29	2.02	1.91	1.87	**2.02**
	O_2	2.35	1.46	1.86	1.78	**1.86**
	O_3	2.42	1.86	1.88	1.78	**1.97**
	Mean	**2.31**	**1.86**	**1.93**	**1.84**	

CD (Soil X Borax) : 0.105

CD (Soil X Organic matter): 0.104

CD (Soil X OM X Borax) : 0.207

1.74 mg kg^{-1} to 1.57 mg kg^{-1} in the treatment without organic matter and with highest dose of OM (15 t OM ha^{-1}) respectively. Here the available B levels at higher doses of organic matter (O_2 and O_3) were critically lower from lower doses (O_0 and O_1).

The highest available B of 1.875 mg kg^{-1} was noticed in the treatment with 12 kg ha^{-1} without organic matter (B_3O_0) which was on par with the treatment combinations of 10 and 15 t OM ha^{-1} without borax (B_0O_2 and B_0O_3 respectively), 3 and 6 kg of borax ha^{-1} without organic matter (B_1O_0 and B_2O_0 respectively), 6 and 12 kg borax ha^{-1} with 5 t OM ha^{-1}(B_2O_1 and B_3O_1). The minimum available B of 1.38 mg kg^{-1} was recorded in the treatment with highest dose of borax and organic matter (B_3O_3) which was on par with B_1O_2 and B_0O_0.

In the low land soils of Elavampadam, the available B decreased from 2.31 mg kg^{-1} at 0 kg borax ha^{-1} to 1.84 mg kg^{-1} at highest dose of borax. Though a decrease in the availability of B was noticed with increasing levels of borax, it was not significant.

The lowest available B of 1.86 mg kg^{-1} was noticed in the treatment with 10 t OM ha^{-1} and the highest of 2.08 mg kg^{-1} in the treatment without organic matter. There was a general decrease in the availability of B with increasing levels of organic matter in the low land soils. Here the available B levels at higher doses of organic matter (O_2 and O_3) were critically lower from lower doses (O_0 and O_1).

The treatment combination of 15 t OM ha^{-1} and 0 kg borax ha^{-1} recorded a maximum availability of boron (2.42 mg kg^{-1}) and was on par with B_0O_1 and B_0O_2. The lowest of 1.46 mg kg^{-1} was found at B_1O_2 (3 kg borax ha^{-1} and 10 t OM ha^{-1}).

In the treatment combinations of borax without OM, both in sandy soils and lateritic soils, available B increased significantly with the levels of borax whereas in low land soils, boron reduced and only B_0O_3 was significantly lower than others.

Table 23. Effect of different levels of organic matter and borax on the availability of B in soils after two months of incubation

Soil	Organic matter / Borax	B_0	B_1	B_2	B_3	Mean
S1	**O_0**	0.93	1.535	1.64	1.73	**1.46**
	O_1	1.53	1.46	1.60	1.48	**1.51**
	O_2	1.50	1.30	1.48	1.42	**1.42**
	O_3	1.65	1.34	1.46	1.34	**1.44**
	Mean	**1.40**	**1.40**	**1.54**	**1.49**	
S2	**O_0**	1.51	1.61	1.67	1.705	**1.62**
	O_1	1.61	1.54	1.53	1.58	**1.56**
	O_2	1.61	1.50	1.57	1.40	**1.52**
	O_3	1.67	1.41	1.50	1.37	**1.48**
	Mean	**1.60**	**1.51**	**1.57**	**1.51**	
S3	**O_0**	1.97	1.99	1.89	1.77	**1.90**
	O_1	2.12	1.81	1.67	1.52	**1.78**
	O_2	2.07	1.73	1.71	1.63	**1.78**
	O_3	2.30	1.71	1.66	1.58	**1.81**
	Mean	**2.11**	**1.81**	**1.73**	**1.62**	

CD (Soil X Borax): 0.019

CD (Soil X Organic matter): 0.018

CD (Soil X OM X Borax): 0.0389

4.2. Effect of different levels of organic matter and borax on the availability of B in soils after two months of incubation

The data on the available B after two months of incubation are given in table 23. In Onattukkara sandy soils, it was observed that available B increases with the levels of applied borax. The treatment with 6 kg borax ha^{-1} recorded the maximum of 1.54 mg kg^{-1} and the treatment without borax recorded the minimum of 1.40 mg kg^{-1}. The treatments without borax and 3 kg borax ha^{-1} were on par and they were significantly different from treatments with 6 and 12 kg borax ha^{-1}.

The treatment with 5 t OM ha^{-1} recorded the maximum available B of 1.51 mg kg^{-1} and it was significantly higher than that of all other treatments of organic matter.

The treatment combination B_3O_0 (12 kg borax ha^{-1} and 0 t OM ha^{-1}) recorded the highest available B of 1.73 mg kg^{-1} and was significantly superior to all other treatments. The application of organic matter @ 15 t ha^{-1} without borax (B_0O_3) recorded an available B of 1.65 mg kg^{-1} which was on par with the treatment with 6 kg borax and 0 t OM ha^{-1} (B_2O_0).

In the lateritic upland soils from Pattambi, the application of borax significantly reduced the amount of available B after two months of incubation. An available B of 1.60 mg kg^{-1} estimated at 0 kg borax ha^{-1} was reduced to 1.51 mg kg^{-1} as the application of borax was raised 3 kg ha^{-1} and was slightly increased to 1.57 mg kg^{-1} when the dose of borax was increased to 6 kg ha^{-1} and it further reduced to 1.51 mg kg^{-1} when the dose was enhanced to 12 kg ha^{-1}. Here B_1 and B_3 were on par.

Application of organic matter significantly reduced the available B. The highest available B of 1.62 mg kg^{-1} was noticed in the treatment without OM and the minimum at highest dose of OM, and all the treatments of OM were found significantly different from each other.

The lowest available B of 1.37 mg kg^{-1} was noticed with highest dose of borax and organic matter (B_3O_3) and the highest of 1.70 mg kg^{-1} in the treatment with highest dose of borax without organic matter (B_3O_0) which was on par with B_2O_0 and B_0O_3. The treatment combinations B_0O_1, B_0O_2, B_1O_0 and B_2O_2 were on par.

In the low land soils of Elavampadam, the availability of B decreased with the increasing levels of borax. The maximum availability of 2.11 mg kg^{-1} was noticed where borax was not applied and the minimum availability of 1.62 mg kg^{-1} at 12 kg borax ha^{-1}. Here all the treatments of borax were critically different. The availability of B was found to get reduced with the increase in the levels of OM. But O_1, O_2 and O_3 were on par. The maximum available B of 2.30 mg kg^{-1} was found where OM was applied @ 15 t ha^{-1} without the addition of borax and the minimum of 1.52 mg kg^{-1} in the combination of 12 kg borax and 5 t OM ha^{-1} (B_3O_1). Here B_1O_2, B_1O_3 and B_2O_2 were on par and all other treatments were critically different.

In the treatment combinations of borax without OM, both in sandy soils and lareritic soils, available B was found to increase with the levels of borax whereas in low land soils, available B reduced with the levels of borax in all the treatment combinations with and without OM while no clear trend of increase in the amount of available B was noticed in the treatment combinations with the levels of OM without borax in all the three soils.

4.3. Effect of different levels of organic matter and borax on the availability of B in soils after three months of incubation

The available boron estimated after three months of incubation are given in the table 24. In the sandy soils of Onattukkara maximum available B of 1.49 mg kg^{-1} was recorded in the treatment receiving 6 kg borax (B_2) and the minimum of 1.37 mg kg^{-1} in the treatment without borax. Though the available B recorded at 12 kg borax ha^{-1} was slightly lower than that at 6 kg borax ha^{-1}, they were on par.

The increase in the dose of OM from 0 t 5 t ha^{-1} increased the available B from 1.41 to 1.48 mg kg^{-1}. Further increase in OM to 10 t ha^{-1}(O_2) reduced the available B to 1.38 mg kg^{-1} which again increased to 1.40 mg kg^{-1} when the dose of OM was enhanced to 15 t ha^{-1} (O_3), but O_2 and O_3were on par.

The maximum availability of B (1.68 mg kg^{-1}) was found in the treatment with 12 kg borax ha^{-1} without OM, and the minimum in the treatment where both borax and OM were not applied (B_0O_0). The treatment with 6 kg borax ha^{-1} without OM recorded an available B of 1.61 mg kg^{-1} and was on par with B_0O_3 and B_2O_1.

In the lateritic upland soils of Pattambi, though the increase in the levels of borax slightly reduced the availability of B, it was not significant. The increase in the levels of OM from 0 to 15 t ha^{-1} reduced the available B from 1.56 to 1.40 mg kg^{-1}. Here O_0 and O_1 were on par, O_2 and O_3 were critically different from each other.

Among the treatment combinations, the minimum availability of B (1.31 mg kg^{-1}) was noticed at B_2O_3 and B_3O_3 and the maximum of 1.63 mg kg^{-1} in the treatment with highest dose of borax without OM (B_3O_0) and on par with B_2O_0, B_1O_0, B_3O_1 and B_0O_3.

In the lowland soils of Elavampadam, the maximum available B of 2.06 mg kg^{-1} recorded at 0 t OM ha^{-1} was reduced to 1.54 mg kg^{-1} upon increase in the dose of OM to 15 t ha^{-1} (O_3). Here all the treatments were significantly different.

The maximum available B of 2.25 mg kg^{-1} was found in the treatment combination B_0O_3 and the minimum of 1.47 mg kg^{-1} at B_3O_3. The treatment combinations with increasing levels of borax without OM decreased the availability of B.

In the sandy soils of Onattukara, in the treatment combination with different levels of OM without borax, the availability of B was found to get increased with the levels of OM, However the treatments with 5 and 10 t OM ha^{-1} were on par. The same trend was noticed with increasing levels of borax without the application of organic matter. Here all the treatment combinations were critically different.

Table 24. Effect of different levels of organic matter and borax on the availability of B in soils after three months of incubation

Soil	Organic matter / Borax	B_0	B_1	B_2	B_3	Mean
S1	**O_0**	0.89	1.48	1.61	1.68	**1.41**
	O_1	1.49	1.42	1.57	1.47	**1.48**
	O_2	1.51	1.30	1.40	1.34	**1.38**
	O_3	1.60	1.27	1.41	1.32	**1.40**
	Mean	**1.37**	**1.36**	**1.49**	**1.45**	
S2	**O_0**	1.43	1.59	1.60	1.63	**1.56**
	O_1	1.57	1.52	1.50	1.60	**1.55**
	O_2	1.51	1.40	1.47	1.34	**1.43**
	O_3	1.61	1.39	1.31	1.31	**1.40**
	Mean	**1.53**	**1.47**	**1.47**	**1.47**	
S3	**O_0**	1.86	1.81	1.72	1.68	**1.77**
	O_1	2.06	1.69	1.55	1.44	**1.68**
	O_2	2.10	1.69	1.66	1.57	**1.75**
	O_3	2.25	1.61	1.58	1.47	**1.73**
	Mean	**2.06**	**1.70**	**1.63**	**1.54**	

CD (Soil X Borax): 0.0181

CD (Soil X Organic matter): 0.0182

CD (Soil X OM X Borax): 0.0366

In the lateritic upland soils of Pattambi, in the treatment combinations of different levels of borax with without the organic matter, the availability of B was found to get increased with the levels of borax, however the B recorded at 3 and 6 kg borax ha^{-1} were on par. Though the increase in the levels of OM without borax significantly increased availability of B, a decrease in the availability was noticed at 10 t OM ha^{-1}.

In the low land soils of Elavampadam, in the treatment combination with different levels of OM without borax, the availability of B significantly increased with the levels of OM. But the increase in the levels of borax with and without OM reduced the availability of B.

Experiment 5

Boron nutrition for rice

5.1. Biometric observations

5.1.1. Tiller production

The data on the number of tillers observed at weekly interval is given in the table 25. The treatments could not produce any significant effect on the total number of tillers. The total number of tillers and productive tillers observed at harvest is given in table 26. The maximum number of tillers was produced in T_4 where borax was applied @ 6 kg ha^{-1}. Only T_4 was significantly different from all other treatments. But T_2, T_3, T_5, T_6, T_7 were on par.

The maximum number of nine productive tillers was produced in T_4 and it was superior to all other treatments. In both T_3 and T_6, seven productive tillers were observed. The minimum number of five productive tillers was observed in control. The treatment, T_4 was superior to all the treatments and T_5 and T_6 were on par with T_3.

5.1.2. Panicle characters

The data on the number of branches per panicle, number of grains per panicle and thousand grain weight are presented in the table 27. There was no significant difference between the treatments with respect to the number of branches per panicle. The maximum number of grains per panicle was observed in the treatment receiving the application of borax @6 kg ha^{-1} and the minimum in T_1. Here T_2, T_3, T_5 and T_7 were on par with T_4.

5.1.3. Thousand grain weight

Data in table 27 shows that the maximum of 30.50 g thousand grain weight was recorded in T_4 and it was superior to all the treatments. T_3, T_2 and T_7 were on par.

Table 25. Effect of borax on number of tillers observed at weekly intervals

Treatment	First week	Second week	Third week	Fourth week
T_1	5.6	7.0	7.3	7.3
T_2	4.6	7.3	8.6	8.6
T_3	4.6	7.0	7.3	7.3
T_4	4.3	7.3	7.6	7.6
T_5	5..0	7.0	7.0	7.0
T_6	5.0	6.6	8.0	7.6
T_7	4.6	6.3	7.3	7.3
CD	NS	NS	NS	NS

Table 26. Effect of borax on number of total tillers and productive tillers at harvest

Treatment	Total tillers	Productive tillers
T_1	5.6	5.0
T_2	7.0	6.0
T_3	7.3	7.0
T_4	9.0	9.0
T_5	7.3	6.6
T_6	7.3	7.0
T_7	7.3	6.3
CD	1.2*	0.50*

Table 27. Effect of borax on number of branches per panicle, grains per panicle and thousand grain weight

Treatment	**No. of branches per panicle**	**No. of grains per panicle**	**Thousand grain weight**
T_1	8.0	97.0	27.60
T_2	8.0	108.6	28.85
T_3	8.6	114.3	29.11
T_4	8.0	117.0	30.50
T_5	7.6	114.3	27.07
T_6	8.6	106.3	27.64
T_7	8.3	110.3	28.27
CD	NS	9.65*	1.01**

Table 28. Effect of borax on grain yield

Treatment	**Grain yield**	
	kg plot^{-1}	**Mg ha^{-1}**
T_1	14.17	7.08
T_2	15.06	7.53
T_3	15.84	7.92
T_4	16.15	8.07
T_5	15.32	7.66
T_6	14.86	7.43
T_7	14.80	7.40
CD	0.61**	0.30**

Table 29. Effect of borax on weight of straw and chaffy grains

Treatment	Straw yield (Mg ha^{-1})	Chaffy grains (kg ha^{-1})
T_1	12.05	162
T_2	12.41	150
T_3	13.43	125
T_4	13.43	133
T_5	12.06	154
T_6	13.85	171
T_7	13.67	154
CD	NS	NS

Table 30. Boron uptake in straw, grain and total uptake

Treatment	Straw		Grain		Total	
	mg $plot^{-1}$	g ha^{-1}	mg $plot^{-1}$	g ha^{-1}	mg $plot^{-1}$	g ha^{-1}
T_1	211.44	105.72	41.62	20.81	253.06	126.53
T_2	258.93	129.47	59.14	29.57	318.08	159.04
T_3	345.25	172.63	65.96	32.98	411.21	205.60
T_4	467.95	233.97	108.01	54.00	575.95	287.98
T_5	240.71	120.35	70.06	35.03	310.77	155.38
T_6	271.46	135.73	65.99	32.99	337.46	168.73
T_7	266.41	133.21	67.02	33.51	333.43	166.72
CD	53.99**	27.01**	5.17**	2.58**	52.52**	26.25**

5.1.4. Grain yield

Grain yield recorded in each treatment in kg plot^{-1} and Mg ha^{-1} is presented in the table 28. The maximum grain yield of 8.07 Mg ha^{-1} was recorded in the treatment which received the application of borax @ 6 kg ha^{-1} (T_4) and the minimum was recorded in the control plot (7.08 Mg ha^{-1}). T_4 and T_3 were on par and T_5, T_6, T_2 and T_7 were on par.

5.1.5. Straw yield and chaffy grains

The straw yield and the weight of chaffy grains recorded in each treatment are presented in the table 29. The highest straw yield of 13.85 Mg ha^{-1} recorded in T_6 and the minimum in T_1 (12.05 Mg ha^{-1}). The maximum weight of chaffy grains (171 kg ha^{-1}) were recorded in the treatment where 10 kg borax was applied and the minimum in T_3 (125 kg ha^{-1}). There was no significant difference between the treatments with respect to the weight of straw as well as chaffy grains.

5.1.6 Uptake of boron

The uptake of boron by straw as well as grains recorded per plot and per ha as well as the total uptake is given in table 30. The maximum uptake of boron in straw (233.97 g ha^{-1}) was noticed in the treatment with 6 kg borax ha^{-1} (T_4) where the maximum grain yield was recorded and the minimum value was recorded in the control (105.72 g ha^{-1}). The uptake of boron in grains also varied significantly with respect to the treatments. Here as well the maximum uptake was recorded in T_4 and the minimum in control. Consequently the lowest total uptake of 126.0 g ha^{-1} was recorded in the control and the highest of 287.98 g ha^{-1} in T_4.

5.2. Soil and plant analysis

5.2.1. Effect of borax on nutrient status of soil at panicle initiation

The data on the electrochemical properties and nutrient contents in the soil at panicle initiation are presented in the table 31 .

The application of different levels of borax had no significant effect on pH, EC and organic carbon status of the soil, while the available phosphorus content of experimental soils varied significantly with respect to the levels of borax. The maximum available P content of 9.70 kg ha^{-1} was found in T_4 and the minimum of 8.08 kg ha^{-1} was noticed in the control plot. However T_4 was on par with T_2, T_3, T_6 and T_7. Available potassium status of the soil was not significantly influenced by the levels of borax.

Secondary and micronutrient status of the experimental soils was influenced by the levels of borax. The data are given in the table 32. Calcium and magnesium content of the soils of the experimental plots were not significantly influenced by the treatment. Available sulphur status varied significantly with respect to the levels of borax. Though maximum sulphur content (20.06 mg kg^{-1}) was found in the control plot it was on par with T_6.

The application of different levels of borax could not produce any significant influence on the available Fe, Mn, Zn and Cu content (Table 33) of soil.

The available boron content of the experimental soils influenced by the level of borax is presented in the table 34. The hot water extractable B increased from 0.80 mg kg^{-1} to 1.20 mg kg^{-1} as the level of borax was enhanced from 0 to 12 kg ha^{-1}.

5.2.2 Fractions of boron at PI

The different fractions of soil boron as well as the total B estimated in the soils of treatment plots are presented in the table 35. T_4 recorded highest RS-B while T_1 recorded the lowest. RS-B increased from lowest value of 0.080 in T_1 (control) to 0.353 in was T_4 further found to be decreased to 0.260 mg kg^{-1} in $T_{7.}$ Specifically absorbed boron was recorded the highest in T_4 (0.567 mg kg^{-1}) and the minimum (0.370 mg kg^{-1}) in the control plot, T_4 was superior to all other treatments, and T_3, T_1, T_2 were on par. Oxide bound B increased with the levels of borax from 4.13 mg kg^{-1} in the control to 4.87 mg kg^{-1} inT_7. Here T_7 was superior to all the treatment, T_6 was on par with T_5 and T_3 was on par with T_2.

Table 31. Effect of borax on electro chemical properties and nutrient content of soil at PI

Treatment	pH	EC (dSm^{-1})	OC (%)	P ($kg\ ha^{-1}$)	K($kg\ ha^{-1}$)
T_1	4.82	0.032	1.56	8.08	168.00
T_2	4.85	0.034	1.39	8.70	151.20
T_3	4.82	0.033	1.23	9.58	148.58
T_4	4.82	0.034	1.25	9.70	170.24
T_5	4.83	0.036	1.30	8.28	159.04
T_6	4.78	0.034	1.16	9.68	153.06
T_7	4.81	0.035	1.29	8.80	160.16
CD	NS	NS	NS	1.04*	NS

Table 32. Effect of borax on secondary nutrient content of soil at PI

Treatment	($mg\ kg^{-1}$)		
	Ca	**Mg**	**S**
T_1	78.80	60.00	8.63
T_2	69.20	59.35	9.14
T_3	71.91	56.55	11.15
T_4	74.45	60.53	12.38
T_5	74.51	57.70	12.50
T_6	73.36	59.50	19.36
T_7	75.51	57.50	20.06
CD	NS	NS	3.878**

Table 33. Effect of borax on content of micronutrient in soil at PI

Treatment	Micronutrient (mg kg^{-1})			
	Fe	**Mn**	**Zn**	**Cu**
T_1	186.33	20.80	3.20	32.0
T_2	183.26	20.47	3.10	31.0
T_3	172.96	19.73	3.10	31.0
T_4	184.83	17.96	4.03	40.3
T_5	177.67	20.60	2.76	27.67
T_6	175.60	24.10	2.93	29.33
T_7	177.10	20.13	4.0	40.0
CD	NS	NS	NS	NS

Table 34. Effect of borax on available B in soil at PI

Treatment	B (mg kg^{-1})
T_1	0.80
T_2	0.82
T_3	0.89
T_4	0.96
T_5	0.78
T_6	0.90
T_7	1.20
CD	0.08**

Table 35. Effect of borax on fractions of B in soil at PI

Treatment	Fractions of boron (mg kg^{-1})					
	RS-B	SA-B	OX-B	OR-B	RES-B	Total-B
T_1	0.080	0.370	4.13	1.22	130.52	136.33
T_2	0.167	0.503	4.31	1.36	132.65	139.00
T_3	0.240	0.453	4.41	1.38	134.45	141.00
T_4	0.353	0.567	4.51	1.37	137.18	144.00
T_5	0.243	0.497	4.57	1.56	137.78	144.67
T_6	0.297	0.433	4.64	1.40	139.56	146.33
T_7	0.260	0.470	4.87	1.29	139.77	146.67
CD	0.045**	0.30**	0.076**	0.117**	1.755**	1.70**

Table 36. Effect of borax on primary and secondary nutrient contents in shoot at PI

Treatment	Primary nutrients (%)			Secondary nutrients (mg kg^{-1})		
	N	P	K	Ca	Mg	S
T_1	0.38	0.26	0.82	915	371	741
T_2	0.41	0.24	0.81	911	573	930
T_3	0.49	0.26	0.82	741	516	908
T_4	0.54	0.26	0.81	778	646	858
T_5	0.43	0.29	0.86	684	476	816
T_6	0.43	0.29	0.86	587	522	613
T_7	0.36	0.25	0.77	703	467	941
CD	0.045**	NS	NS	NS	NS	91**

Table 37. Effect of borax on content of micronutrients in shoot at PI

Treatment	Micronutrients (mg kg^{-1})			
	Fe	Mn	Zn	Cu
T_1	1393.3	197.80	66.37	2.17
T_2	1010.67	176.67	60.33	1.80
T_3	1050.00	179.00	84.03	2.17
T_4	993.33	199.00	56.00	1.93
T_5	530.00	213.67	55.77	1.73
T_6	340.00	208.92	66.90	1.47
T_7	310.00	230.63	57.33	2.20
CD	106.43**	NS	11.58**	NS

Table 38. Effect of borax on boron content in shoot and root at PI

Treatment	B (mg kg^{-1})	
	Shoot	Root
T_1	3.30	25.26
T_2	5.20	27.76
T_3	5.63	31.73
T_4	6.13	29.93
T_5	5.96	33.66
T_6	3.70	34.86
T_7	3.40	28.73
CD	0.5633**	4.35**

OR-B increased linearly from T_1 (1.22 mg kg^{-1}) up to T_5(1.56 mg kg^{-1}) and reduced to 1.29 mg kg^{-1} in T_7. Whereas T_7 recorded highest value for RES-B (139.77 mg kg^{-1}) and the lowest in the control plot (130.52 mg kg^{-1}) RES-B increased linearly with the levels of borax. The same trend was observed in the case of total borax also it varied from 136.33 mg kg^{-1} to 146.67 mg kg^{-1}.

5.2.3. Nutrient content in shoot at panicle initiation

The primary and secondary nutrients estimated in shoot samples at PI are presented in the table 36. Highest content of nitrogen was noticed in T_4 (0.54 per cent) and the minimum at T_7 (0.36 per cent). Though T_4 recorded the highest it was on par with T_3.

Total phosphorus, potassium, calcium and magnesium content in shoot were not significantly influenced by the levels of borax, but the total sulphur content in shoot was significantly influenced by the treatments. A highest value of 941.66 mg kg^{-1} was estimated at T_7 and lowest value of 741.6 mg kg^{-1} at T_1. Though significant, the change in S content was not linear at higher levels of borax.

Table 37 shows the micronutrient content of shoot samples at PI. Iron and zinc varied significantly with respect to the levels of borax. Highest Fe content was noticed in T_1 (1393 mg kg^{-1}) and was found reduced linearly with the levels of borax whereas Zn content was highest in T_3 (84 mg kg^{-1}) and lowest in T_4. Though Mn content increased with levels of borax, it was not significant.

5.2.4. Total boron content in shoot and root at panicle initiation

Table 38 shows the total boron content estimated both in shoot and root at PI. A maximum of 6.13 mg kg^{-1} of boron was estimated in the shoot samples of T_4 and a minimum of 3.30 mg kg^{-1} of B in samples of T_1. Though T_4 was highest, it was on par with T_3 and T_5. Total B in root samples was maximum in T_6 (34.86 mg kg^{-1}) and minimum in T_1 (25.26 mg kg^{-1}). T_5 recorded 33.66mg kg^{-1} of total boron, and was on par with that of T_6 and T_3.

5.2.5. Correlation coefficients of available B, fractions of soil B with content of B in shoot at PI

Data in table 39 show that available B had very high positive correlation with RS-B (0.645**), OX-B (0.838**) and residual boron (0.788**). Readily soluble B had a very high positive correlation with SA-B (0.759**), OX-B (0.556**) and RES-B (0.629**). Boron content of shoot was significantly correlated with RS-B (0.521*). Specifically adsorbed B had significant positive correlation with OR-B (0.526**) and RES-B (0.456*). The B content in shoot was also correlated with specifically adsorbed B (0.572*) and OR-B (0.597**).

5.2.6. Path analysis

Path coefficients of different fractions of B indicating the direct and indirect effects on available B at PI are given in the table 40. The direct effect of RS-B on hot water extractable B at PI was moderate. The indirect effect of OX-B and RES-B through RS-B was low. While the direct effect of oxide bound B on available B was high as indicated by the path coefficient of 0.6352. The indirect effect of RS-B and RES-B through OX-B on available B was also high. The direct effect of RES-B on available B was negligible.

The path coefficients explaining the direct as well as indirect effects of SA-B, OX-B and RES-B on RS-B are presented in the table 41. Specifically adsorbed B had a high direct effect (0.5988) on RS-B and the indirect of OX-B and RES-B through SA-B on readily soluble B was moderate. Oxide bound B had a negligible direct effect on RS-B and RES-B had a moderate direct effect on RS-B.

The path coefficients showing the direct and indirect effects of fractions of soil B on the content of boron in shoot at PI are presented in the table 42. RS-B had a high direct effect (0.5976) on content of B in shoot. SA-B had high direct effect on B in shoot through RS-B while the boron bound to organic matter in soil had a moderate indirect effect through RS-B. Organically bound B had a high direct effect on content of B in shoot. The indirect effect of RS-B and SA-B through OR-B on the content of B in shoot at PI was moderate. The direct effect of SA-B on the content of in Shoot was low.

Table 39. Correlation between fractions of B and content of B in shoot at PI

	Available boron	**RS-B**	**SA-B**	**OX-B**	**OR-B**	**RES-B**	**boron in shoot**
Available B	1.00						
RS-B	0.645**	1.00					
SA-B	0.156	0.759**	1.00				
OX-B	0.838**	0.556**	0.371	1.00			
OR-B	0.320	0.313	0.526*	0.235	1.00		
RES-B	0.788**	0.629**	0.456*	0.877**	0.372	1.00	
B in shoot	0.313	0.521*	0.572*	0.093	0.597**	0.013	1.00

(** sigificant at 1.00 % level, * significant at 5.00 % level))

Table 40. Path coefficient of different fractions to available B at panicle initiation

	RS-B	**OX-B**	**RES-B**	**Correlation coefficient**
RS-B	**0.2460**	0.3504	0.0481	0.6445**
OX-B	0.1357	**0.6352**	0.0672	0.8381**
RES-B	0.1533	0.5571	**0.0772**	0.7876**

(Values on diagonal are direct effects and values on horizontal lines are indirect effects)

Table 41. Path coefficient of different fractions to RS- B at panicle initiation

	SA-B	OX-B	RES-B	Correlation coefficient
SA-B	**0.5988**	0.0331	0.1270	0.7589**
OX-B	0.2224	**0.0891**	0.2441	0.5556**
RES-B	0.2731	0.0782	**0.2784**	0.6297**

(Values on diagonal are direct effects and values on horizontal lines are indirect effects)

Table 42. Path coefficient of different fractions to boron content in shoot at panicle initiation

	RS-B	SA-B	OR-B	Correlation coefficient
RS-B	**0.5976**	0.1159	0.2050	0.9185**
SA-B	0.4482	**0.1545**	0.2551	0.8578**
OR-B	0.2526	0.0813	**0.4849**	0.8188**

(Values on diagonal are direct effects and values on horizontal lines are indirect effects)

5.2.7. Effect of borax on nutrient status of soil at harvest

The data on electrochemical properties, OC, P and K at harvest is given in the table 43. pH and EC were not influenced by the treatment, while OC status of the soil was significantly influenced by the levels of borax. The control plot recorded the maximum OC content (1.23 per cent) and T_2 recorded the lowest (0.099 per cent) but no linear relationship of OC was observed with the levels of borax. Available P and K also were significantly influenced by the application of different levels of borax. Available P was found to reduce from T_2 (10.53) to T_7 (8.40) and T_2 was on par with T_3 which was on par with T_4, T_6 and T_7. Available K was highest in the control plot and the lowest in T_6. Potassium content in the soil was reduced slowly from the control treatment and then reduced drastically after T_4.

The data on available Ca and Mg, content of soil as influenced by the treatment are given the table 44. Both available Ca and Mg content of the soil did not significantly differ with respect to the levels of borax application. But the available sulphur was found to reduce from 18.77 mg kg^{-1} to 8.40 mg kg^{-1}as the level of borax was raised from 0 to 12 kg ha^{-1}.

The available Fe, Mn, Zn and Cu status of the soils from the treatments plots are presented in the table 45. None of the elemental status in soil was significantly differed with respect to the treatment.

Available B content (table 46) of the soils of the treatment plots varied significantly with respect to the levels of borax. Plant available B increased from 0.85 to 1.32 mg kg^{-1} when the borax was enhanced from 0 to 12 kg ha^{-1}.

5.2.8. Fraction of boron in soil at harvest.

The data on total boron in soil as well as its various fractions estimated at harvest are presented in the table 47. The treatments had significant difference with respect to the readily soluble boron and it had maximum value at T_3 (0.293 mg kg^{-1}) and very low value of 0.053 mg kg^{-1} at T_1. Though T_3 recorded the highest it was on par with T_4, T_5 and T_7.

Table 43. Effect of borax on electro chemical properties and nutrient content of soil at harvest

Treatment	**pH**	**EC (dSm^{-1})**	**OC (%)**	**P (kg ha^{-1})**	**K(kg ha^{-1})**
T_1	4.59	0.04	1.23	6.81	110.58
T_2	4.63	0.041	0.099	10.53	101.94
T_3	4.68	0.046	1.14	9.69	107.95
T_4	4.63	0.038	1.06	8.81	109.62
T_5	4.68	0.036	1.03	7.80	89.40
T_6	4.66	0.039	1.71	8.43	83.62
T_7	4.64	0.039	1.15	8.40	89.80
CD	NS	NS	0.135*	1.33**	9.17**

Table 44. Effect of borax on secondary nutrient content of soil at harvest

Treatment	**Secondary nutrient (mg kg^{-1})**		
	Ca	**Mg**	**S**
T_1	75.65	60.35	18.77
T_2	75.81	59.70	17.96
T_3	75.96	58.25	15.30
T_4	75.55	58.61	11.87
T_5	76.95	59.00	11.32
T_6	75.83	57.01	10.98
T_7	75.75	59.13	8.40
CD	NS	NS	2.76**

Table 45. Effect of borax on micronutrient content of soil at harvest

Treatment	Micronutrient (mg kg^{-1})			
	Fe	Mn	Zn	Cu
T_1	159.93	19.40	3.13	6.50
T_2	153.16	21.80	3.76	5.93
T_3	163.00	20.90	3.40	6.30
T_4	161.73	20.06	3.00	6.36
T_5	158.13	22.20	2.93	6.26
T_6	160.30	20.56	2.30	5.56
T_7	163.36	23.00	3.50	6.80
CD	NS	NS	NS	NS

Table 46. Effect of borax on available B in soil at harvest

Treatment	B (mg kg^{-1})
T_1	0.85
T_2	0.94
T_3	0.95
T_4	0.99
T_5	1.04
T_6	1.27
T_7	1.32
CD	0.155**

SA-B had maximum value of 0.353 mg kg^{-1} at T_5 and a minimum of 0.110 mg kg^{-1} at T_1. Similar to RS-B, treatments were also significantly different with respect to content of SA-B in soil. Oxide bound-B was highest at T_7 (4.96 mg kg^{-1}) but it was on par with T_6, T_5, T_4, T_1. OR-B had a maximum value of 1.607 mg kg^{-1}in T_5 and minimum of 1.210 mg kg^{-1} at T_1. OR-B was significantly influenced by the application of different levels of borax.

Both RES-B and Total-B were also significantly influenced by the levels of borax. In both the cases, T_1 recorded lowest and T_7 recorded the highest value. Both RES-B and TB increased linearly with the levels of borax when its dose was raised from 0 to 12 kg ha^{-1}. Though both were significantly differed over the control T_4, T_5, T_6 were on par with T_7.

5.2.9. Nutrient content in straw at harvest

The data on primary and secondary nutrient contents estimated in straw samples are given in table 48. Highest content of nitrogen was noticed in T_4 (0.470 per cent) and the lowest in T_1 (0.307 per cent) The nitrogen content in shoot increased up to T_4 and then reduced. Though T_4 recorded highest it was on par with T_3.

The treatment had not significantly influenced the total P, K, Ca and S content of straw while the Mg content on shoot varied significantly with respect to the treatments.

Table 49 shows the total micronutrient content in straw samples at harvest. Fe content in shoot increased linearly from T_1 (256.60 mg kg^{-1}) to T_4 (850.00 mg kg^{-1}) and then decreased. Total Mn content also recorded the highest value of 579.33 mg kg^{-1}in T_4 and the lowest in T_7 (369.33 mg kg^{-1}).

Total Zn in straw also varied significantly with respect to the levels of borax. The content of Zn also was highest in T_4 and the lowest in T_7. The total copper content was not influenced significantly by the treatments.

Table 47. Effect of borax on fractions of B in soil at harvest

Treatment	Fractions of boron (mg kg^{-1})					
	RS-B	SA-B	OX-B	OR-B	RES-B	Total-B
T_1	0.053	0.110	4.32	1.210	128.30	134.00
T_2	0.147	0.153	4.38	1.313	131.67	137.66
T_3	0.293	0.213	4.30	1.407	133.22	139.33
T_4	0.263	0.283	4.90	1.457	134.43	141.33
T_5	0.257	0.353	4.95	1.607	135.16	142.33
T_6	0.193	0.283	4.94	1.507	135.74	142.66
T_7	0.230	0.300	4.96	1.540	136.30	143.33
CD	0.039**	0.042**	0.149**	0.072**	3.214**	3.214**

Table 48. Effect of borax on primary and secondary nutrient contents in straw at harvest

Treatment	Primary nutrient (%)			Secondary nutrient (mg kg^{-1})		
	N	P	K	Ca	Mg	S
T_1	0.307	0.09	0.94	2828	536	633
T_2	0.323	0.08	0.87	3560	525	733
T_3	0.453	0.07	0.92	4876	561	633
T_4	0.470	0.09	0.91	2996	566	741
T_5	0.380	0.06	0.98	3370	451	675
T_6	0.380	0.09	0.97	3154	597	441
T_7	0.317	0.09	0.94	3064	561	683
CD	0.0735**	NS	NS	NS	71**	NS

Table 49. Effect of borax on micronutrient content in straw at harvest

Treatment	Micronutrient (mg kg^{-1})			
	Fe	Mn	Zn	Cu
T_1	256.66	449.27	96.47	1.30
T_2	480.00	474.33	147.90	1.80
T_3	848.33	546.66	151.90	1.37
T_4	850.00	579.33	156.10	1.50
T_5	440.00	486.00	122.63	1.73
T_6	343.33	408.46	115.33	1.53
T_7	276.66	369.33	71.83	0.58
CD	48.18**	121.76**	9.250**	NS

Table 50. Effect of borax on primary and secondary nutrient contents in grain at harvest

Treatment	Primary nutrient (%)			Secondary nutrient (mg kg^{-1})		
	N	P	K	Ca	Mg	S
T_1	0.85	0.288	0.21	83.57	587	1218
T_2	0.93	0.31	0.23	71.63	575	1138
T_3	0.76	0.26	0.23	27.57	509	1078
T_4	1.12	0.29	0.23	52.33	509	1116
T_5	0.81	0.286	0.23	44.26	507	1158
T_6	0.84	0.280	0.23	87.50	594	1131
T_7	0.81	0.29	0.26	61.07	516	1198
CD	0.055**	NS	NS	5.65**	26 **	80.16*

5.2.10. Analysis of nutrients in grain

The primary and secondary nutrients estimated in the grain samples are given in the table 50. Except P and K, all the elements were significantly influenced by the levels of borax. Highest nitrogen content of 1.12 per cent was recorded in the treatment which received the application of borax @ 6 kg ha^{-1}. At higher levels of borax, nitrogen content in grain was found to get reduced. Calcium content was highest in T_6 and lowest in T_3. Total Mg reduced linearly from T_1 (587.0 mg kg^{-1}) to T_5 (507.47 mg kg^{-1}) and then increased.

Total S content in grain also varied significantly with respect to the levels of borax. Highest S content was noticed in T_1 and the lowest of 1078.00 mg kg^{-1}in $T_{3.}$

Table 51 shows the content of total micronutrients estimated in grain at harvest. Total Fe content reduced linearly with the levels of borax. Fe, Mn, Zn and Cu varied significantly with respect to the levels of borax. Highest Mn content in grain was recorded in T_7 (47.87 mg kg^{-}1) and the minimum in T_1 (18.43 mg kg^{-1}). Zn content was highest in T_6 and the lowest in T_1. Though the Zn content in grain was significantly influenced by the treatments, there was no linear relationship with the treatments. T_7 recorded the highest and the lowest in T_4 for copper in grain. Though the treatments resulted in significant difference in Cu content, there was no relationship with respect to the levels of borax.

5.2.11. Total boron content in straw, root and grain

Total B content in straw, root and grain recorded at harvest is given in table 52. Total content of boron analysed in straw samples had maximum value of 17.33 mg kg^{-1} in T_4 and the minimum of 8.77 mg kg^{-1} in T_1. Boron content increased linearly with the levels of applied borax up to T_4 and decreased thereafter with the levels of borax. Maximum content of 32.33 mg kg^{-1} of B in root samples was estimated in T_7 and a minimum of 23.33 mg kg^{-1} in T4. Grain sample analysis revealed a maximum content of B in T_4 (5.70 mg kg^{-1}) and the minimum in T_1 (2.93 mg kg^{-1}).

Table 51.Effect of borax on micronutrient content in grain at harvest

Treatment	Micronutrient (mg kg^{-1})			
	Fe	Mn	Zn	Cu
T_1	514.6	18.43	31.63	3.93
T_2	384.66	31.40	55.13	2.17
T_3	382.0	32.90	29.87	1.37
T_4	209.0	42.77	40.33	1.23
T_5	111.33	42.40	67.23	2.63
T_6	111.67	40.00	88.10	4.00
T_7	107.33	47.87	71.67	4.67
CD	16.12**	5.07**	28.92**	0.551**

Table 52. Effect of borax on boron content in straw, root and grains at harvest

Treatment	Boron (mg kg^{-1})		
	Straw	Root	Grain
T_1	8.77	25.12	2.93
T_2	10.36	21.58	3.93
T_3	12.76	24.34	4.16
T_4	17.33	23.36	5.70
T_5	9.73	31.06	4.47
T_6	9.80	29.15	4.3
T_7	9.67	32.33	4.40
CD	0.76**	3.59**	0.480**

5.2.12. Correlation coefficients of available B, fractions of soil B with content of B in shoot at harvest

Data in table 53 show that hot water extractable B had high significant correlation with SA-B (0.931**), OX-B (0.739**), OR-B (0.981**) and RES-B (0.831**). But the correlation between the B in straw, grain and yield were not significant. RS-B had significant correlation with SA-B (0.718**), OR-B (0.698**) and RES-B (0.602**) and B in straw (0.540*), grain (0.616**) and yield (0.674**). There were high positive significant correlation with between oxide bound B, OR-B, and RES-B with SA-B. Boron content in straw and grain also had positive correlation with SA-B. Boron in straw had positive correlation with content of B in grain and grain yield.

5.2.13. Path analysis

Table 54 shows the direct as well as the indirect effects of different fractions of soil B on available B content in the soil at harvest. Organically bound B had a very high direct effect on available B as indicated by the path coefficient of 1.0569. The indirect effect of SA-B through OR-B was very high and the indirect effect of OX-B and RES-B through OR-B was high. The specifically adsorbed B had a high direct negative effect on available B. But RES-B had a high direct positive effect on available B at harvest and the indirect effect of SA-B, OX-B and OR-B through RES-B was moderate.

Table 55 shows the path coefficients indicating direct and indirect effects of different fractions on RS-B at harvest. Direct effect of SA-B on RS-B at harvest was very high as indicated by the path coefficient of 1.1630. The indirect effects of OX-B (0.9674), OR-B (1.1074) and RES-B (0.8291) through SA-B on RS-B were high. OX-B had a high negative direct effect on RS-B and also OR-B, SA-B and RES-B produced a indirect negative effect through OX-B on RS-B. The direct effect of OR-B on RS-B was negative and low. The direct effect of RES-B on RS-B was moderate as indicated by the path coefficient 0.2138 and the indirect effect of SA-B, OX-B and OR-B through RES-B on RS-B was low.

Table 53. Correlation between fractions of B and content of B in straw, grain and yield

	Available boron	**RS-B**	**SA-B**	**OX-B**	**OR-B**	**RES-B**	**boron in straw**	**Boron in grain**
Available boron	1.00							
RS-B	0.289	1.00						
SA-B	0.931**	0.718**	1.00					
OX-B	0.739**	0.424	0.832**	1.00				
OR-B	0.981**	0.698**	0.952**	0.748**	1.00			
RES-B	0.831**	0.602**	0.713**	0.619**	0.672**	1.00		
Boron in straw	0.204	0.540*	0.190	0.138	0.106	0.124	1.00	
Boron in grain	0.202	0.616**	0.573**	0.493*	0.444*	0.492*	0.818**	1.00
Grain yield	0.113	0.674**	0.330	0.154	0.346	0.010	0.744**	0.571**

(** sigificant at 1.00 % level, * significant at 5.00 % level))

Table 54. Path coefficient of different fractions to available B at harvest

Fractions of B	SA-B	OX-B	OR-B	RES-B	Correlation coefficient
SA-B	**-0.3273**	0.0247	1.0064	0.2276	0.9314**
OX-B	-0.2723	**0.0296**	0.7910	0.1916	0.7399**
OR-B	-0.3117	0.0222	**1.0569**	0.2137	0.9811**
RES-B	-0.2334	0.0184	0.7102	**0.3180**	0.8312**

(values on diagonal are direct effects and values on horizontal lines are indirect effects)

Table 55. Path coefficient of different fractions to RS- B at harvest

Fractions of B	SA-B	OX-B	OR-B	RES-B	Correlation coefficient
SA-B	**1.1630**	-0.4960	-0.1018	0.1524	0.7176**
OX-B	0.9674	**-0.5963**	-0.0800	0.1323	0.4235*
OR-B	1.1074	-0.4463	**-0.1069**	0.1436	0.6978**
RES-B	0.8291	-0.3692	-0.0718	**0.2138**	0.6019**

(values on diagonal are direct effects and values on horizontal lines are indirect effects)

Table 56. Path coefficients of different fractions to content of B in grain

Fractions of B	RS-B	SA-B	OX-B	OR-B	RES-B	Correlation coefficient
RS-B	**0.5110**	0.7544	0.0772	-0.7571	0.0390	0.6164**
SA-B	0.3667	**1.0513**	0.1517	-1.0331	0.0366	0.5732**
OX-B	0.2164	0.8745	**0.1823**	-0.8120	0.0318	0.4930*
OR-B	0.3566	1.0014	0.1364	**-1.0850**	0.0345	0.4436*
RES-B	0.3076	0.7495	0.1129	-0.7290	**0.0513**	0.4922*

(values on diagonal are direct effects and values on horizontal lines are indirect effects)

Table 56 shows the path coefficients indicating the direct and indirect effects of different fractions of B in soil on the content of boron in grains. The direct effect of RS-B on the content of B in grain was high as indicated by the path coefficient of 0.5110 and SA-B, OX-B, OR-B and RES-B produced a high indirect effect on grain B through RS-B. The specifically adsorbed B had a very high direct effect on grain B as indicated by the path coefficient of 1.0513. All other fractions of B in soil had a high indirect effect on the content of B in grains through SA-B. The organically bound B had a very high direct negative effect on the content of B in grains. The indirect effects of all other fractions of B in soil on B in grains through OR-B were high and negative. The direct effect of OX-B on the content of B in grains was low and the indirect effect of all other fractions through OX-B was also low. RES-B had a negligible effect on B in grains.

Discussion

5. Discussion

Sixty five representative samples from 23 AEUs coming under five Agro ecological zones of the state have been characterized initially. From these, thirty one samples (including one from the location of field experiment) were selected based on electrochemical properties and the content of hot water extractable boron and were subjected to fractionation of soil boron. In the succeeding experiment six major soils were selected from 31 samples to study the pattern and thermodynamics of boron adsorption. An incubation experiment was conducted in the laboratory to study the effect of added organic matter on the adsorption of B in three different soil types. A field experiment was also conducted to optimize the level of boron for rice nutrition. In this chapter, the result of all these experiments are presented in chapter 4 and are discussed critically with supporting studies from the literature.

Experiment 1

5.1 Electro chemical properties and available nutrient status.

The data on the electrochemical properties and available nutrients status are presented in the table 6.

5.1.1 Soil pH

The soil pH ranged from 2.96 to 6.28 with a mean value of 4.89. The acid sulphate/saline soils of *Kayal*, *Kaipad*, *Kole* and *Pokkali* are extremely acidic (George, 2011) with pH less than 4.4. Thirty per cent of the soil samples (fig. 3.) under study were very strongly acid (pH 4.5 -5.0) which included soils from southern and northern coastal sandy plains, northern central laterite, northern laterite, southern and central foot hills northern foot hills, southern high hills and Kumily dry hills. Majority of the soils (40 per cent) under study were strongly acidic (5.1 – 5.5). The soils of Onattukara sandy plain, southern central laterite, Marayoor dry hills, Attapady dry hills, eastern and central plateau of Ambalavayal, Palakkad central plain, low lands of Nalleppilly fall under this category. Black cotton soils of Chittoor, uplands soils Nalleppilly in the Palakkad eastern plain were slightly acidic/near neutral in soil reaction. The study reveals that 90 per cent soils of the state are highly acidic. Acid sulphate/saline soils as well as soils from mid land laterite, dry hills and foot hills were confronted with the problem of soil acidity requiring liming to maintain productivity and health. This would also mean that any fertility management in soils of different AEUs should begin with acidity management to ensure better physical, chemical and biological soil environment.

5.1.2. Electrical conductivity

The electrical conductivity of the soils of the AEUs ranged from 0.01 to 15.2 dSm^{-1}. The acid sulphate/saline soils of *Kayal*, *Kaipad*, *Kole* and *Pokkali* land have shown comparatively higher EC indicating effect of sea water inundation. Among these soils, one sample from *Pokkali* and two samples from *Kaipad* lands were having EC > $4dSm^{-1}$ making it problematic due to salinity. George (2011) also reported that soils of *Pokkali* have EC > $4dSm^{-1}$. The high salinity of these soils is due to periodic inundation of sea water, as these lands are not protected from the direct entry of sea water. The *Kole* and *Kuttanad* lands escape from the ill effects of salinity because of the spillways/bunds constructed to prevent the entry of salt water.

5.1.3. Organic carbon

The organic carbon content of soils of AEUs of Kerala ranged from as low as 0.25 per cent to as high as 5.53 per cent. Seventeen per cent of the soils (fig. 4.) under study which included soils from southern and northern coastal plains and *Onattukara* sandy plain are very low in organic carbon with content less than 0.76 per cent. The soils from upland and low lands of central and eastern plains of Palakkad, eastern and central plateau of Wayanad, soils from southern and southern central laterite are medium in organic carbon content with a status between 0.76 and 1.5 per cent. The soils of southern and northern high hills, Kumily dry hills, *Pokkali*, *Kole* and *Kuttanad* are rich in organic carbon content > 1.5 per cent. Thampatty and Padmakumar (1999) reported that soils of *Kuttanad* and *Pokkali* are rich in organic matter.

The results point to the fact that the soils of coastal sandy plain and lateritic belts came under poor to medium fertility class with respect to organic carbon. As the OC status of soil is an index of available nitrogen, the deficiency of N as well as low microbial activity could be expected in these soils. Submerged soils with high OC *viz. Kuttanad, Kole, Pokkali* and *Kaipad* may not give a true information on N status as the stabilization of C-N mineralizaion becomes incomplete under anaerobic condition with a C:N ratio usually more than 20 : 1. This would also mean that N deficiency could be anticipated even with high carbon levels.

5.1.4. Available phosphorus

The available phosphorus status of the soils of the AEUs of the state ranged from as low as 3.63 to as high as 300.16 kg ha^{-1} (table 6 and fig.5) Both *Kayal* and *Karappadam* soils of *Kuttanad* and northern laterite (Panniyoor) soils are of poor phosphorus status. Bridgit (1999) also reported that lateritic soils of Kerala are low in available P. Extremely high values of P reported in sandy soils of Edavilangu is attributed to low P fixation leading to accumulation of applied P in the labile pool whereas very low values of P in the soils of *Kuttanad*, is due to high fixation by Al, Fe and Zn under acidic condition as evidenced by the high status of these elements in these soils (Table 7).

5.1.5. Available potassium

Available potassium status of soils varied from as low as 42.9 to as high as 1103.60 kg ha^{-1}. Sandy soils of coastal and *Onattukara* plains are very poor in available potassium. Sixty per cent of the soils of AEUs are poor to medium in potassium fertility (fig. 6). Soils of *Pokkai, Kaipad* soils, Kumily dry hills, Wayand eastern plateau, Palakkad central plains and some soils from Palakkad eastern plain are very rich in potassium. The high potassium reported in the soil of Pampadumpara (Kumily Dry hills) might be due to the fact that the samples were drawn from well managed cardamom plantation. Sandy soils of coastal plain and *Onattukara* plains are very poor in available potassium. Lack of 2:1 type clay and coarse texture of soils results in low retention of K and even the applied potassic fertilizer would be lost by the leaching unless need based split application is followed.

5.1.6. Available Sodium

The acid sulphate/saline soils of *Kuttanad, Pokkali, Kole* and *Kaipad* lands reported high values for Na in soil. As these soils are subjected to sea water inundation the sodium status of these soils increased.

Fig. 3. pH of soils of different AEUs of Kerala

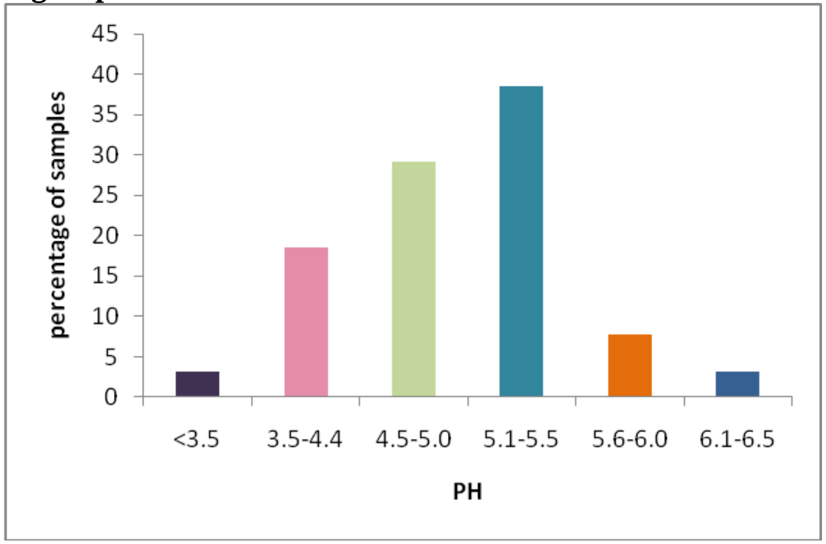


Fig. 4. Organic carbon status of soils of different AEUs of Kerala

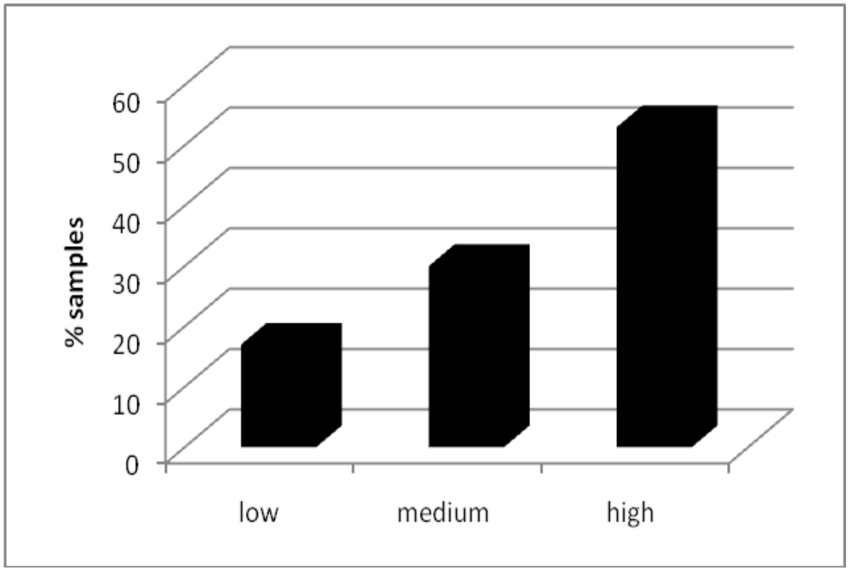


Fig.5. Available phosphorus status of soils of different AEUs of Kerala

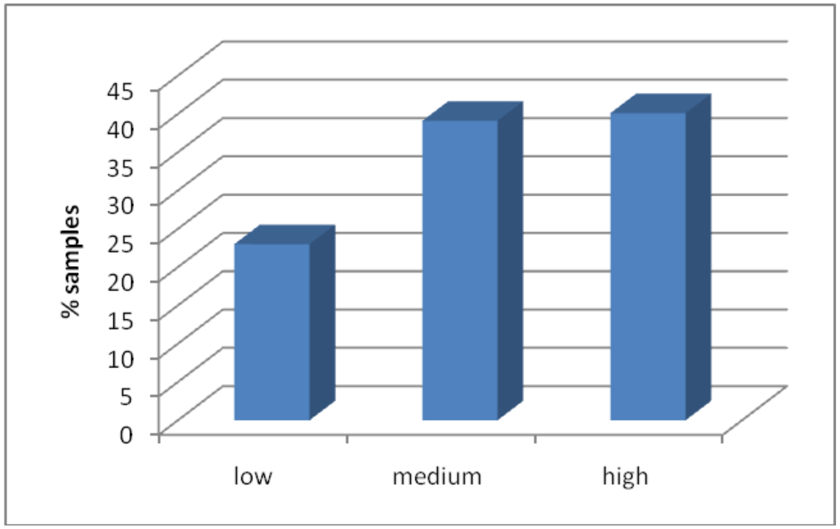


Fig. 6. Available potassium status of soils of different AEUs of Kerala

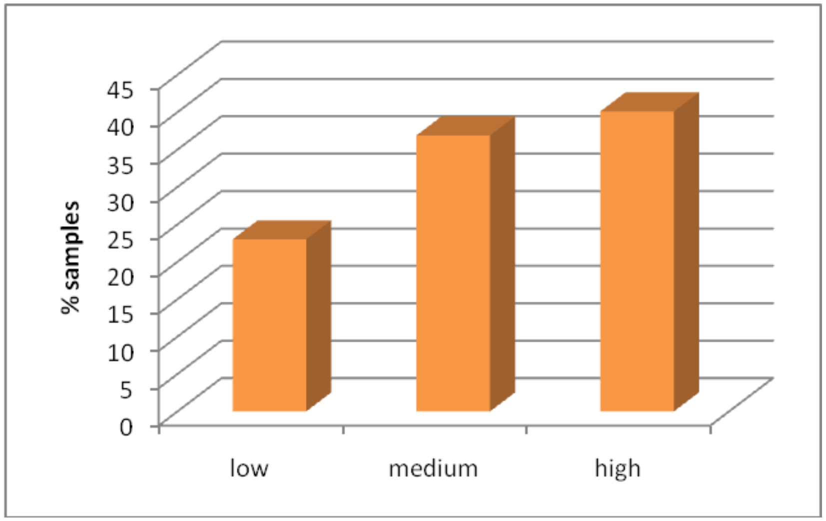


Fig. 7. Available calcium status of soils of different AEUs of Kerala

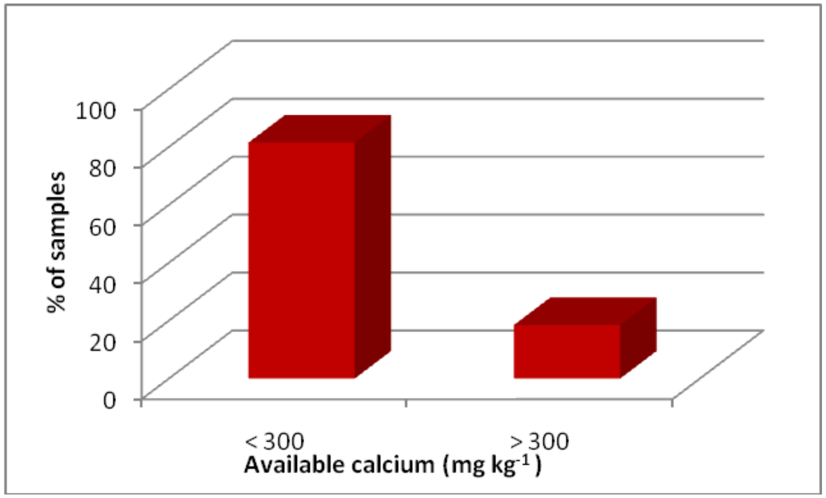


Fig. 9. Available copper status of soils of different AEUs of Kerala

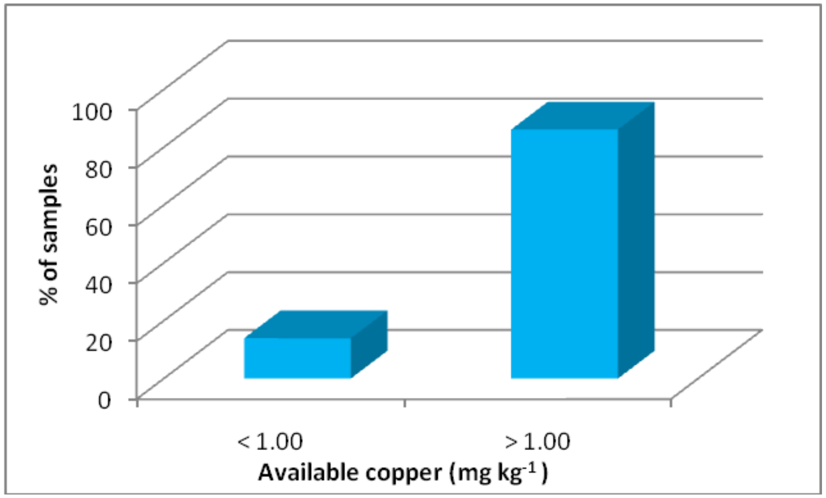


Fig. 8. Available sulphur status of soils of different AEUs of Kerala

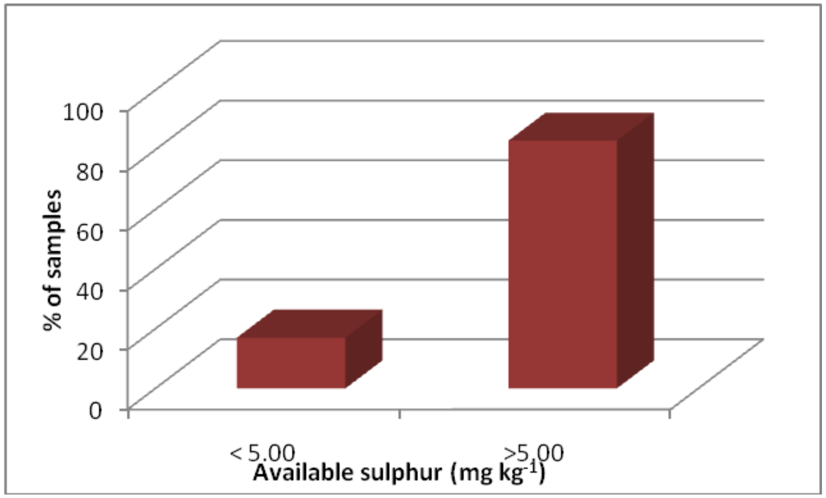
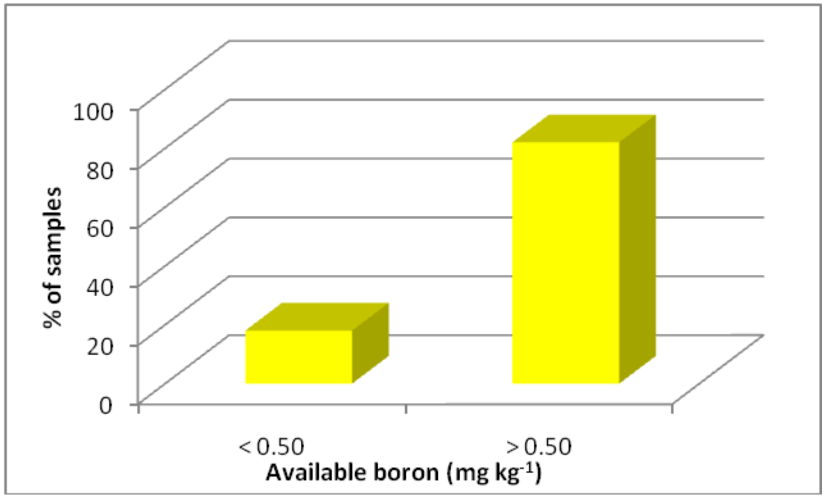


Fig. 10.Available boron status of soils of different AEUs of Kerala



5.1.7. Available calcium

The data in table 6 and fig. 7 show that 82 per cent of the soils of the AEUs are deficient in calcium with status less than 300 mg kg^{-1} (1.5 cmol(+) kg^{-1}). Available calcium status in soils of AEU$_S$ varied widely from as low as 17.9 to 657 mg kg^{-1}. Soils of Marayoor dry hills and Palakkad eastern plain (Nalleppilly and Chittor) were sufficient in calcium content, the effect of which is well reflected in pH. These results clearly indicate the role of low rainfall on retention of calcium. The soils of coastal sandy plains, high hills are very low in calcium content due to high rainfall which leaches calcium. The very low status of Ca in the midland lateritic soils is attributed to the leaching of calcium from soil as the process of laterisation progresses.

5.1.8. Available magnesium

A perusal of the data of magnesium status reported in the soils of the AEUs of the state reveals 100 per cent deficiency of Mg with a content < 120 mg kg^{-1}(1 cmol(+) kg^{-1}). Tropical climate itself leads to leaching losses of Mg as in the case of Ca. Further imbalanced fertilizer application and non-inclusion of magnesium fertilizers in crop culture might have lead to such a situation. Results on low status of Ca and Mg warrants mandatory application of sources of these two elements as amendments before planning for any fertility management.

5.1.9. Available sulphur

The data in table 6 shows that available sulphur status in soils of AEUs varied from 2.08 to 593.75 mg kg^{-1}. A very low percentage of the samples are deficient in sulphur (fig. 8) particularly upland soils of pattambi, Mavelikkara, Kavalangad and Vythiri. Comparatively low sulphur deficiency in the state might be an integral effect wide spread use of factomphos as a NP fertilizer. High level of S is as expected in soils of *Pokkali* and *Kaipad* lands being acid sulphate/saline.

5.1.10. Available micronutrients

The data on 0.1M HCl extractable micronutrients (Fe, Mn, Zn and Cu) in soils of AEUs of Kerala shows high Fe in majority of soils mainly *viz. Kuttanad, Pokkali, Kole, Kaipad*, lateritic soils etc. George (2011) also reported that soils of *Kuttanad, Pokkali,* and *Kole,* are high in Fe. Presence of Iron rich parent materials and leaching of basic materials form the surface layers of the soils due to heavy rain (in laterite soils) could be the reason for Fe toxicity in these soils.

Available Mn contents of the soils ranged from 2.35 to 54.91 mg kg^{-1}. None of the samples under study were deficient in Mn. Similar to iron, manganese also affects the crop growth. High status of these elements reported in the soils of *Kuttanad, Kole, Pokkali* and mid land laterite is attributed to the same reason as discussed in the case of Fe.

The content of Zn in soils of AEUs varied from 0.73 to 37.91 mg kg^{-1}. Similar reports were made by Praseedom and Koshy (1975). Only two samples (Panniyoor-1 and Neriamangalam-2) under study reported values below critical level (1.00 mg kg^{-1}). Zinc being comparatively mobile in soil results in accumulation due to continuous application. The same reason pointing to the fact that Zn application should be recommended on soil test basis. Under intensive agriculture, the use of Zn containing fertilizers resulted in change in available Zn status from deficient to sufficient and even to toxic level within a period of a decade.

The available copper status of the soils ranged from 0.09 to 33.2 mg kg^{-1}. Praseedom (1970) and Venugopal (1980) also reported the same range in soils of Kerala. Soils of Cherthala and one sample from Sholayoor have shown deficiency of copper. High status (fig. 9) might have resulted from the use of Cu based fungicides as in the case of Zn. The data clearly indicate that no special measures are to be taken to manage this nutrient in soils of the state. However the chances for toxicity to sensitive crops cannot be over ruled so that care should be taken for need based application of Cu also.

5.1.11. Available boron

The data in table 6 shows that hot water extractable boron in soils varied from as low as 0.05 to 7.96 mg kg^{-1} with a mean of 1.37 mg kg^{-1}. Similar range was reported in soils of Punjab by Katyal and Agarwala (1982). Eighteen per cent of samples under investigation are deficient in B (fig. 10) with content less than 0.5 mg kg^{-1}. Thirty per cent samples are having boron content between 0.5 and 1.00 mg kg^{-1} and 34 per cent of samples have reported a content of hot water extractable B between 1.00 and 2.00 mg kg^{-1}. Soils of southern and northern coastal plains, low lands of Pattambi are deficient in boron due to high leaching and phosphorus status in soil. The toxic levels of boron reported in *Pokkali* and *Kaipad* soils might be due to sea water inundation as the direct entry of sea water is not checked by any control measures. George (2011) also reported very high levels of B in soils of *Pokkali.*

The predominance micronutrients in soils of the different AEUs of Kerala followed the order Fe > Mn > Zn > Cu > B. The same sequence excepting B was reported by Balasubramaniam (1975) in soils of Periyakulam in Tamil Nadu.

5.1.12. Exchangeable cations, cation exchangeable capacity and percentage base saturation

Exchangeable cations *viz*. K Na, Ca, Mg, Al, Fe, Mn, Zn and Cu extracted by 0.01M $BaCl_2$, CEC, PBS (percentage base saturation) are given in table 7 and 8.

The data on the 0.01 M $BaCl_2$ extractable exchangeable cations show that potassium ranged from 110.0 (0.28 cmol(+) kg^{-1}) to 465.0 mg kg^{-1} (1.18 cmol(+) kg^{-1}) with a mean of 0.48 cmol(+) kg^{-1}. The amount of exchangeable Na was found to range from 63 (0.27 cmol(+) kg^{-1}) to 1857 mg kg^{-1} (8.10 cmol(+) kg^{-1}) with a mean of 0.9 c mol (+) kg^{-1}. The exchangeable calcium ranged from 167.8 (0.84 cmol(+) kg^{-1}) to 1277.2 mg kg^{-1} (6.80 cmol(+) kg^{-1}) with a mean of 3.7 cmol(+) kg^{-1}. Whereas the exchangeable Mg varied from 1.99 (0.016 cmol(+) kg^{-1}) to 341.1 mg kg^{-1} (2.84 cmol(+) kg^{-1}). Exchangeable Al ranged from 0.01mg (0 cmol(+) kg^{-1}) to 481.2 mg kg^{-1} (5.84 c mol (+) kg^{-1}.

A perusal of the data on exchangeable cations showed that the most dominant cation in the exchangeable sites was calcium followed by Na, K, and Al in that order. The dominance of cations on the exchangeable sites is in the following order Ca > Na > K > Al > Mg. The same sequence was reported in lateritic soils by Geetha (2008). Contribution of Fe, Zn and Cu to the exchange surface was negligible as evidenced by the very low values.

Cation exchange of the soils ranged from 1.66 to 14.93 with a mean of 6.28 cmol(+) kg^{-1}. The high values of CEC (>10 cmol(+) kg^{-1}) reported in soils of *Karappadam, Pokkali, Kaipad* lands could be due to large amount of cations *ie*. Na and K in the water soluble and non specifically adsorbed form which might have got extracted by 0.01 M $BaCl_2$. All other soils under study were with CEC < 8.5 cmol(+) kg^{-1} as expected since the soils are dominated by 1:1 type kaolinitic clay minerals. The percentage base saturation of soils of different AEUs varied from 60.28 to 99.7. As the soils are with very low CEC and in most of the cases calcium alone occupies more than 50 to 60 per cent of exchangeable sites, the values of PBS would not give a true information on the fertility status of soil (Seena, 2000).

5.1.13. Soil Texture

The soils of Cherthala (AEU-1) are sandy in texture (table 9) constituting more than 90 per cent of sand, where as *Kayal* and *Karappadam* soils of *Kuttanad* are clayey with clay content more than 40 per cent. Soils of *Pokkali* are loamy whereas *Kaipad* soils are sandy loam in texture. The soils of mid land laterite are sandy clay loam to sandy loam in texture. The majority (50 per cent) of the soils in different AEUs of Kerala are sandy loam in texture. This is due to the prevailing tropical climate with high rainfall leading to migration of clay resulting in accumulation of coarser fractions at the surface. In contrast to this *Kuttanad* soils being the deltaic area of different rivers are formed by dominant clay fractions.

5.1.13. Sesquioxide

Sesquioxide content of the soils of different AEUs ranged from 0.5 to 22 percent (table 9). Low sesquioxide content reported in sandy soils of Edavilangu and Cherthala are due to lesser amount of Fe and Al in these soils whereas high content of sesquioxide reported in the soils of northern and north central laterite (Panniyoor and Pattambi) could be due to the accumulation of Fe and Al oxides in the surface layers during the course of laterisation.

5.1.14. Anion exchange capacity

Table 9 show that anion exchange capacity of soils varied from 1.54 to 5.26 cmol(-) kg^{-1}. The highest AEC was observed in Pampadumpara soils and the lowest was in Cherthala soils. AEC is a measure of capacity of surface positive charges to retain anions in soil. AEC results either from broken edges of 1:1 type clay or from pH dependant charges mainly from organic functional groups.

5.1.15. Correlation between electrochemical properties and nutrient status of the soils.

Available B was correlated positively and significantly with EC, K, Na, Fe, sulphur and CEC (table 10). The negative significant correlation of available B with pH would mean that availability increases with soil acidity as evidenced by the high values of B in *Pokkali*, *Kuttanad*, and *Kaipad* soils. Similar reports were made by Rashid (2005) in soils of Pakisthan. The increased availability of B at lower pH could be due to high solubilisation of different forms of B. The high significant positive correlation of available B with EC, K, Na (both available and exchangeable forms) underlines the effect of salts of boron mainly K and Na borates on the salinity status of the soil which is very well evidenced by the high values of K, Na and B so also EC in the soils of *Pokkali, Kaipad* and *Kuttanad.*

Positive correlation of available B with Fe indicates the association of B with iron. The retention of boron by Fe and Al oxyhydroxide in absolutely depended on pH and it is high at alkaline pH. Solubilisation of these oxyhydroxides at low pH releases the associated boron as evidenced by the significant negative correlation of pH and positive correlation of Fe and Al with available B.

Regression analysis including the most important parameters significantly correlated with available boron yielded the following equation explaining 84.5 per cent variability

Available B = - 1.001 + 0.385 pH** – 0.135 EC** +0.002 Na** + 0.018 S* – 0.003 Ex. Na* (R^2=0.845)

The above equation clearly indicates that effects of pH, EC, Na, S and Ex. Na in governing the available B. The significant negative correlation of pH with Fe, Al and sulphur indicate the major role played by these acidic ions in reducing the pH of the soils of Kerala rendering it acidic in reaction. The negative significant correlation between OC and pH indicate the clear role of organic matter on releasing H^+ ions associated with -COOH, -OH and -NH_2 groups and thereby increasing the acidity and these dissociated ions in turn act as sites for binding cations. The significant positive correlation exhibited by CEC with exchangeable Na, K and Al clearly indicate the role of these cations on the exchange sites.

Experiment 2

5.2.1. Fractions of boron in soil

The data on various fraction as well as total boron is soils of AEUs of Kerala and their percentage distribution in presented in table 11 and 12. Fig. 11 and 12 depicts the amount as well as percentage distribution of all fractions except residual B.

The readily soluble boron (RS-B) in soils varied from 0.1 to 2.48 mg kg^{-1} which accounted 0.14 to 2.07 per cent of total boron with a mean of 0.59 per cent. Similar ranges were reported by Datta *et al*. (2002) in soils of different locations in India. This pool of B in soil, which includes dissolved plus B adsorbed non-specifically on edges of clays and other variable charged surfaces. The low values of RS-B reported in coastal sandy plains and foot hills could be due to high rainfall and leaching losses.

Specifically adsorbed boron (SA-B) ranged from 0.16 to 2.6 mg kg^{-1} accounting 0.14 to 2.96 per cent of total soil boron with a mean of 0.86 per cent. This fraction probably originates from the weakly binding sites of both organic and inorganic constituents especially that is adsorbed to specific sites in soil such as Fe and Al oxyhydroxides (Hou *et al*., 1994) which itself explains the low and high values of SA-B in Cherthala and *Kaipad* soils.

Oxide bound B (OX-B) in soils of different AEUs ranged from 0.5 to 7.8 mg kg^{-1} constituting 0.85 to 4.31 per cent of total soil boron with a mean of 2.31 per cent. Similar mean values are reported by Hou *et al.* (1994 and 1996). OX-B actually represents the fraction of soil B that is bound to Al and Fe oxides as well as layer silicate clay minerals as evidenced high SA-B in *Karappadam*, *Kayal,* northern laterites, northern and southern central laterites where the content of Fe & Al oxides are high. The adsorption by unit weight (specific adsorption) is greater and more spontaneous for aluminium than iron oxides due to higher surface area of aluminium than oxides due to higher surface area of aluminium oxides.

Fig. 11. Fractions of B (excluding RES-B) in soils of AEUs in Kerala

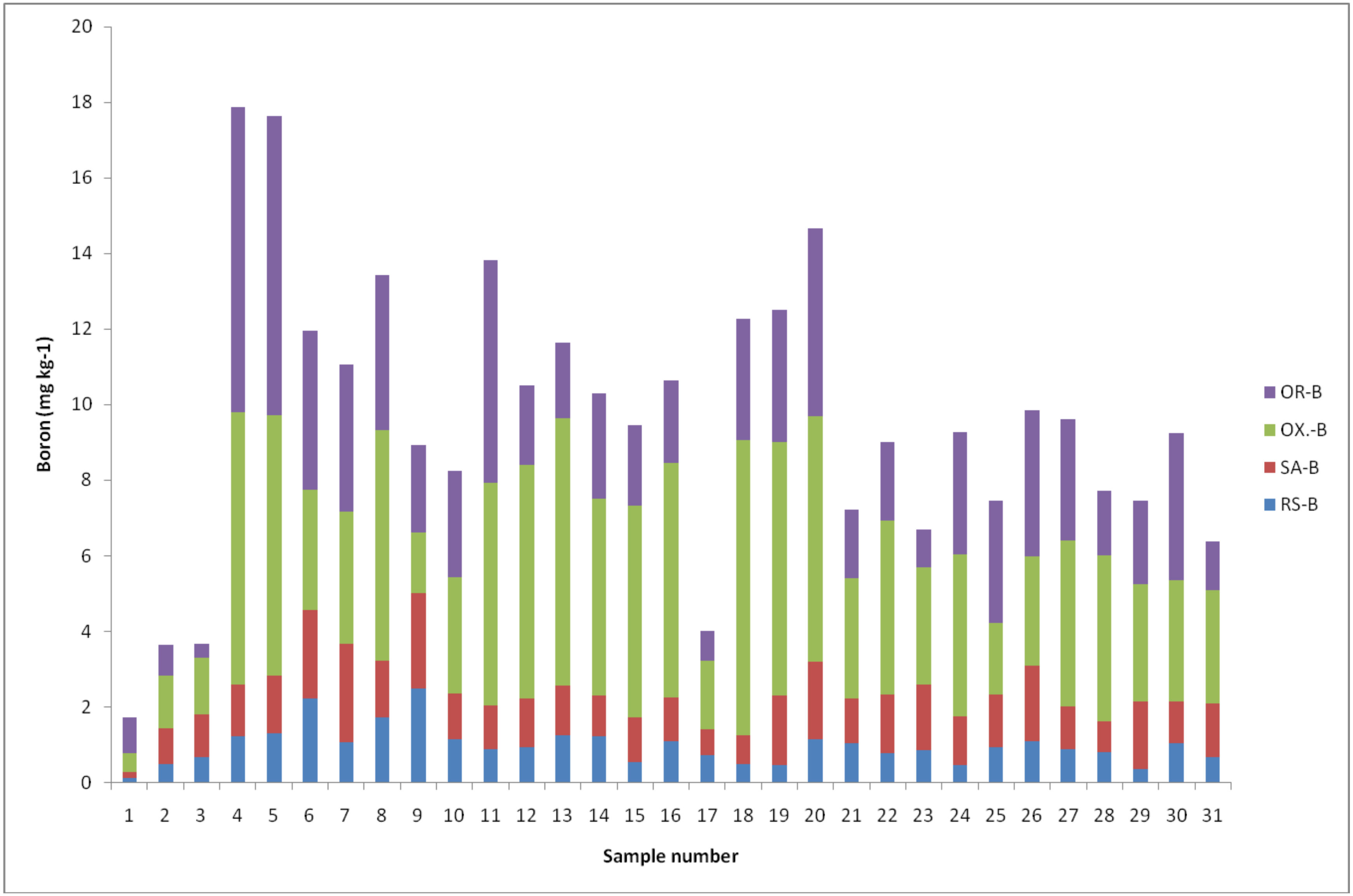
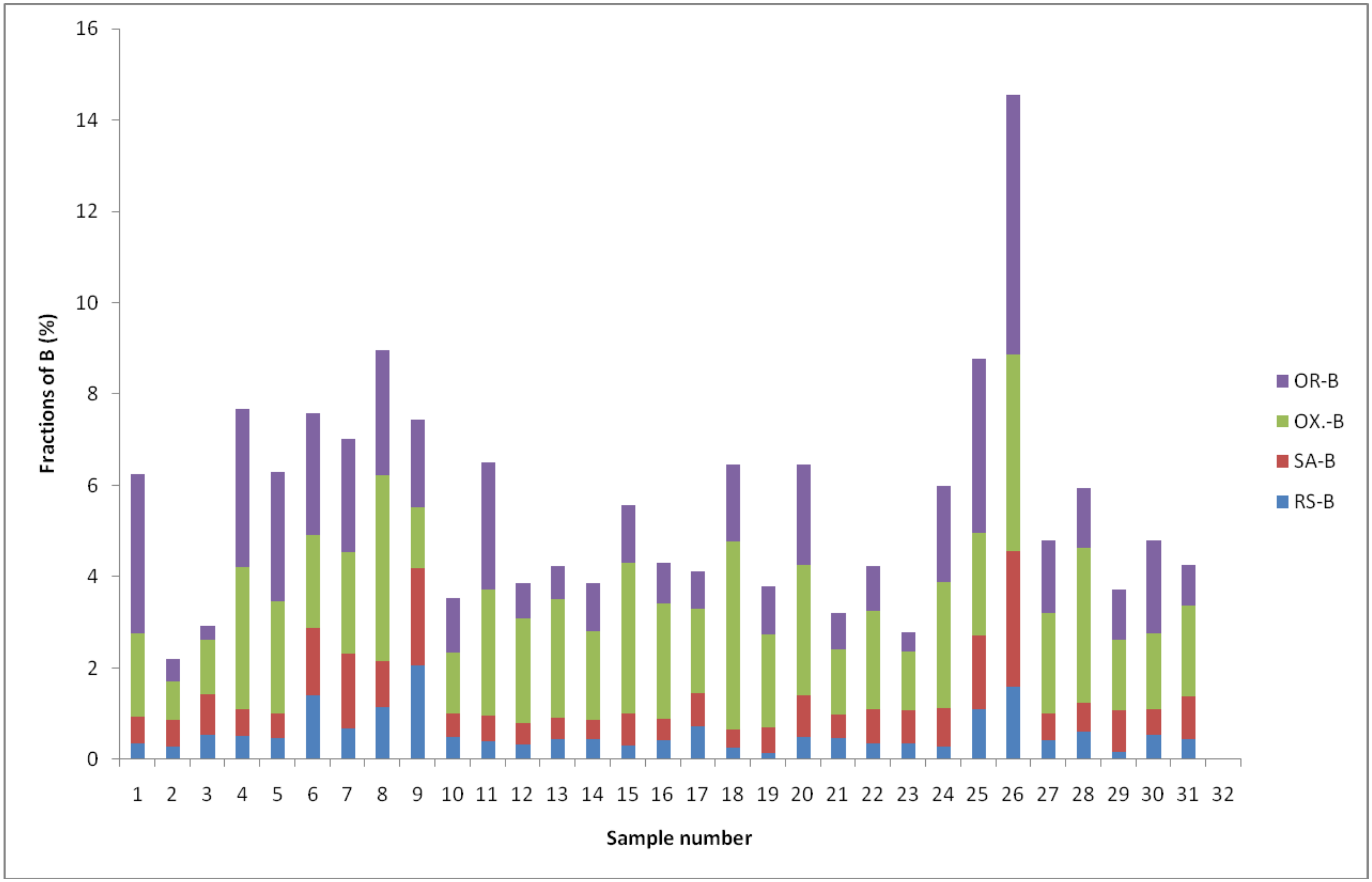


Fig. 12. Percentage distribution of different fractions of B (excluding RES-B) in soils of AEUs in Kerala



The mechanism of adsorption might be ligand exchange with reactive surface hydroxyl groups that mainly explains the adsorption of anions.

Organically bound form of B in soils ranged from 0.38 to 8.1 mg kg^{-1} accounting to 0.3 to 5.7 per cent of total soil B with mean status of 1.79 per cent. Organically bound-B represents the fraction of soil B retained by humus. Compared to mineral constituents organic constituents adsorb more amount of B on a weight basis. The highest OR-B recorded in *Karappadam* soils of *Kuttanad* and the lowest in sandy soils of *Onattukara* sandy soils explains the clear role of organic matter in the retention of boron.

The dominant fraction, RES-B ranged from 25.78 to 317.51 mg kg^{-1} which accounted 85.44 to 97.81 per cent of total B in soil with a mean of 94.45 per cent. Similar ranges were reported by Datta *et al*. (2002) in soils of different locations in India. This fraction represents fraction of soil B occluded in the structural constituents of clays and sesquioxides.

A perusal of data on percentage distribution of the different fractions of B in soil reveals their relative dominance in the following order

RES-B > OX-B > OR-B > SA-B > RS-B

Total boron content in soils ranged from 27.5 to 330 mg kg^{-1}. This is close to the ranges (31.0 - 355 mg kg^{-1}) reported by Datta *et al*. (2002) in soils of India and was well within the reported ranges (7- 630 mg kg^{-1}) in Indian soils (Kanwar and Randhawa, 1974). Very low amount of total B reported in sandy soils of Cherthala, Kayamkulam (*Onattukara*), Wandoor (northern foot hills) could be attributed to several factors such as highly weathered loose textured soils, low content of sesquioxide, clay and organic matter which act as sink/reservoir for different fractions of boron. The opposite trend of high levels of fractions as well as total B in soils of *Kuttanad* is also attributed to the reverse situations to the above reasons.

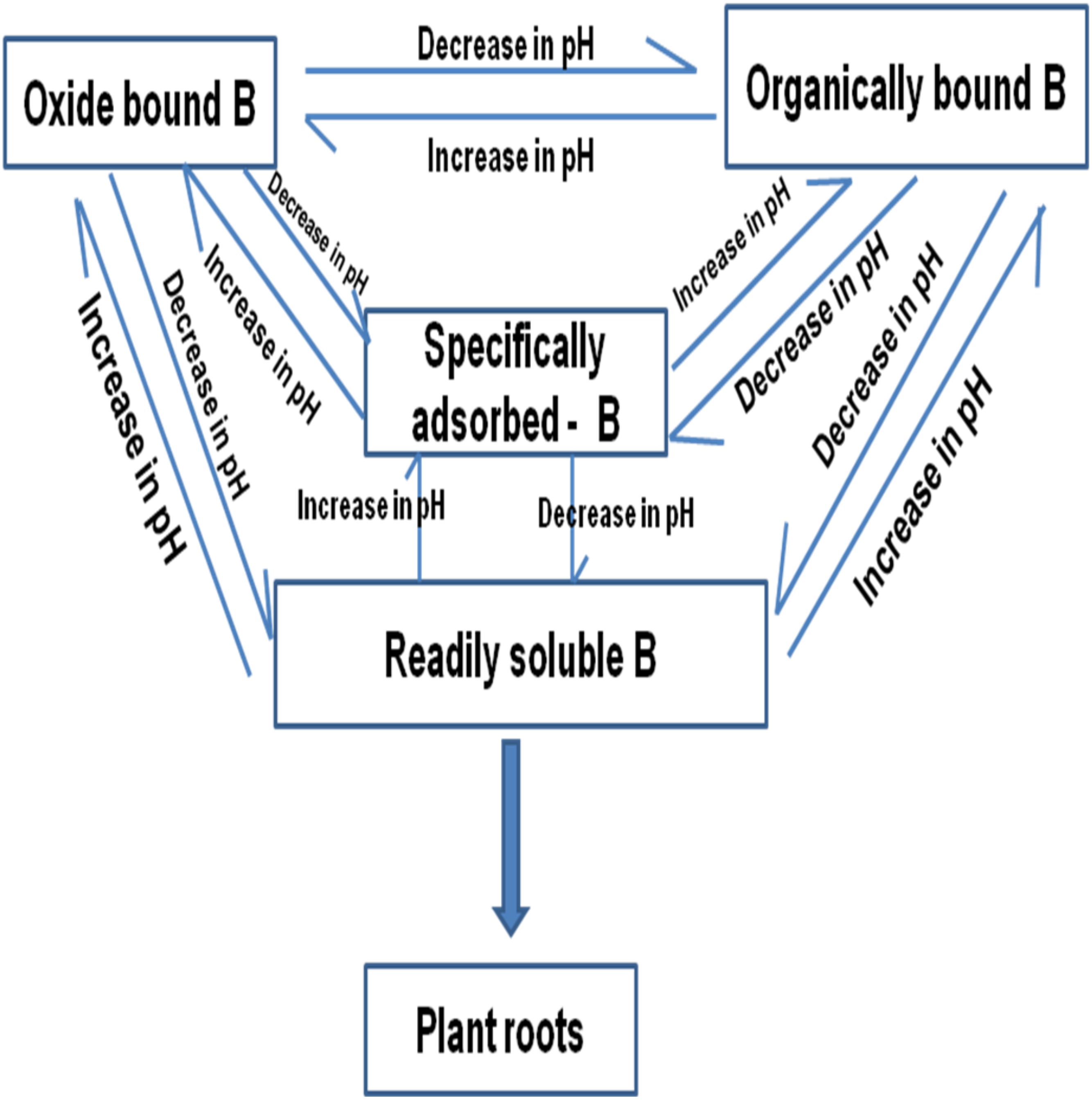
5.2.2. Correlations between the fractions, B with electrochemical properties and nutrient contents of soil.

Correlation coefficients of B fractions with different parameters is presented in table 14 and 15. Significant positive correlation of the RS-B with SA-B and OR-B indicates the contribution of SA-B and OR-B to readily soluble pool of B in soil and it explains that as the readily soluble (pool constituting dissolved B and nonspecifically adsorbed B) is depleted it will be replenished immediately by SA-B followed by OR-B in that order. The weak correlation of RS-B with RES-B and total-B indicates the negligible contribution made by this fraction to RS-B. The significant positive correlation of oxide bound boron with OR-B and RES-B could be explained in the back ground of significant positive correlation of OR-B with RS-B, that is the oxide bound-B might be regrouped into:

1. Labile form:- complexed with organic matter which could replenish the depletion of RS-B
2. Non labile form:- resistant form associated with RES-B and hence the total boron, this fraction being totally unavailable for plant absorption

The significant negative correlation of RS-B with pH would mean that this pool of B increases with decrease in pH as evidenced by the high value of RS-B reported in soils of *Kuttand*, *Pokkali* and *Kaipad*. The increased RS-B at low pH could be due to solubilisation of different forms of B and the formation of boric acid which is water soluble. The significant negative correlation of SA-B, OX-B and OR-B with pH explains the possible existence of dynamic equilibrium between these fractions. The most dominant among these fractions being oxide bound will release borate ion which will contribute to readily soluble fraction or bound to the pH dependant positive charges of functional groups of humic fractions (especially when the pH decreases) thereby contributing to OR-B. Part of the same might be adsorbed to the specific sites by ligand exchange contributing to SA-B. Ultimately the equilibrium in each of these fractions with RS-B tends to shift towards the formation of RS-B. This can be represented as in fig. 13.

Fig. 13. Dynamic equilibrium among fractions of boron in soil



Significant positive correlation of EC, K, Na (neutral normal ammonium acetate and barium chloride extractable), S, Fe with RS-B and SA-B could be due to direct effect of highly soluble salts of B such as Na and potassium borate, on the total soluble salt content in soil which is very well evidenced by high values of these elements in soils of *Pokkali*, *Kaipad* and *Kuttanad*. RS-B also significantly correlated with silt indicating the presence of B in the finer fractions of soil. The significant negative correlation of RS-B with sand content indicate that there would be less amount of RS-B in loose textured soils as it is subjected high leaching as evidenced by the low values of RS-B in soils of Cherthala, Kayamkulam and Edavilangu.

A step up regression equation including all the parameters significantly correlated with readily soluble boron finally yielded the following equation.

1. $\text{RS-B} = 0.783 + 0.002\ \text{Na}^{**}$ ($R^2 = 0.543$)
2. $\text{RS-B} = 0.762 + 0.003\ \text{Na}^{**} - 0.091\ \text{EC}^{**}$ ($R^2 = 0.663$)
3. $\text{RS-B} = 0.6366 + 0.003\text{Na}^{**} - 0.0960\ \text{EC}^{**} + 0.001\ \text{K}^{*}$ ($R^2 = 0.71$)

4 $\text{RS-B} = 1.0000 + 0.002\ \text{Na}^{*} - 0.082\ \text{EC}^{**} + 0.0014\ \text{K}^{**}$
$- 0.0006\ (\%\ \text{sand})$ ($R^2 = 0.75$)

5\. $\text{RS-B} = 1.284 + 0.003\ \text{Na}^{**} - 0.062\ \text{EC}^{**} + 0.001\ \text{K}^{**}$ –
$0.009\ (\%\text{sand})^{**} - 0.005\ \text{Ex. Mg}^{**}$ ($R^2 = 0.798$)

The above equations clearly indicate that sodium is the single most important factor in predicting readily soluble boron status explaining 54.3 per cent variability indicating that readily soluble B would be associated with sodium as sodium borate. Inclusion of electrical conductivity improved the predictability from 54.3 per cent to 66.3 per cent which explain the indirect effect of salinity on RS-B in terms other soluble boron salt like potassium borate. This is further supported by improvement is predictability from 56 to 71 per cent by including K in equation. Further inclusion of sand and exchangeable magnesium improved the predictability to 79.8 per cent.

Similar to RS-B, SA-B also positively and significantly correlated with K, Na, S, Cu, Fe, Ex. K, Ex. Na, Ex. Mg, Ex. Fe and CEC and silt and not with clay, sand and sesquioxide. Similar reports were also made by Xu *et al.* (2001) in soils of China and Datta *et al.* (2002) in soils of India and Hou *et al.* (1994). The step up regression analysis including all the parameters correlated for SA-B yielded the following relations

1. SA-B = 1.234 + 0.003 S* ($R^2 = 0.52$)
2. SA-B = 1.108 + 0.002 S** + 0.0006 Ex. Mg** ($R^2 = 0.602$)
3. SA-B = 0.959 + 0.002 S** + 0.006 Ex. Mg** + 0.001 K* ($R^2 = 0.667$)

The above equation indicate that sulphur alone can explain 52 per cent of the variability in SA-B and the inclusion of Ex. Mg and available potassium improved the predictability to 66.7 per cent concludes the influence of sulphur on specific adsorption of B as these elements might have got affinity to the same sites of adsorption, however it require further detailed investigation.

The significant positive correlation of OX-B with Ex-Na, Ex-Al, Ex-Mn and clay and sesquioxide (0.986**) could be due to the fact that this fraction of soil B adsorb to the Fe-Al oxide (sesquioxide) and Fe and Al oxyhydroxide and Mn-Oxyhydroxide especially amorphous hydrous oxide minerals. The regression equation including all the parameters having significant correlation with OX-B yielded the following single regression equation obtained with sesquioxide as the dominant independent variable that could explain 97 per cent variability.

OX-B = 0.830 + 0.299 (% sesquioxide)** ($R^2 = 0.973$)

OR-B bound B is significantly and positively correlated with OC (0.712**), Fe Cu, Fe, Al, CEC, Silt, Clay and sesquioxide and negatively with sand. Significant positive correlation of OC with OR-B is also reported by Datta *et al.* (2002). The highest correlation coefficient of OR-B with OC of soil explains the retention of boron by organic matter in soil. The positive correlation of clay with OR-B could be explained in terms of close association of clay with organic matter as clay organic complexes. This is further substantiated by significant correlation of Ex. Mg, Ex. Al, Mn, Cu and CEC as these cations are bound to humic functional groups probably through borate clay complexes.

The positive correlation of OR-B with CEC is due to direct influence of organic matter on CEC of soils. High significant negative correlation exhibited by OR-B with sand could be explained in terms of the low status of organic matter in sandy soil. Step up regression analysis including all the parameters correlated with OR-B yielded the following equations.

1. OR-B = 7.468 - 1.072 (% sand)** ($R^2 = 0.556$)
2. OR-B = 4.224 – 0.049 (% sand)** + 0.660 OC** ($R^2 = 0.677$)
3. OR-B = 4.782 – 0.052 (% sand)** + 0.051 OC** + 0.184 Cu* ($R^2 = 0.726$)
4. OR-B = 4.328 – 0.048 (% sand)**+ 0.0479 OC**+ 0.198 Cu*
   + 0.108 Ex. Cu* ($R^2 = 0.798$)

These above equations clearly indicate that 55.6 per cent of the variability in OR-B could be explained by percentage sand fraction in soils. The inclusion of organic carbon status of soils improved the predictability by 12.10 per cent and it increased by 10.10 per cent by the further inclusion of available and exchangeable copper.

RES-B was significantly and positively correlated with OC, Clay, sequioxide and AEC which confirms that residual B is the structural constituent of amorphous oxyhydroxide minerals and sequioxide. Positive correlation of OC and RES-B could be explained in terms of close association of OC with clay (Datta *et al.*, 2002 ; Xu *et al.*, 2001). Regression analysis including all the parameters which had significant correlation with RES-B yielded the following equation which indicate that 51.4 per cent of the variability in RES-B could be explained by the content of sesquioxide

.

RES-B = 97.929 + 7.071 (% sesquioxide)** ($R^2 = 0.514$)

The total content of born in soil in significantly positively correlated with OC, sesquioxide and clay. The regression analysis yielded the following equation with sesquioxide as independent variable. This would mean that as in residual fraction substantial amount of B is associated with sesquioxide. The residual fraction which constitutes more than 90 per cent of total boron and hence substantial amount were adsorbed in sesquioxide.

TB = 102.212 + 7.535 (% sesquioxide)** ($R^2 = 0.550$)

Experiment 3

Adsorption study

5.3.1. Q-I relationship

Quantity – intensity relationship with respect to the six soils varying in physico-chemico properties and representing different AEUs were studied at two temperature *viz*. 25 and 40^{0}C. From the data obtained, Q-I curves were plotted with the amount of B adsorbed on Y axis and the equilibrium concentration of B in the solution on the X axis. The concentration of B in solution after equilibration for 24 hours was considered as intensity factor. The amount of B adsorbed on solid phase at equilibration was considered as the quantity factors. The Q/I curves were fitted with these data and intercepts and slopes were computed from the best fit curves using regression analysis (figures from 14 to 24).

The intensity factor is a measure of B in solution that is immediately available for absorption by the plants and quantity factor is the one that explains the capacity of the soil to replenish the level of boron in soil solution over a period. The slope of Q-I curve is the buffer power which explains how the level of boron in solution (intensity) varies with the unit change in quantity factor. All the soils could give best fit curves explaining more than 50 per cent variability both at 25 and 40^{0}C with the sole exception of *Onattukara* soils at 40^{0}C. This would mean that there exists a linear relationship between the solid phase-solution phase boron equilibrium, though the mechanism of adsorption- desorption process might vary.

A perusal of data in table 16 show that at 25^{0}C, *Kole and Kayal* soils exhibited almost equal buffer power (0.64 and 0.62 Lkg^{-1}). Buffer power is the change in quantity factor with respect to unit change in intensity factor ($\Delta Q/\Delta I$). Greater values of buffer power would mean that greater will be the ability of a given soil to release B from the exchange phase to the solution phase when B is depleted in solution phase and vice versa for boron gain by the soil solution. The highest buffer power indicated by *Kole and Kayal* land soils clearly indicate that these soils have got a greater power to retain boron on solid phase and replenish its level in solution as and when it is depleted by the plant uptake or leaching losses. Negative buffer power values in soils of *Onattukara* indicate practically no capacity for the soil to replenish the solution B.

Fig. 14. Quantity – intensity curve for soil of Pattambi at 25^0C

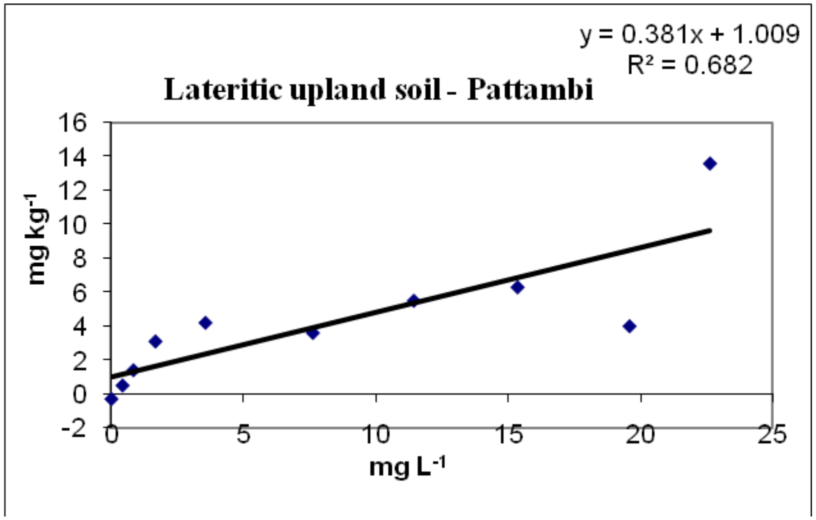


Fig.15. Quantity – intensity curve for low land soil of Elavampadam at

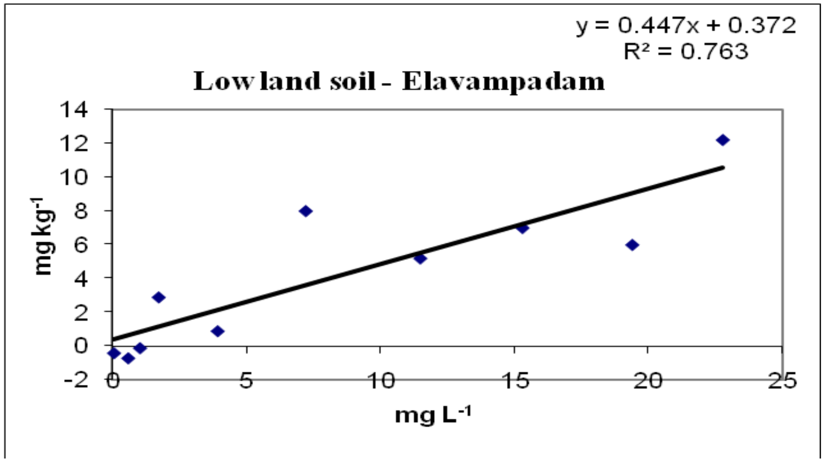


Fig.16. Quantity – intensity curve for sandy soil of *Onattukara* at 25^0C

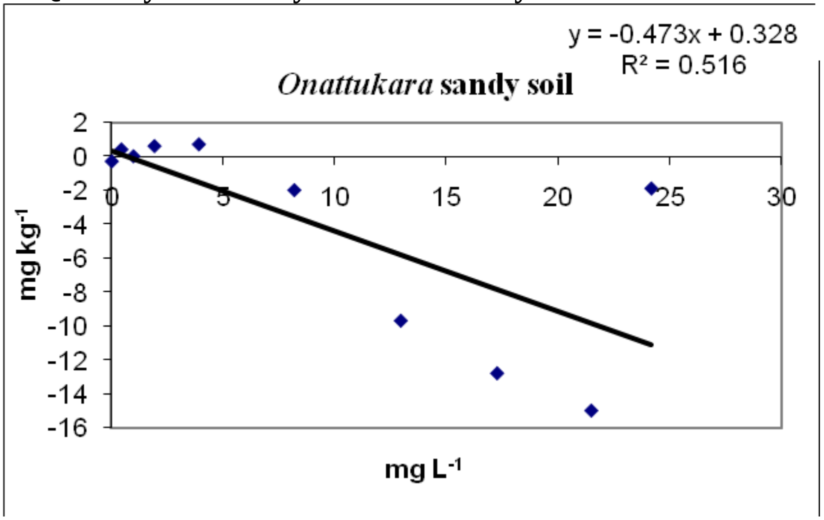


Fig.17. Quantity – intensity curve for black soil of Chittoor at 25^0C

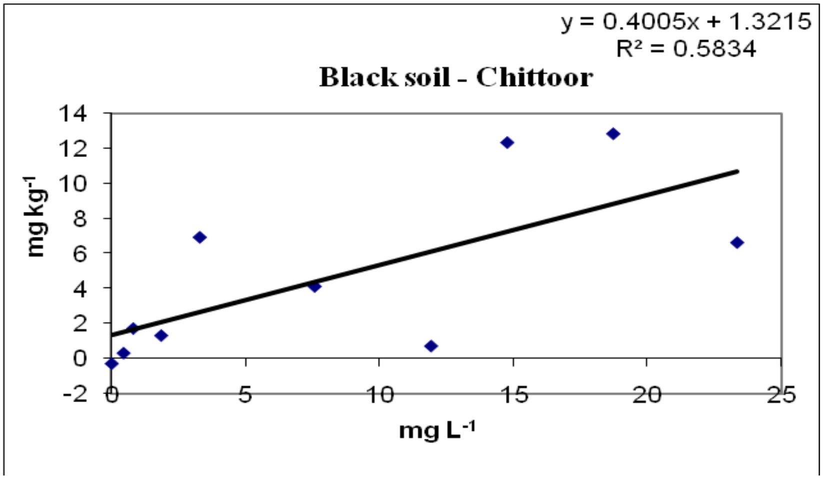


Fig.18. Quantity – intensity curve for *Kole* land soil at 25^{0}C

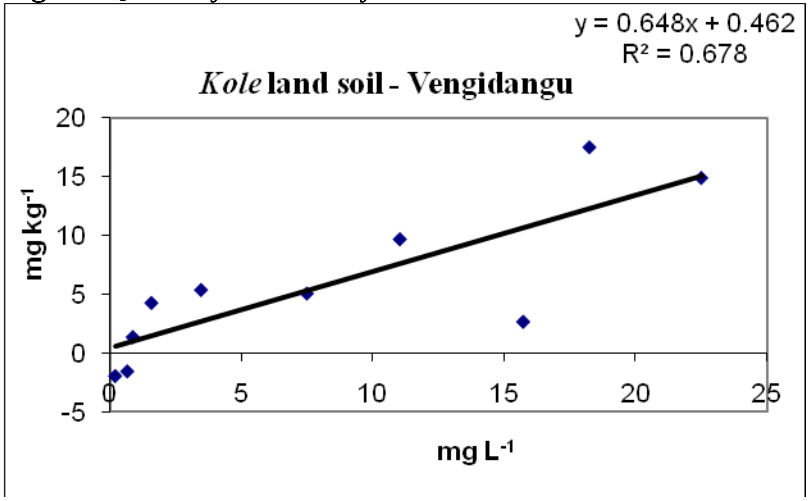


Fig.19. Quantity – intensity curve for *Kayal* land soil at 25^{0}C

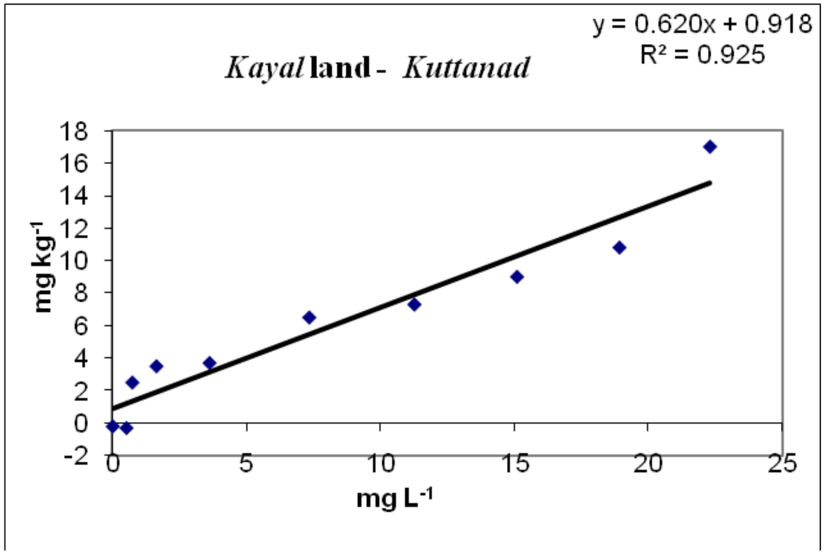


Fig. 20. Quantity–intensity curve for soil of Pattambi at 40^{0}C

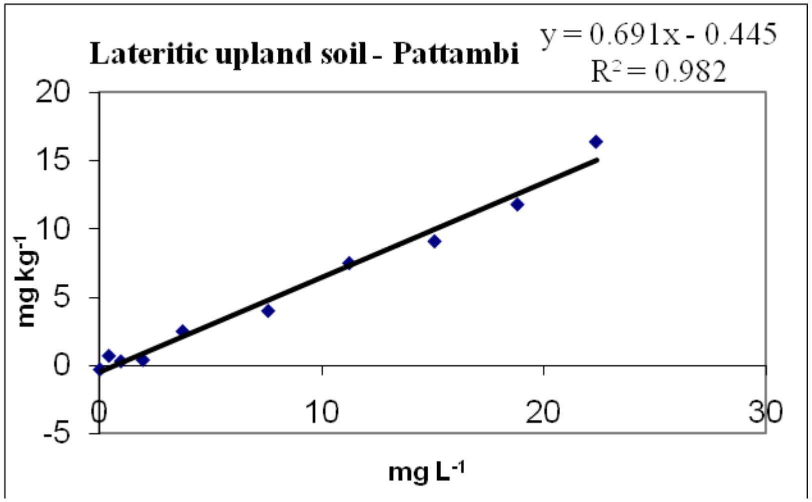


Fig.21. Quantity – intensity curve for low land soil of Elavampadam at 40^{0}C

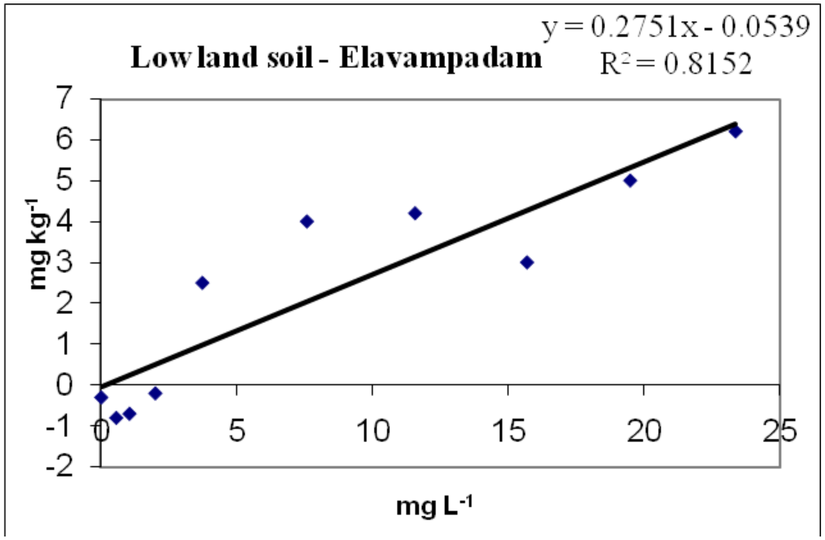


Fig. 22. Quantity – intensity curve for black soil of Chittoor at 40^0C

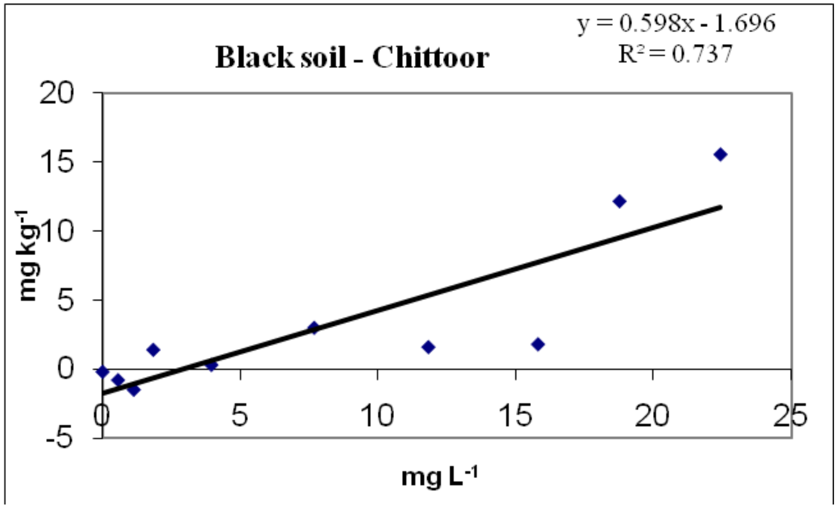


Fig. 23. Quantity – intensity curve for *Kole* land soil at 40^0C

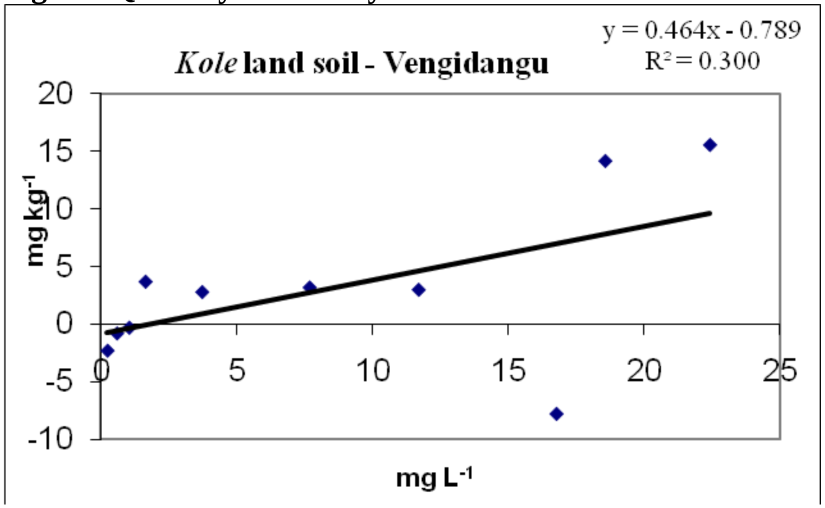
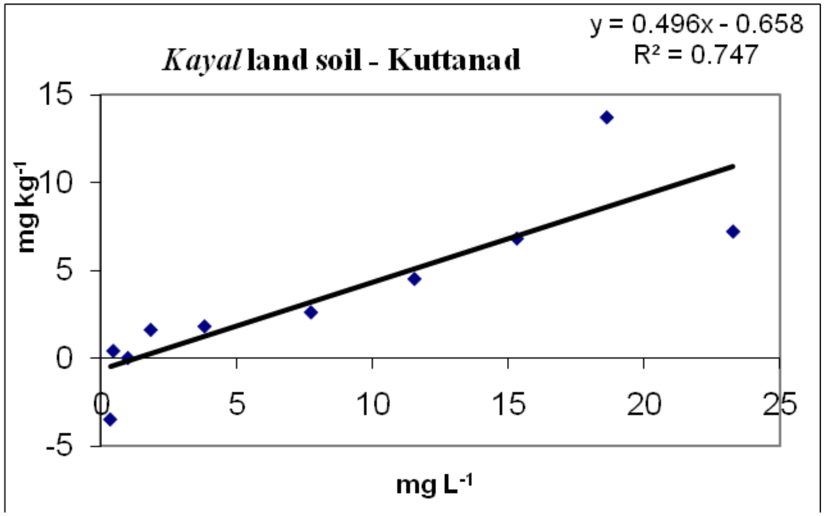


Fig.24. Quantity – intensity curve for *Kayal* land soil of *Kuttanad* at 40^0C



Positive intercepts of Q-I curves at 25^0C, indicate the requirement of a minimum amount of boron at the solid phase below which there will not be any desorption. As the temperature was raised to 40^0C (table 17) intercepts became negative in all the soils indicating desorption from the solid phase below equilibrium concentration. At 40^0C, the buffer power almost doubled in Pattambi and black soils, whereas it decreased in all other soils. The reduced buffer power at 40^0C in soils of *Kole, Kayal* lands and low lands of Elavampadam clearly indicate that the sites of adsorption in these soils are purely organic which might have lost their specificity due to denaturing of specific functional groups at elevated temperature. Whereas in the lateritic, black cotton and sandy soils the sites of adsorption are mainly inorganic *ie.* oxide and oxy hydroxide surfaces whose specificity might have enhanced at higher temperatures.

5.3.2. Adsorption isotherms and thermodynamics of adsorption

The data from adsorption experiment at 25 and 40^0C were fitted into Langmuir and Freundlich equations. Table 18 and figure 25 and 26 show that data for only two soils could be fitted into the linear form of Langmuir equation explaining more than 50 per cent variability. Actually this adsorption isotherm was developed to describe adsorption of gas onto a clean solid surface and it is strictly obeyed only for a uniform adsorbent surface without lateral interaction, implying constant free energy of adsorption irrespective of surface coverage. The failure of adsorption data to fit into Langmuir equation could be attributed to the involvement of more than one type of sites with different binding energies at the concentration range selected for the study. The adsorption maxima was high for *Kayal* land soils and very low in *Onattukara* soils. This is due to the fact that high amount of clay and organic matter offered sites for maximum adsorption and the abundance of these sites might have resulted in low binding energy in *Kayal* land soils. At 40^0C, the failure of Langmuir equation in these soils indicates the development of different sites of adsorption with different binding energies.

The thermodynamic parameters of boron adsorption are presented in the table 21. The free energy of adsorption (ΔG^0) is a measure of how much the concentration of boron must diminish starting with activity of boron equal to unity, before reaching equilibrium. The greater the adsorption, the more negative is the value of free energy.

Fig. 25. Langmuir adsorption isotherm for *Onattukara* soil at 25^{0}C

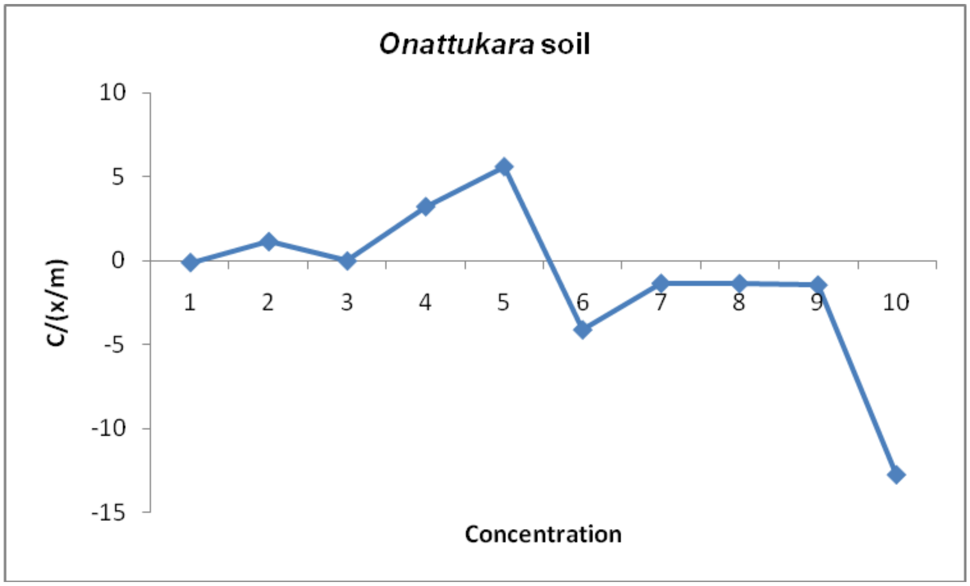
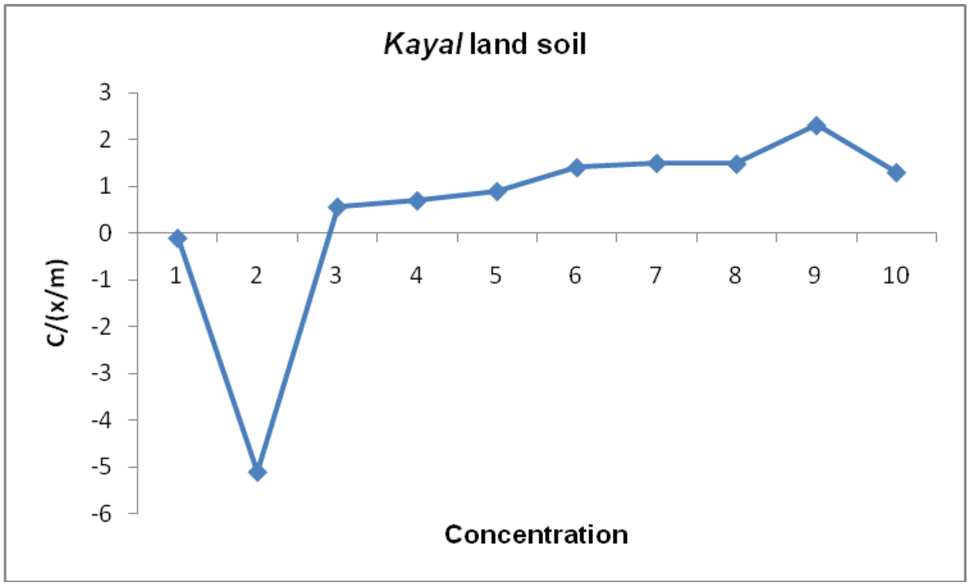


Fig. 26. Langmuir adsorption isotherm for *Kayal* land soil at 25^{0}C



Enthalpy change (ΔH^0) indicates the nature of heat change associated with the process. Positive values of ΔH^0 indicate that the adsorption process is endothermic in nature while the negative values indicate that the process is exothermic in nature. Entropy change (ΔS) explains the degree of disorder or spontaneity of the process. Higher positive values of ΔS are indicators of more disorder or spontaneous nature of adsorption.

Freundlich adsorption isotherm equations and constants for the soils at 25 and 40^0C are given in tables 19 and 20 respectively and depicted in figures from 27 to 36. The adsorption data of *Onattukara* soils could not be fitted into Freundlich equation at both the temperatures. Adsorption data at both the temperatures for all the soils except *Onattukara* soils could be well fitted to Freundlich adsorption isotherm. This assumes that the affinity for adsorption decreases exponentially with the increase in surface coverage which is more logical in real situation. The constant K represents the amount adsorbed at unit solution concentration or in other words it is the specific adsorption *ie*. amount adsorbed per unit solution concentration (Sureshkumar, 1993). At 25^0C, the values of K were higher for black soil, *Kole* and *Kayal* soils in that order while it was less than half of the values in Elavampadam and Pattambi soils revealing more adsorption capacity for the first three soils *ie*. black, *Kole* and *Kayal* soils which might be due to high clay content or organic matter or both. The values of K decreased for all the soils when the temperature was raised from 25 to 40^0C which means that the amount adsorbed per unit solution concentration decreased. The highest decrease was observed in the case of black cotton soil. The value of K was highest for this soil at 25^0C (2.58) reduced to the lowest (0.26) among the soils at 40^0C. This soil is an exception with increase in free energy of adsorption from 0.2336 to 2.30 indicating the adsorption becoming less spontaneous. Further negative values of enthalpy change indicate that the adsorption is exothermic and entropy is also negative suggesting the nature of adsorption is in an orderly fashion. In brief, the increase in temperature reduced the adsorption in black soils. Vermiculite being the dominant clay mineral due to shrinkage with the increase in temperature reduced the surface area which ultimately decreased the amount adsorbed.

Kole and *Kuttanad* soils also showed a similar trend with respect to Freundlich K (K_F) value and thermodynamic parameters the reason being quite different. Here higher temperature might have lead to the change in the sites associated with organic matter probably reducing the surface area.

Fig. 27. Freundlich adsorption isotherm for soil of Pattambi at 25^0C

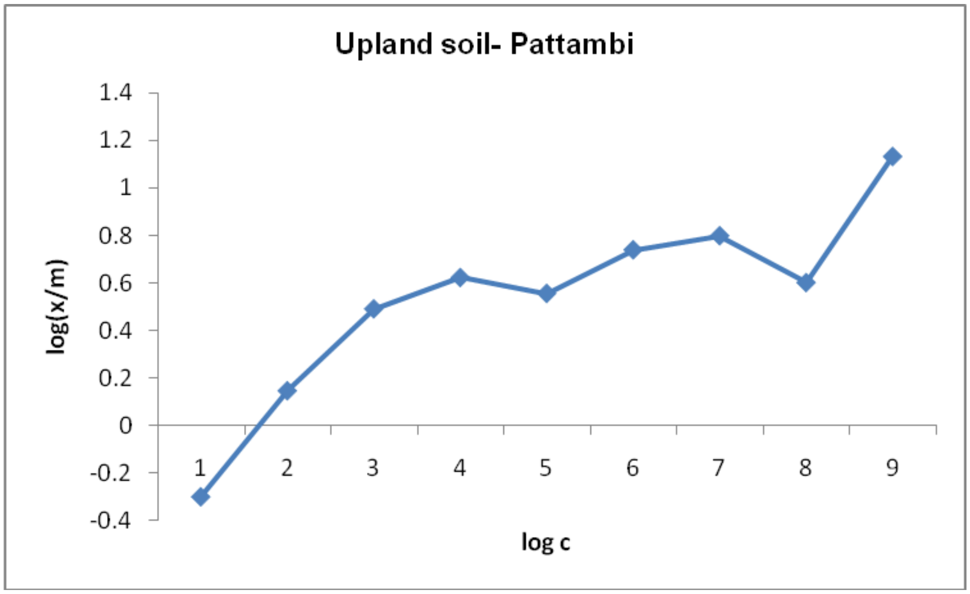


Fig. 28. Freundlich adsorption isotherm for soil of Elavampadam at 25^0C

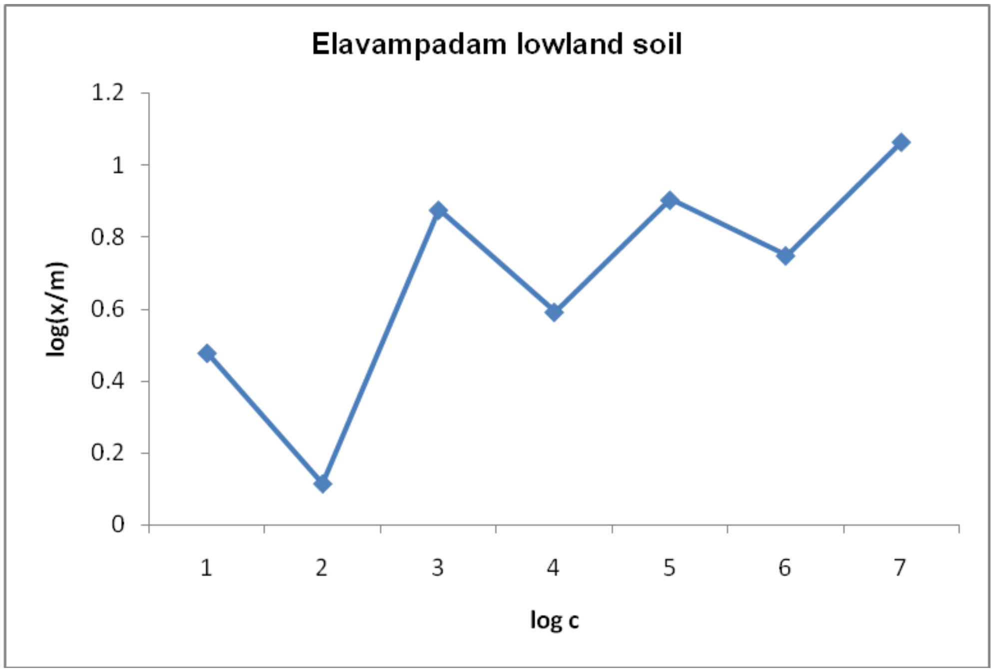


Fig. 29. Freundlich adsorption isotherm for black soil of Chittoor at 25^{0}C

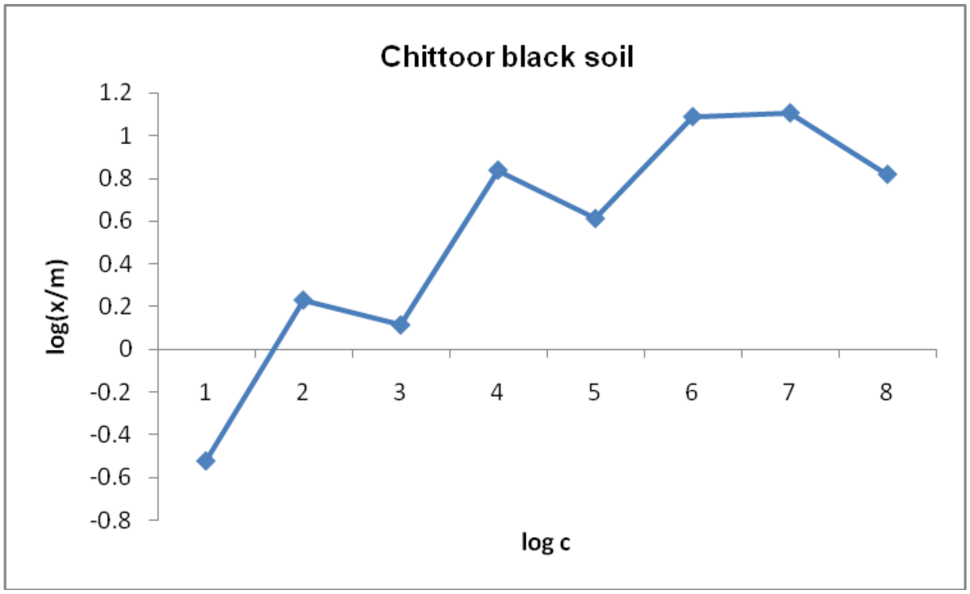


Fig. 30. Freundlich adsorption isotherm for *Kole* land soil at 25^{0}C

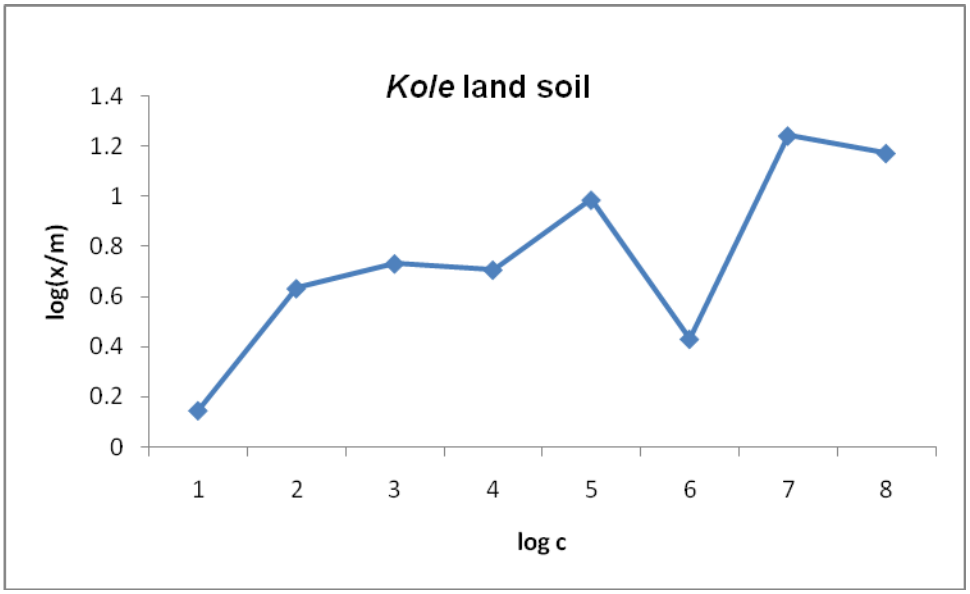


Fig.31. Freundlich adsorption isotherm for *Kayal* land soil at 25^{0}C

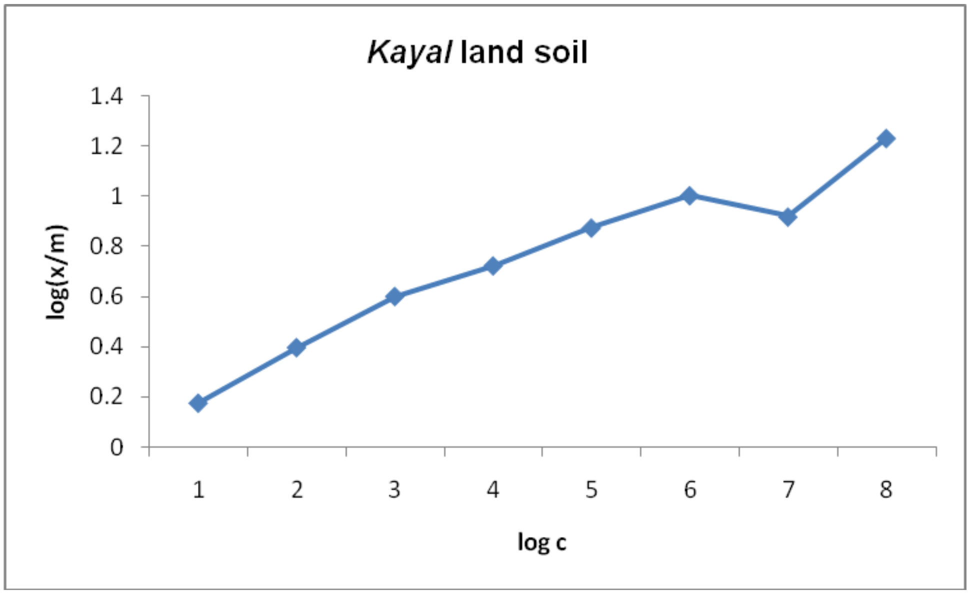


Fig. 32. Freundlich adsorption isotherm for soil of Pattambi at 40^{0}C

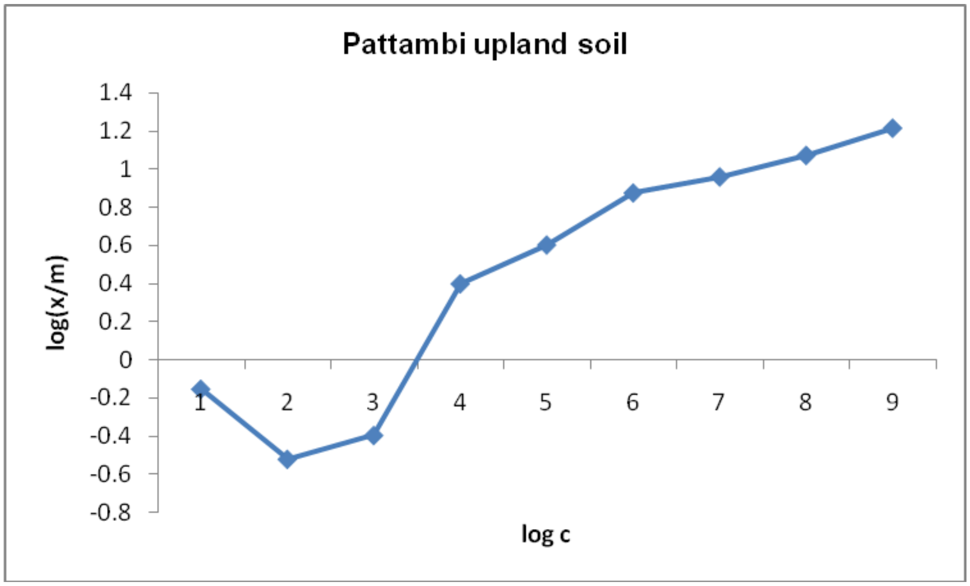


Fig. 33. Freundlich adsorption isotherm for soil of Elavampadam at 40^{0}C

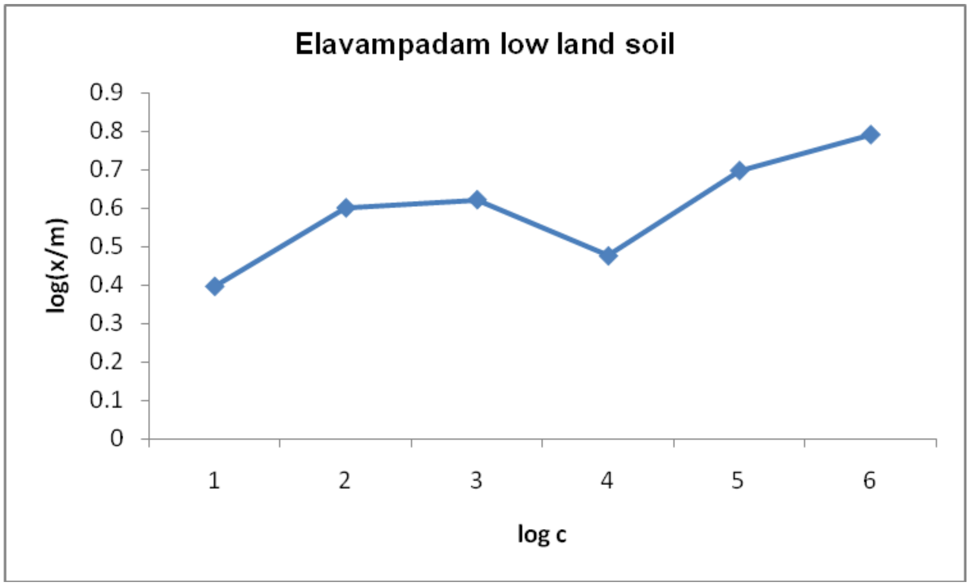


Fig. 34. Freundlich adsorption isotherm for black soil of Chittoor at 40^{0}C

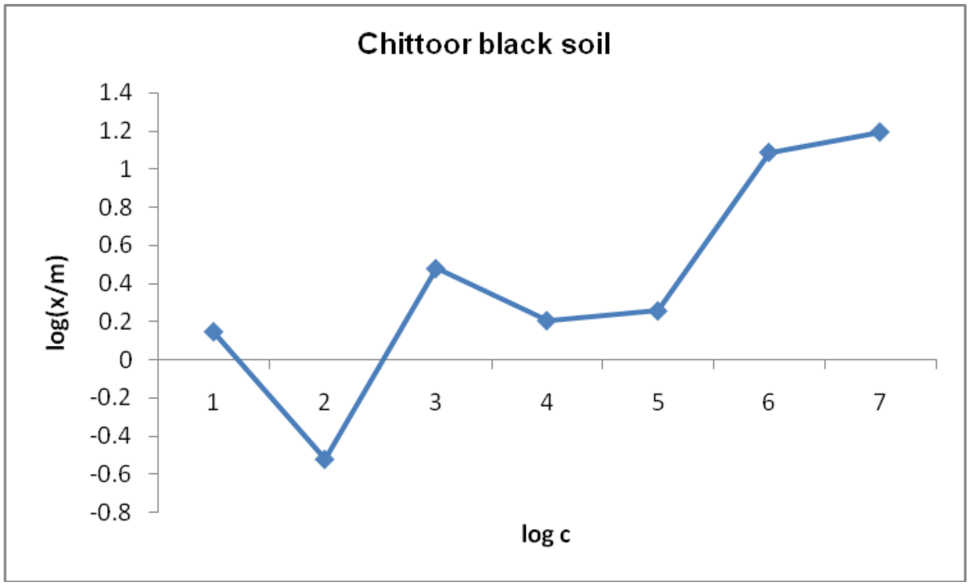


Fig.35. Freundlich adsorption isotherm for *Kole* land soil at 40^0C

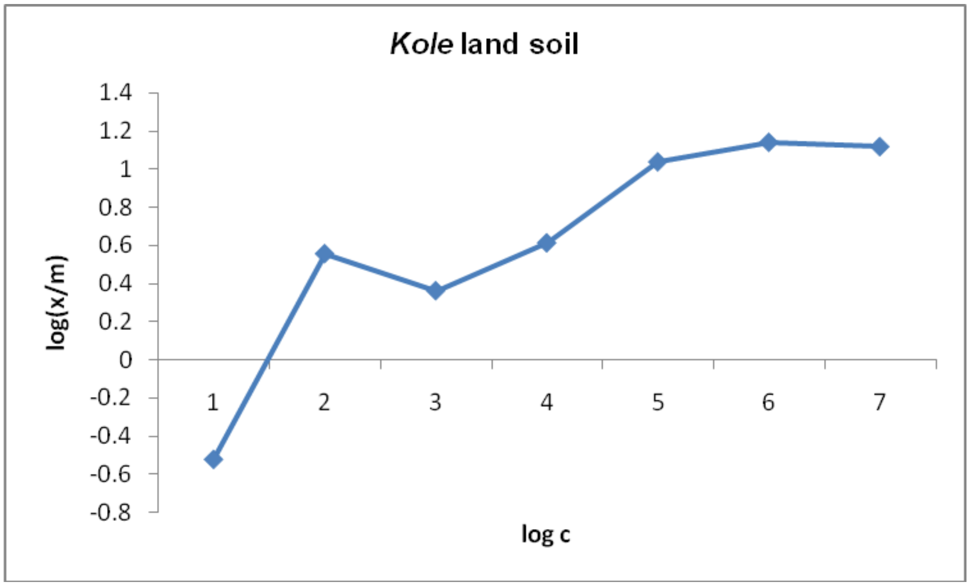
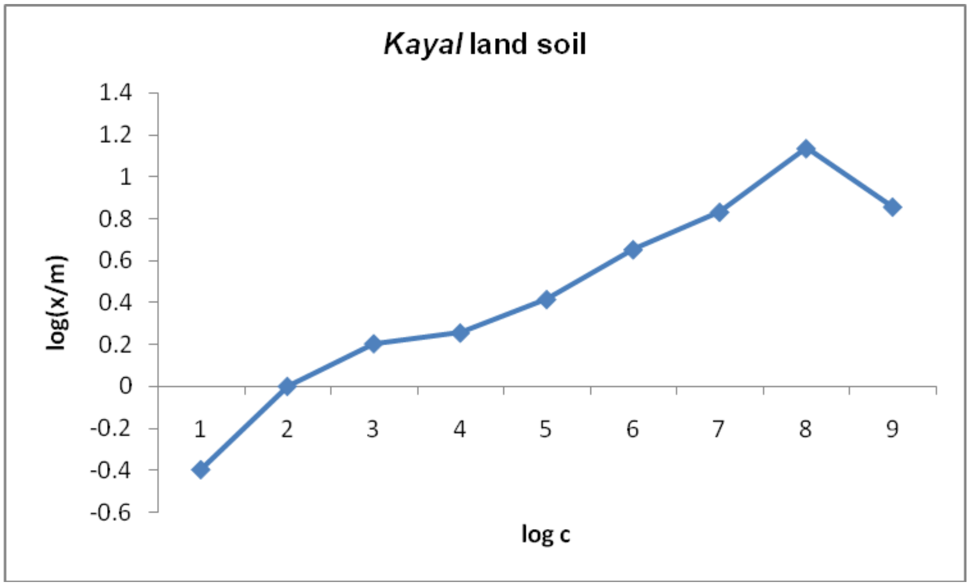


Fig. 36. Freundlich adsorption isotherm for *Kayal* land soil at 40^0C



In Pattambi and Elavampadam soils, K_F though decreased, the adsorption increased with increasing temperature indicating endothermic spontaneous nature of adsorption. This is supported by decrease in free energy, increase in enthalpy and positive entropy. The reason for the difference in adsorption pattern in *Kole* and *Kuttanad* (both acid sulphate) soils is to be further investigated. However, the influence of organic matter showed more quantitative effects in *Kayal* soils in comparison with the *Kole* soils where the organic matter is almost double in *Kayal* soils. So also the case with the total surface area, which is much higher in *Kayal* soils due to high organic matter and clay.

Experiment 4

The available B status recorded in three soils viz. *Onattukara* sandy soil (S_1), lateritic upland soil (S_2) and low land soils from Elavampadam (S_3) at one month, two months and three months after incubation are given in table 22, 23 and 24 and the interaction effect is depicted in figures 37, 38 and 39 respectively. After one month of incubation, in sandy soils of *Onattukara* the application of 6 kg borax ha^{-1} significantly improved the available boron status from 1.43 to 1.60 mg kg^{-1} and reduced to 1.53 mg kg^{-1} up on further increase in the dose of borax to 12 kg ha^{-1}. The increase in the availability of boron up to 6 kg borax ha^{-1} could be due to the increase in the amount of RS-B. The decrease in availability at higher doses might have resulted from adsorption of B. The application of organic matter @ 5t ha^{-1} increased the availability of B but it was found reduced at higher levels of organic matter. Though the application of borax without the addition of organic matter resulted in the increase in the content of boron in soils, the available B recorded in the treatment with 6 and 12 kg ha^{-1} were on par emphasizing that available B increases in sandy soils upon addition of borax up to 6 kg ha^{-1} which reduces on further increase in borax due to adsorption. On perusal of the data on available B estimated at different levels of borax with the increase in levels of organic matter clearly indicate that adsorption of boron increases with the amount of added organic matter.

Both in the lateritic soils and low land soils of Elavampadam, though insignificant, a slight change in boron availability was noticed upon increase in the levels of borax. This could be due to adsorption of very small amount of boron on Fe and Al oxide and oxyhydroxides. The means of available B recorded at different levels of organic matter application also show that the decrease in availability of B resulted from increase in adsorption of B with the increase in levels of added organic matter. In the treatment combination of B_0 (0 kg borax ha^{-1}) with increasing levels of organic matter resulted in significant increase in the content of available B both in lateritic upland and low land soils of Elavampadam while the available B recorded at 0 t OM ha^{-1} exhibited a different trend in these soils. The available B increased from 1.56 mg kg^{-1} at B_0O_0 to 1.87 mg kg^{-1} at B_3O_0 in the soils of Pattambi could be explained as the increase in the amount of RS-B with the increase in the levels of borax while in the lowland soils, available B decreased with the levels of borax from 2.17 (B_0O_0) to 1.95 (B_3O_0) mg kg^{-1}. The decrease in availability might have resulted from adsorption of B by comparatively high amount of clay fraction present

Fig. 37. Interaction between organic matter and borax on availability of B after one month of incubation

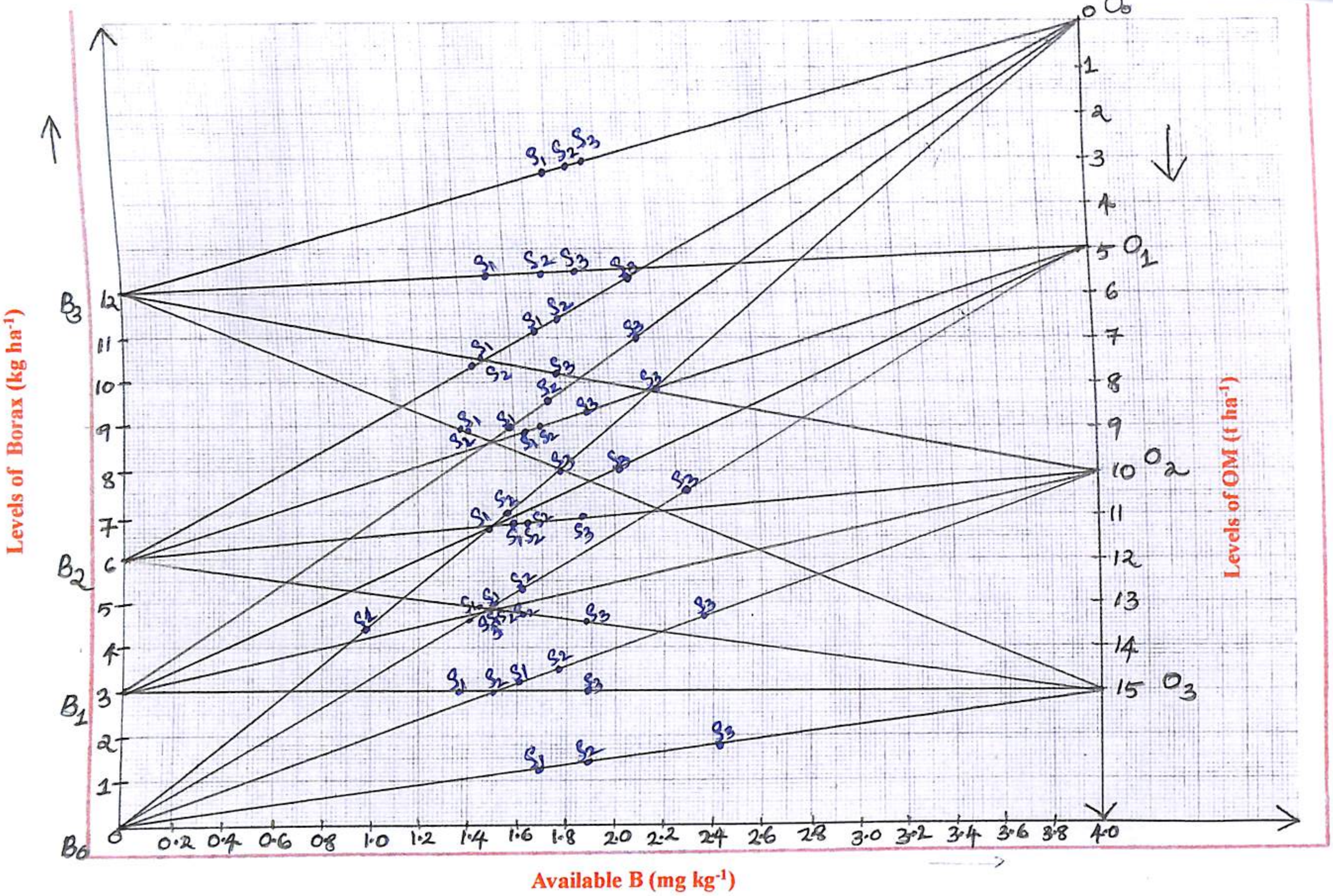
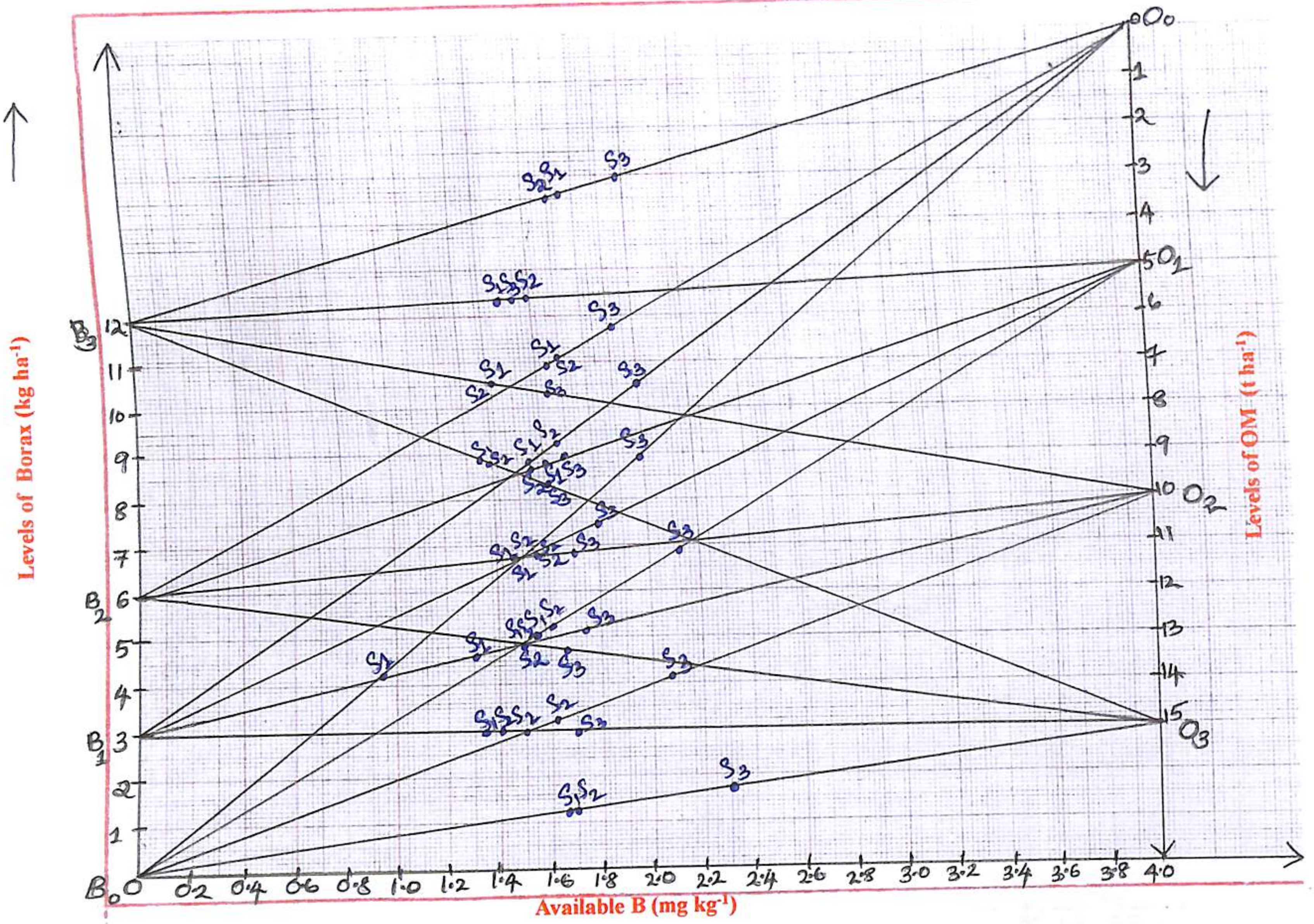


Fig. 38. Interaction between organic matter and borax on availability of B after two months of incubation



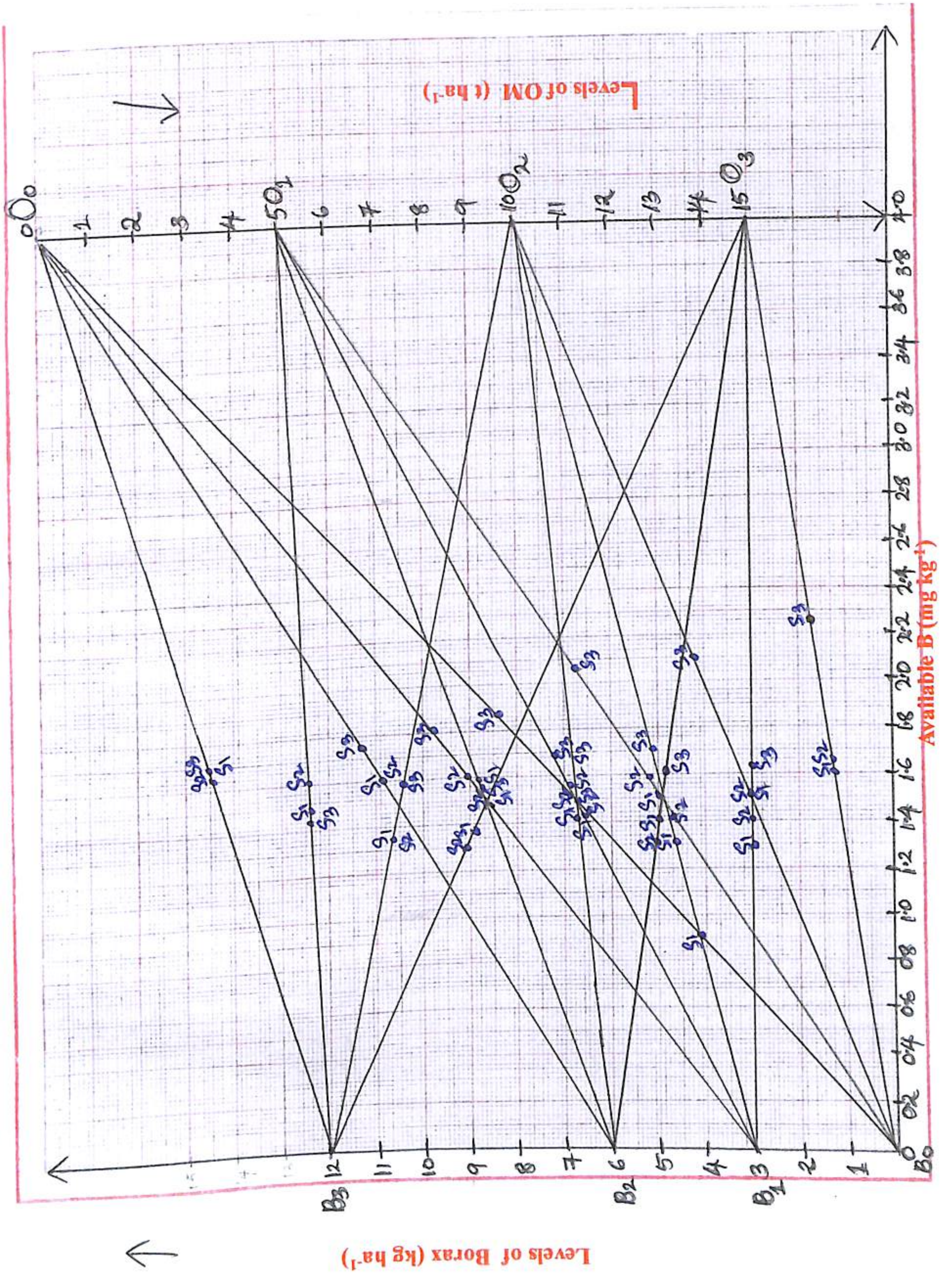


Fig. 39. Interaction between organic matter and borax on availability of B after three months of incubation

Fig. 40. Effect of 0 t OM ha^{-1} at different levels of borax on B availability in *Onattukara* soil

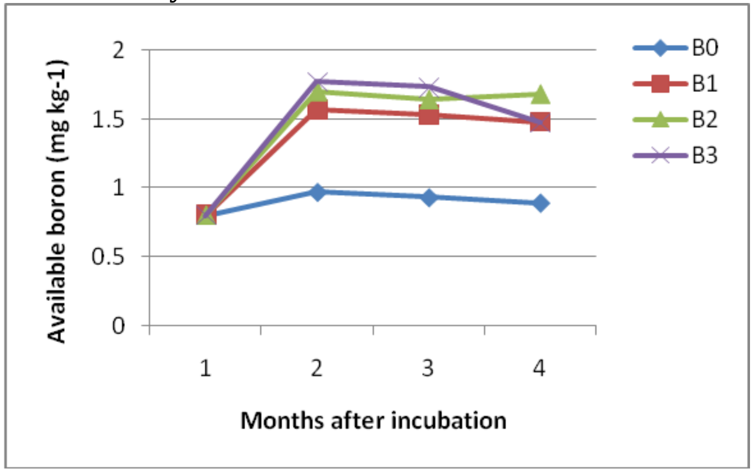


Fig. 41. Effect of 5 t OM ha^{-1} at different levels of borax on B availability in *Onattukara* soil

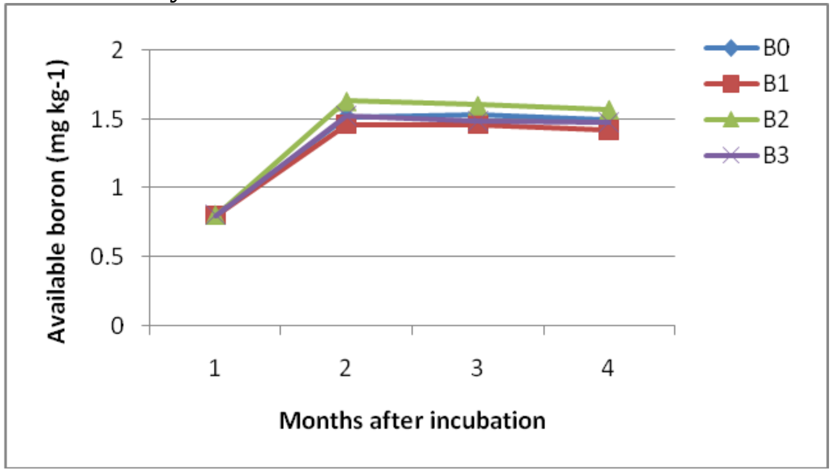


Fig. 42. Effect of 10 t OM ha^{-1} at different levels of borax on B availability in *Onattukara* soil

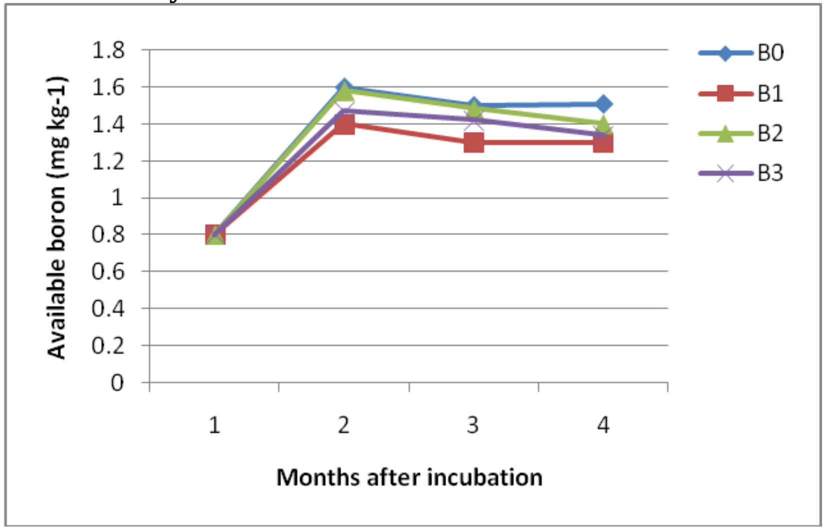


Fig. 43. Effect of 15 t OM ha^{-1} at different levels of borax on B availability in *Onattukara* soil

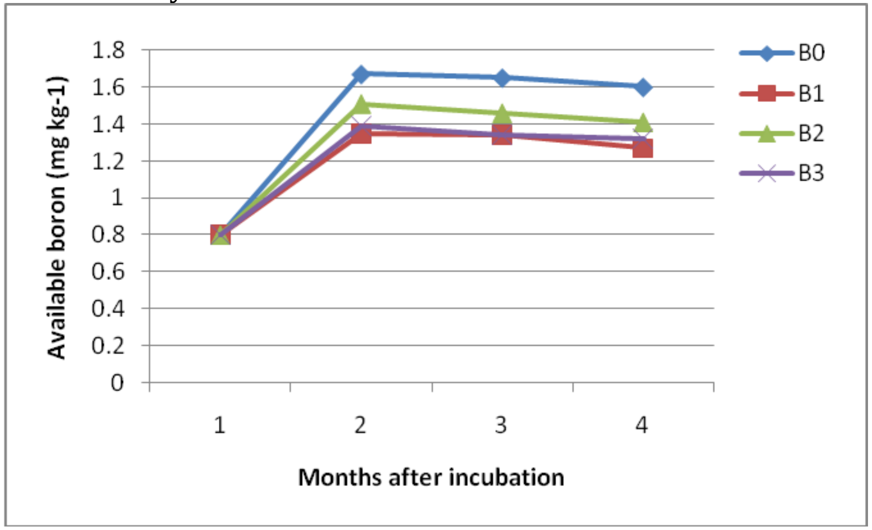


Fig. 44. Effect of 0 t OM ha^{-1} at different levels of borax on B availability in Pattambi soil

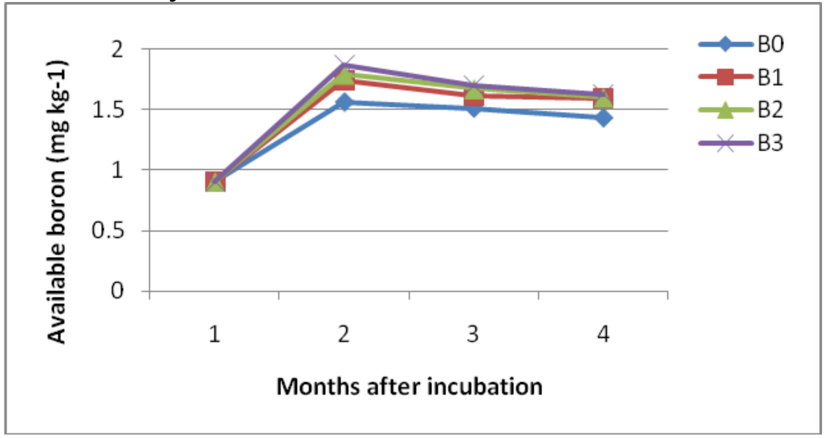


Fig. 45. Effect of 5 t OM ha^{-1} at different levels of borax on B availability in Pattambi soil

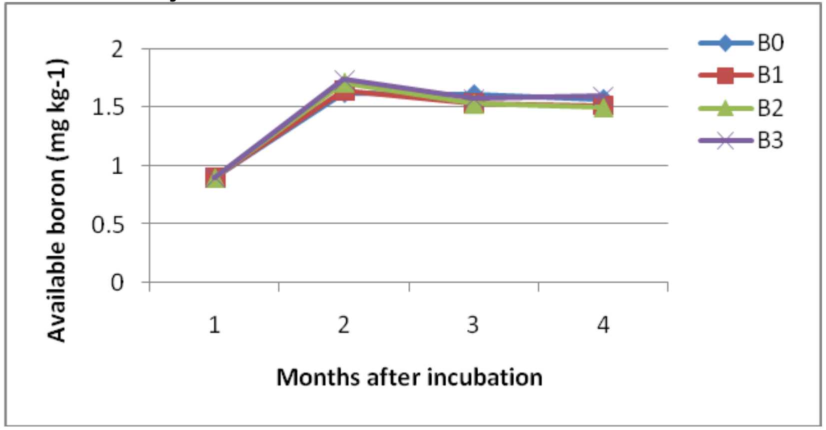


Fig. 46. Effect of 10 t OM ha^{-1} at different levels of borax on B availability in Pattambi soil

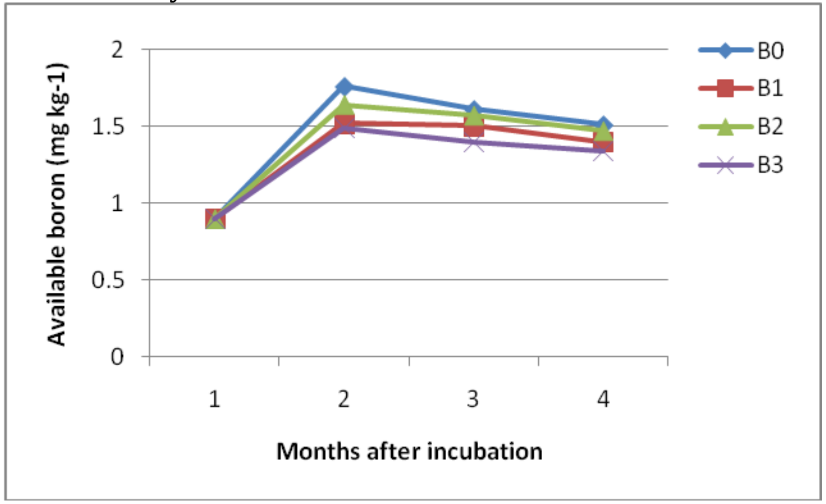


Fig. 47. Effect of 15 t OM ha^{-1} at different levels of borax on B availability in Pattambi soil

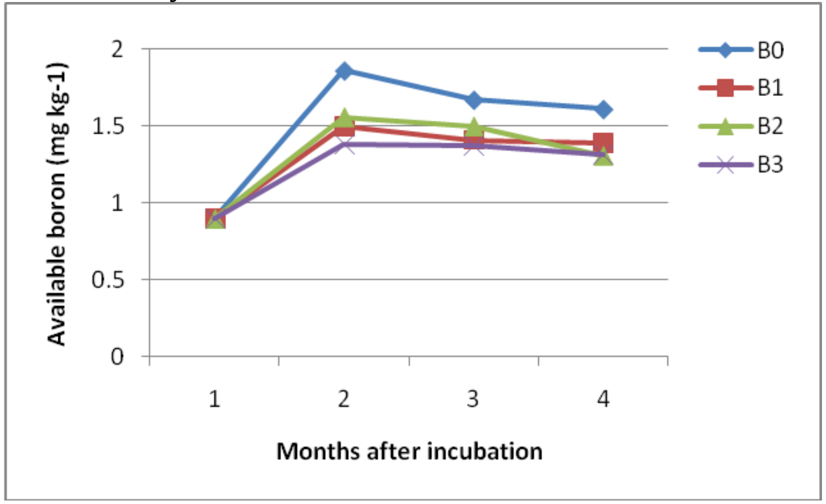


Fig. 48. Effect of 0 t OM ha^{-1} at different levels of borax on B availability in Elavampadam soil

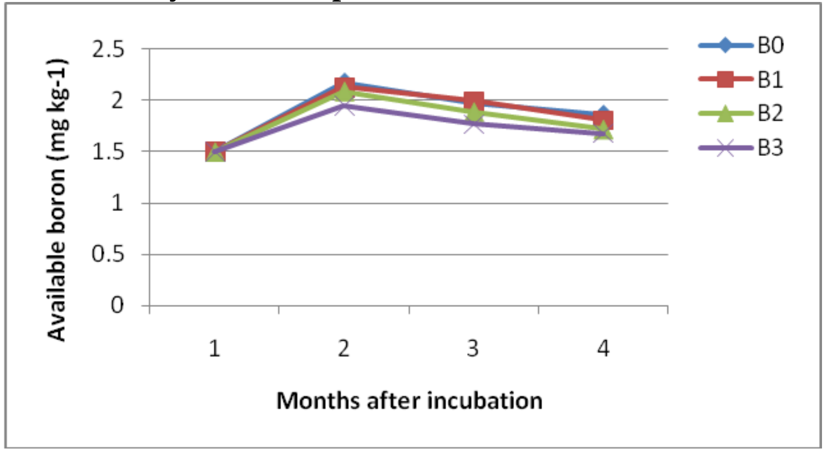


Fig. 49. Effect of 5 t OM ha^{-1} at different levels of borax on B availability in Elavampadam soil

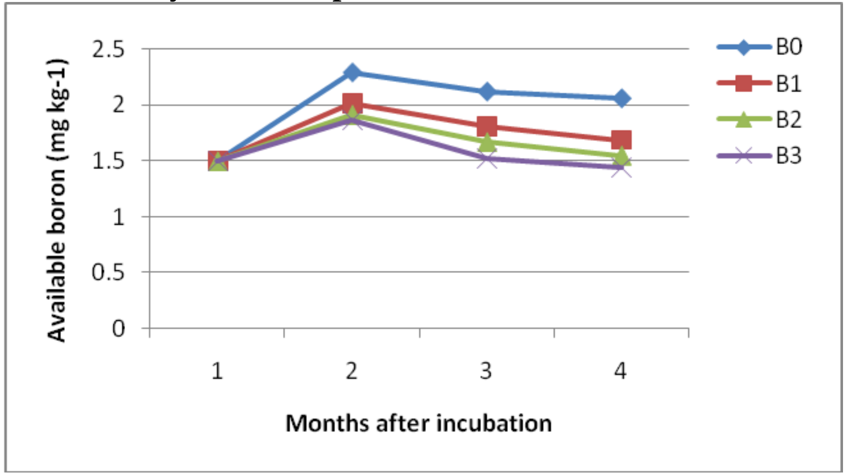


Fig. 50. Effect of 10 t OM ha^{-1} at different levels of borax on B availability in Elavampadam soil

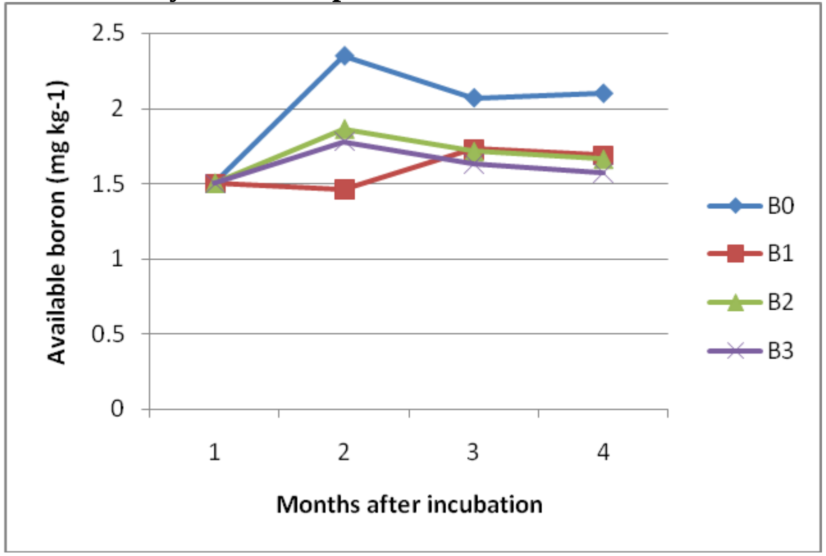
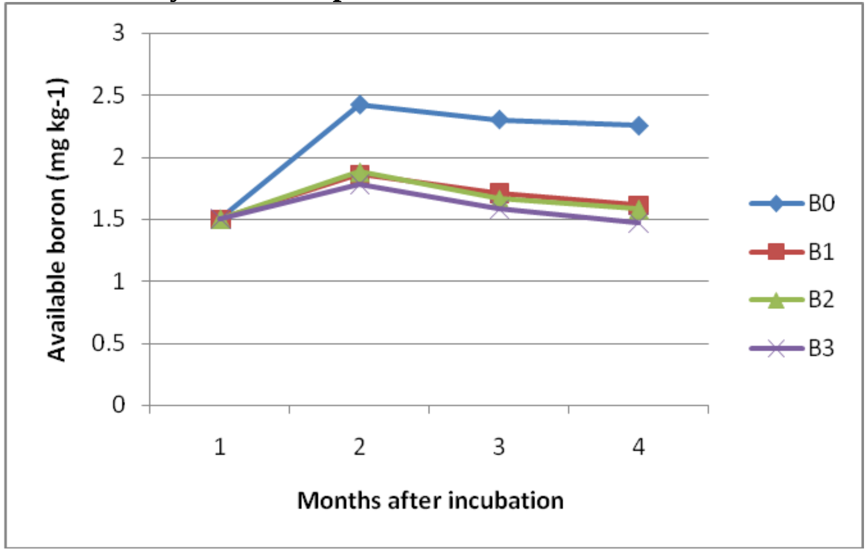


Fig. 51. Effect of 15 t OM ha^{-1} at different levels of borax on B availability in Elavampadam soil



in this soil. This is further supported by the adsorption data where K_F was more in the lowland soils of Elavampadam suggesting more amount of adsorption per unit equilibrium concentration.

After two months of incubation also the mean values of boron recorded show that treatment with 6 kg borax ha^{-1} was significantly superior to all other doses of borax and the decrease in boron was noticed at higher levels of borax meaning that the process of adsorption is still in progress. The available B recorded at different levels of borax without OM was highest at 12 kg borax ha^{-1} and critically different from all other treatments clearly indicate that increase in availability of B with increases in doses of borax. The available B recorded at 6 kg borax without OM, and 15 t OM ha^{-1} without borax were on par which means that 15 t OM ha^{-1} is contributing the same amount of boron to the available pool as that of applying 6 kg borax ha^{-1}. The availability of B reduced at increasing levels of borax combined with increase in organic matter indicates the enhanced adsorption of boron by the added organic matter. The decreased availability of boron with increase in levels of borax is associated with the levels of organic matter clearly indicates the role of organic matter in adsorption of B. Increase in OM levels without borax as well as increasing levels of borax without OM in majority of the cases increased the available B. Treatment combinations of different levels of borax without organic matter, increased the availability of B from 1.43 to 1.63 mg kg^{-1} in lateritic soils while it decreased from 1.86 to 1.68 mg kg^{-1} in the low land soils. The decreased boron availability with the increasing levels of borax could be due to adsorption by the comparatively higher amount of clay present in this soil whereas the increase in the levels of OM without the addition of borax increased the boron availability in both the soils. In different treatment combinations of borax combining with higher levels of organic matter resulted in decrease in availability of B and the decrease is more pronounced in the low land soils which might have resulted from the adsorption of B by clay and organic matter. Even after three months the availability of boron as well as its adsorption pattern followed the same trend as that in the previous time intervals which indicate that the adsorption of B by organic matter is a slow and steady process.

Availability pattern of boron over the period of incubation is depicted in fig. 40 to 51. In nutshell the following are the patterns of interaction of organic matter and borax in all the three soils. After one month of incubation in all the soils, in treatments without application of OM and borax slightly increased the availability of boron and maintained almost constant level thereafter. Application of borax at different levels without OM increased the available B after one month and maintained a constant level thereafter. When 5 t OM ha^{-1} was applied it was found that boron was released to the available pool after one month of incubation with and without borax application suggesting that the release was from organic matter. Further increase in duration of incubation did not make any significant increase or decrease in available boron or it maintained a constant level of available pool. When 10 t OM ha^{-1} was applied a substantial increase in the available boron was observed after one month of incubation at different levels of applied borax, thereafter it showed a slight decrease indicating adsorption of boron by higher levels of organic matter. When 15 t OM ha^{-1} was added similar to other treatments there was a substantial increase in available B initially and a slight decrease thereafter. However it is to be specifically noted that at this level of organic matter (15 t OM ha^{-1}), the available B was highest in the treatment without any borax application and it was lowest at higher levels of borax 6 and 12 kg ha^{-1}. The above observations point to the fact that either organic matter or borax independently could maintain sufficient amount of B in the soil. However, when both are applied together depending up on the quantities of their application B was adsorbed by organic matter and maintained a constant release. These observations have practical significance especially under acidic coarse textured soils for retention of applied boron without leaching losses *ie.* organic matter level should be maintained for realizing long term effect of applied B otherwise need based split application of borax is to be followed to minimize the losses and to increase efficiency.

Experiment 5

5.5.1. Biometric observations

Table 25 shows that application of borax could not produce any significant change in the tillering of rice during a period of one month after transplanting. One of the most important components contributing to the yield of the crop is number of tillers per plant. However it is controlled by environmental factors and the genetic make-up of the plant. This is in conformity with the reports of Shafiq and Maqsood (2010).

Data in table 26 show that a maximum of nine tillers were observed in T_4 at harvest and was superior to all the treatments. With respect to number of productive tillers in T_4 all the nine tillers produced were productive. In all other treatments all the tillers were not productive. It is very well clear from the data that boron has significant role on total number of tillers and their productivity at later stages as evidenced by the significant improvement in the same over the control. The reason for this could be the presence and utilization of B at the reproductive stages of growth. This is agreement with the reports of Shafiq and Maqsood (2010).

Table 27 Shows that the number of branches per panicle is not affected by the application of borax. Application of borax @ 2 kg ha^{-1}(T_2) significantly increased the number of grains per panicle over the control and the highest number of grains per panicle was observed in T_4 (117.0) where the borax was applied @ 6 kg ha^{-1}. Further increase in the dose of borax reduced the number of grains per panicle. Lower number of grains produced with the higher rates of borax might be due to the toxic effect of boron. Thousand grain weight increased with the doses of borax up to T_4 (30.50g) where the borax was applied @ 6 kg ha^{-1} and it was critically superior to all other treatments. This would mean that boron has also got a role in making the grains bold. This may be due to the boron mediated translocation and accumulation of photoassimilates in the grain favouring heavier grains. The lighter grains produced at the higher levels of borax might have resulted from the toxic effect of boron in rice. This is line with the reports of Hussain *et al.* (2005) and Shafiq and Maqsood (2010).

Fig. 52. Effect of borax on thousand grain weight

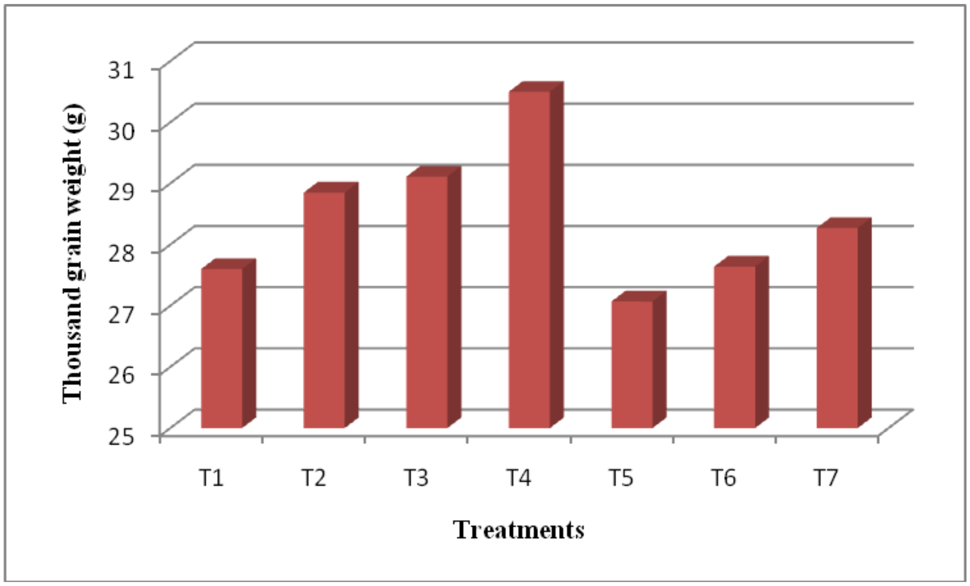
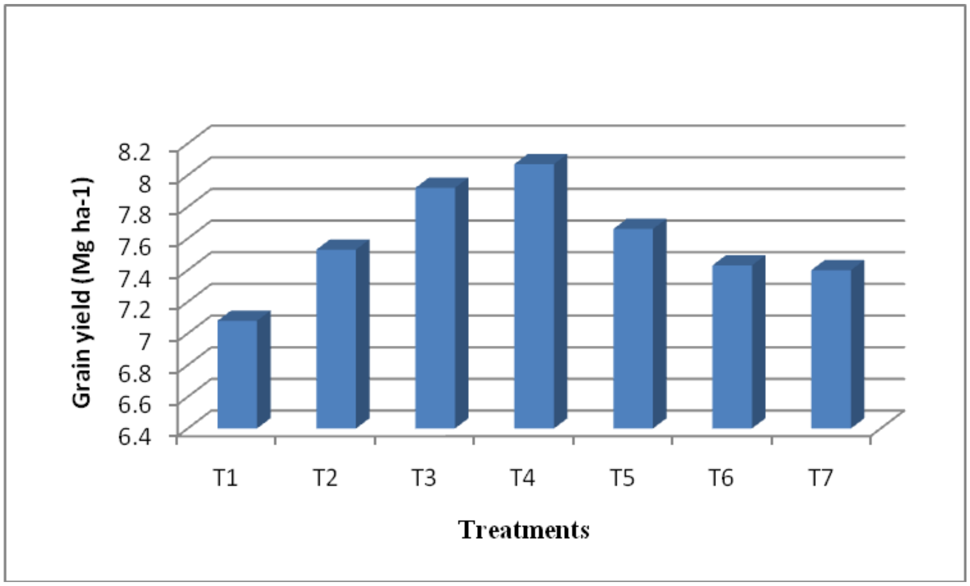


Fig. 53. Effect of borax on grain yield



Grain yield of rice (table 28 and fig. 53) show that there was a significant increase in grain production by the application of 2 kg borax ha^{-1} over the control and increased significantly with increasing doses of borax. The maximum yield of 16.15 kg plot^{-1} (8.07 Mg ha^{-1}) was noticed in T_4 where borax was applied @ 6 kg ha^{-1} and it reduced up on further increase in borax. Yield increases with B accrued because of reduced panicle sterility (on lower portion of the ear) and increased productive tillers per hill. Post-harvest grain shedding is also reduced with improved B nutrition. Also, B deficiency in rice causes an uneven crop maturity. Optimum B dose for effective management of B deficiency in rice is 0.75 kg ha^{-1}(Rashid *et al*., 2004; 2006). The treatment with 8 kg borax recorded yields significantly lower than T_4 and it is on par with T_6, T_7 and T_2. These results agree to the findings of Rashid *et al.* (2004), Diana and Beni (2006), Shafiq and Maqsood (2010). Response curve to find out the optimum dose of borax for rice was plotted with the levels of borax on X axis and the corresponding yield on Y axis (Panse and Suktame, 1978) and is presented in fig. 54. The optimum dose identified from the response curve is 5.5 kg borax ha^{-1} which could be rounded to 6 kg borax ha^{-1}. This is in proximity to the optimum dose (7.5 kg borax ha^{-1}) fixed by Rashid *et al.* (2004) for soils of Islammabad in Pakistan.

Fig. 54. Response curve showing the effect of levels of borax on grain yield of rice

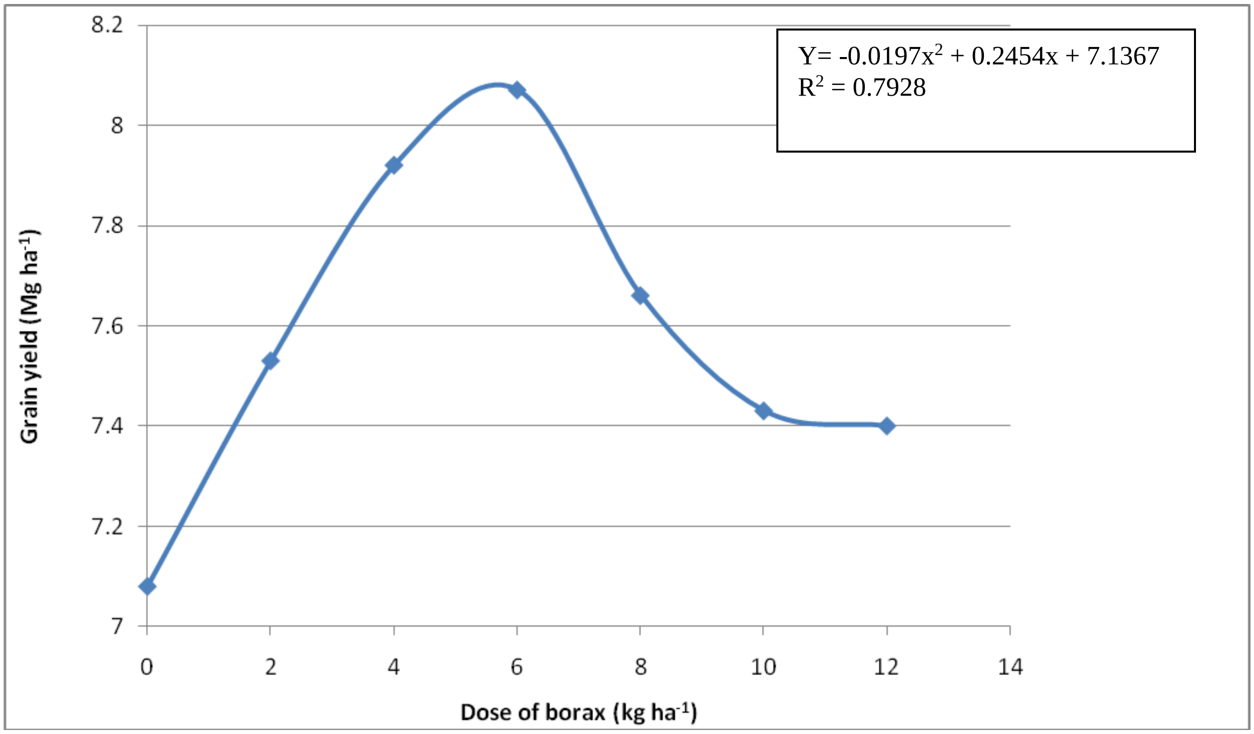


Fig. 55. Effect of borax on uptake of boron in straw and grains

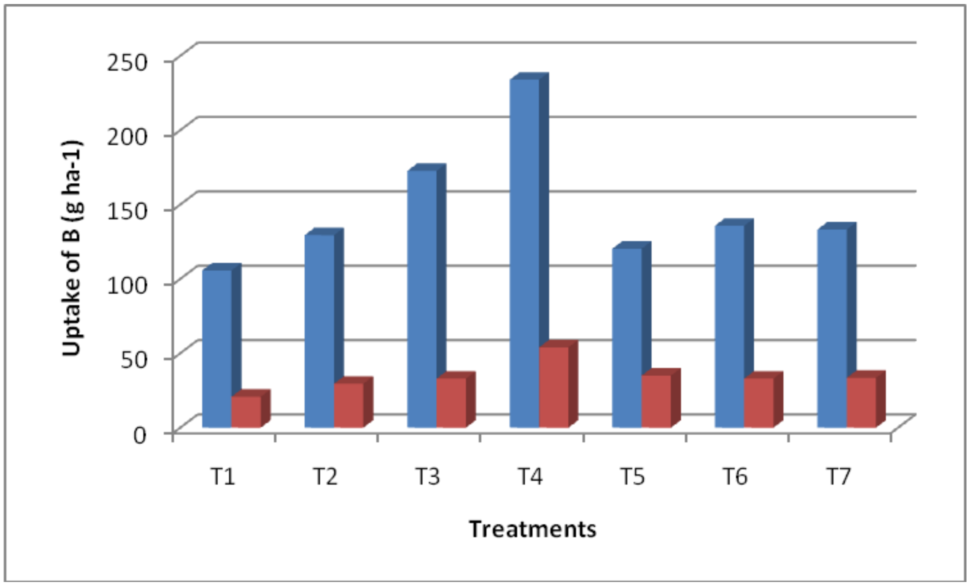
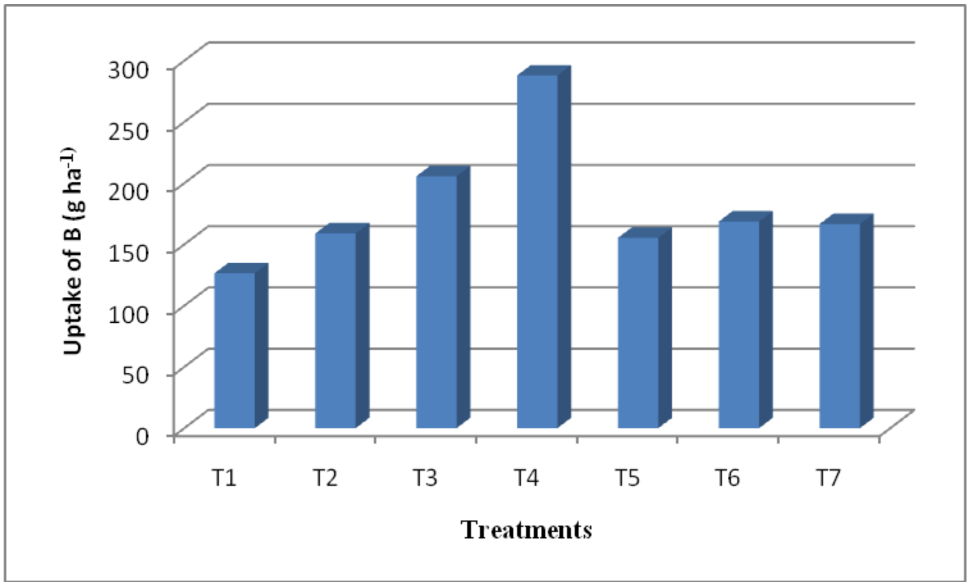


Fig. 56. Effect of borax on total uptake of boron



There was a slight increase in the straw yield (table 29) in response to the borax application but the increase was statistically not significant. The maximum straw yield of 13.85 Mg ha^{-1} was recorded in T_6 whereas the minimum was in control (12.05 Mg ha^{-1}). These results are similar to those of Husain (2006) and Shafiq and Maqsood (2010) who could not observe any significant change in straw yield in response to the boron fertilizers. The data on percentage chaffy grains recorded in different treatments did not show any trend with respect to the doses of borax.

Data on both per plot and per ha boron uptake in straw, grain as well as total uptake are presented in the table 30 and depicted in figures 55and 56. The maximum uptake of 233.97 g boron ha^{-1} in straw was noticed in the treatment with 6 kg borax ha^{-1} where the maximum grain yield was recorded and the minimum of 105.72 g ha^{-1} in the control. Though T_6 recorded the maximum straw yield, the uptake was low which would mean that boron requirement for highest straw yield might be same 6 kg ha^{-1} which gave the maximum grain yield. Hence it could be concluded that boron absorption at both levels might be same and due to dilution effect by larger biomass a lower content was recorded in T_6. The uptake of boron in grains also varied significantly with respect to the different treatment levels of borax. Here also the maximum yield was noticed in T_4 and the minimum in the control treatment. This is as expected due to higher grain yield in T_4.

In brief, it is well evident from the biometric observations and yield data that boron has got critical role in the productivity of tillers, number of grains per panicle and thousand grain weight which ultimately resulted in increased grain yield and nutrient uptake.

5.5.2. Effect of borax at panicle initiation stage

Data in tables (31, 32, 33 and 34) show the effect of borax on electrochemical properties, primary, secondary and micronutrients (Fe, Mn, Zn and Cu) in soil at the panicle initiation stage. The application of borax showed no effect on pH, EC, OC, K, Ca, Mg and the micronutrients. These results are in line with the reports of Rashid *et al.* (2004). Only P and S were affected by the treatments. The highest available P of 9.70 kg ha^{-1} was recorded in T_4 and the minimum of 8.08 kg ha^{-1} in the control plot. Though T_4 recorded the highest it was on par with T_3, T_6 and T_7. The lowest value of available P in the control could be attributed to the reason that in the absence of boron, plants might have absorbed more quantities of P by the same absorption sites. Available sulphur had lowest value in the control plot (8.63 kg ha^{-1}) and it increased significantly to 20.06 kg ha^{-1} in T_7 where the highest dose of borax (12 kg ha^{-1}) was applied. The available boron in soil increased linearly with the doses of borax from 0.80 in control to 1.20 mg kg^{-1} at T_7. The increase in available B could be attributed to the increase in readily soluble boron fraction in soil.

Table 35 shows that the application of borax had significant effect on the different fractions of soil boron. Both readily soluble B and specifically adsorbed B had the lowest values in the control treatment and it increased linearly up to T_4 *ie*. treatment which produced maximum grain yield. Further increase in the doses of borax reduced these fractions. Similar reports were made by Diana and Reni (2006) in lettuce that SA-B, RS-B and OR-B increased up to a particular level of boron fertilizer during crop session of lettuce. Organically bound boron had maximum value of 1.56 mg kg^{-1} in T_5 and then reduced. Here T_2, T_3, T_4 were on par and T_6 and T_7 were on par. Both the oxide bound B and residual boron increased linearly with the doses of borax. The direct and indirect influence of fractions on available B as indicated by the path coefficients suggest that roots were absorbing B from readily soluble pool of B as well as from the OR-B. specifically adsorbed B has no direct effect on available B but its indirect effect through RS-B suggest that it is a labile form of B in soil which is in immediate equilibrium with RS-B.

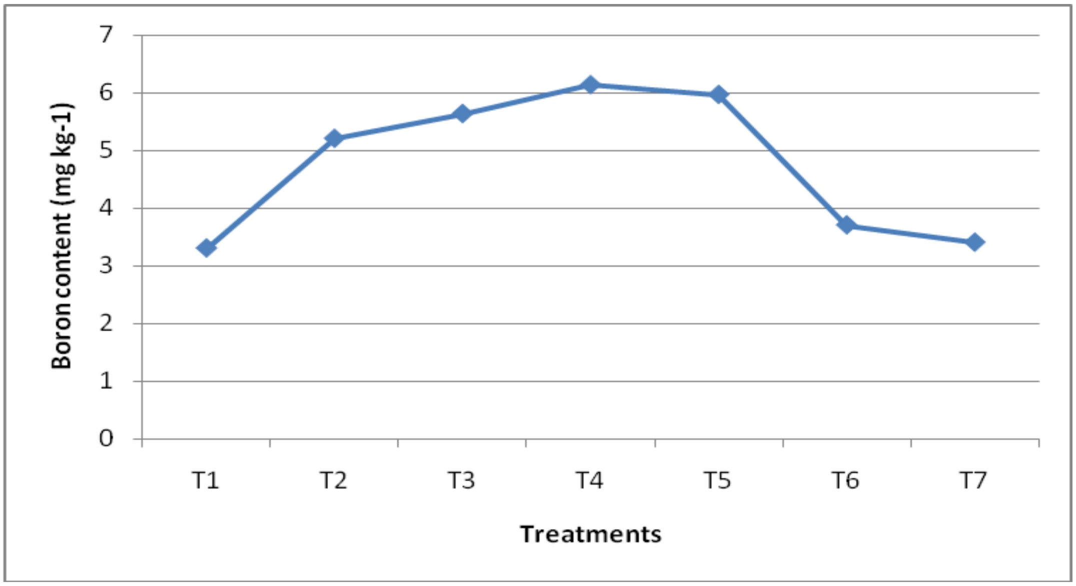
Effect of borax on primary, secondary and micronutrients (Fe, Mn, Zn and Cu) are presented in tables 36 and 37. The data show that the treatments did not produce any significant effect on the content of P, K, Ca, Mg, Mn and Cu. These observations are in line with the findings of Rashid *et al*. (2004) that P, K, Ca, Mg concentration in leaves of wheat did not vary significantly with increase in the doses of boron fertilizers while the total N, S, Fe and Zn content in shoot samples were significantly influenced by the treatments. Total nitrogen had the highest value of 0.54 per cent in T_4 and the lowest in T_7 indicating an inverse relationship between nitrogen content and levels of borax applied which could be due to reduced absorption of nitrate ions in presence of borate ions particularly at higher concentrations of the latter. Though the treatments had significant influence on total sulphur content in shoot, it did not show any clear trend. However the synergistic effect of S and B could be attributed to the above observation. The total Fe content reduced linearly from T_1 to T_7, whereas zinc content in shoot did not show any trend with respect to the borax applied.

The maximum content of 6.30 mg boron kg^{-1} was noticed (table 38 and fig. 57) in the shoot samples of the treatment with 6 kg borax ha^{-1} (T_4) and the minimum in the control. Though B at T_4 was the highest it was on par with T_3 and T_5. This would mean that at balanced status of nutrients in soil, boron will not be absorbed beyond a particular limit. Similar reports were made in wheat by Shafiq and Maqsood (2010) that the content of boron in leaves did not increase linearly with the levels of boron fertilizers.

Application of borax also had significant influence on the content of boron in roots. Though the treatments with 4, 6, and 8 kg borax ha^{-1} were significantly different over the control, they were on par. However it is clear from the data that with the increase in levels of borax there is an increase in the content of boron in roots which might be accumulation of reversibly adsorbed boron on the root surface which increased with the levels of boron in soil solution.

The correlation coefficients between available B, fractions of B and the content of B in shoot is given in table 39. The contribution of RS-B, OX-B and RES-B to the available pool is evident from the highly significant positive correlation between available B and these fractions. Path coefficients (table 40) indicate that the direct effect of oxide bound boron on available B at PI was high as evidenced by the path coefficient of 0.6352 and the direct effect of RS-B was moderate. The indirect effect of RS-B and residual B through Oxide bound B was high whereas the indirect effect of OX-B and RES-B through RS-B was low. The readily soluble boron was found significantly and positively correlated with SA-B, OX-B and RES-B. The path analysis (table 41) clearly indicates that direct effect of specifically adsorbed boron on readily soluble B was high indicating the contribution made by SA-B to RS-B which establishes the immediate dynamic equilibrium between these two. The Oxide bound boron and residual boron was also contributing to RS-B through SA-B as indicated by the moderate indirect effect of OX-B and RES-B through SA-B.

Fig. 57. Effect of borax on content of boron in shoot at panicle initiation



The content of boron in shoot is highly significantly correlated with RS-B, SA-B and OR-B and not correlated with available B. Similar reports were made by Sims and Johnson (1991), Tsalidas *et al.* (1994) and Jin *et al.* (1987). The direct effect of RS-B and OR-B on the content of boron in shoot at panicle initiation stage was high as indicated by the path coefficients of 0.5976 and 0.4849 respectively (table 42) while that of SA-B was low. The indirect effect of SA-B and OR-B through RS-B on the content of B in shoot clearly indicates the existence of dynamic equilibrium between these fractions of boron in soil. The indirect effect of RS-B and SA-B through OR-B was moderate. This would mean that plant roots mainly absorb boron from RS-B, SA-B and OR-B.

5.5.3. Effect of borax at harvest stage

Data in tables 43, 44, and 45 depicts the effect of borax on the electrochemical properties and available nutrient content of soil at harvest. pH, EC, available Ca, Mg and micronutrients (Fe, Mn, Zn and Cu) were not influenced by the difference in the levels of application of borax. Similar reports were made by Shafiq and Maqsood (2010). While OC, P, K and S status in soil were significantly influenced by the treatments. Organic carbon status of soils was found to decrease significantly with the levels of borax except at $T_{6.}$ Available P was found to decrease from T_2 with the increase in levels of borax though linearity is absent. Lower levels of P at higher levels borax might have resulted from higher concentration of borate ions in soil which in turn hindered the availability of P in soil. Available S status of soil decreased linearly from 18.77 mg kg^{-1} (T_1) to 8.40 mg kg^{-1}(T_7) might have resulted from higher plant absorption at lower levels of borax.

Similar to the trend at PI, available boron increased linearly with the levels of borax at harvest stage also (table 46). This could be due to the increase in the amount of readily soluble B in soil. Data on the effect of borax on different fractions of boron is given in table 47. With respect to fractions of B in soil the same trend at PI is observed at harvest stage also. RS-B, SA-B and OR-B reached a maximum value either at T_4 or T_5 and it got decreased thereafter while OX-B and RES-B increased linearly with the levels of borax. These observations are in close line with the findings of Diana and Beni (2006). The comparison of fractions at PI and harvest reveals that the amount of RS-B, SA-B and RES-B decreased while OX-Band OR-B made a slight increase or rather remain unaltered at the harvest stage. This would mean that the plant absorption might have taken place from RS-B, SA-B, OR-B, OX-B in that order which is same as the trend observed at PI. But the slight increase or no change in OX-B and OR-B further establishes the existence of dynamic equilibrium particularly at the later stage of plant growth. Data in table 48 show that content of P, K, S and Ca in straw at harvest were not affected by the treatments. Content of N had highest value of 0.47 per cent at T_4 and reduced to a lower value at T_7 indicating reduced absorption of boron at higher levels of borax which might be due to reduced absorption of nitrate ions in the presence of borate ion in soil solution particularly at higher concentrations of the latter.

Though the content of Mg in straw significantly differed in response to different levels of borax no clear trend was observed. The content of Fe, Mn and Zn had significant difference with respect to the levels of borax as revealed by the data in table 49. All these elements had low values in the control treatment and the highest values at T_4. Further increase in the levels of borax reduced the content of these elements.

Data on the effect of borax on primary, secondary and micronutrients in grains are given in tables 50. Content of P and K recorded in grain samples were not found to be affected by the treatments whereas the content of N and S in grains were different in response to the treatments. Similar to the trend in shoot at PI, the lowest nitrogen content of 0.85 per cent was noticed in control and increased to a maximum value of 1.12 per cent in T_4 thereafter it reduced upon increase in the doses of borax and it seems that at higher concentrations of boron in soil solution, absorption and translocation of N to the sink is affected.

The content of Mg in grains varied from 507.47 to 587.0 mg kg^{-1}. It showed a decreasing trend in response to the increase in levels of borax. This is opposite to the trend that is observed in shoot. The higher levels of Mg recorded in the grains might be due to selective translocation. The content of Ca in grains was found to decrease with the increase in the levels of borax though linearity was absent whereas sulphur did not show any clear trend with the increase in levels of borax. However all the treatments recorded values lower than control.

The content of Fe, Mn, Zn and Cu in grains (table 51) was significantly affected by the difference in the levels of borax. Content of Fe had maximum value in the control (514.60 mg kg^{-1}) and the lowest value in T_7 (107.33 mg kg^{-1}). The content of Fe showed a decreasing trend with the increase in the levels of borax which is opposite to the trend observed in straw. Higher accumulation in straw resulted from lesser translocation to grains. Manganese and Zn content in grain was found to increase with the doses of borax even though linearity was lacking.

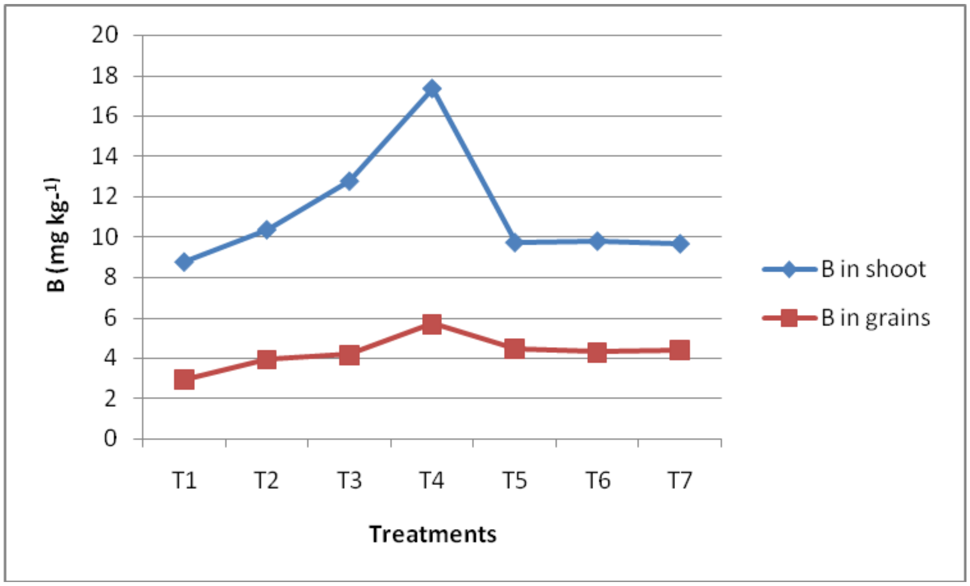
The content of B in straw (table 52 and fig.58) was lowest in the control with 8.77 mg boron kg^{-1} and increased linearly with the levels of borax and recorded the highest at T_4 with 17.33 mg boron kg^{-1} and was superior to all the treatments. Upon further increase in levels of borax, content of B in straw was reduced. This would mean that at balanced status of nutrients in soil, boron will not be absorbed beyond a particular limit. Similar reports were made in wheat by Shafiq and Maqsood (2010) that the content of boron in leaves did not increase linearly with the levels of boron fertilizers.

Application of borax also had significant influence on the content of boron in roots. Though the treatments with 8, 10, and 12 kg borax ha^{-1} were significantly different over the control, but were on par. The lower values recorded in treatments with 2, 4 and 6 kg borax ha^{-1} than control treatment could be due to translocation of B as evidenced by high values recorded in straw and grains in these treatments.

Maximum content of B in grain was recorded in T_4 (5.70 mg kg^{-1}) and the minimum in the control treatment (2.93 mg kg^{-1}). Boron in grains increased (fig. 57) linearly with the levels of borax up to T_4 (where the maximum content of B in straw was recorded) and then reduced.

Correlation studies between available B, fractions of B, with the content of B in straw as well as the grains given in table 53 show that there exists a high significant positive correlation of SA-B, OX-B, OR-B and RES-B with available B indicating that at later stages of plant growth these fractions have their own role in controlling the availability of B in soil. Path coefficients in table 54 show that the direct effect of OR-B on the available B in soil at harvest was very high as indicated by the path coefficient of 1.0569 and RES-B also had high direct effect on available B

Fig. 58. Effect of borax on content of boron in shoot and grain at harvest



as path coefficient being 0.3180. Specifically adsorbed B had high negative direct effect on available B. The indirect effect of SA-B, OX-B and RES-B through organically bound B was also high. This indicates that organically bound B contributes highly to available B and all other fraction except RS-B were also contributing to available B through OR-B.

Readily soluble B was highly significantly correlated with SA-B, OR-B, OX-B and RES-B. Path coefficients (table 55) indicate that the direct effect of SA-B on RS-B at harvest was very high. The indirect effect of oxide bound B, organically bound B and RES-B through SA-B was also high. This further establishes the existence of dynamic equilibrium between all these fractions and it gives the clear indication of contribution from different fractions in supplementing B to the pool of readily soluble B and hereby affecting the plant nutrition. The oxide bound B has got a high negative direct effect on RS-B, the indirect effects of SA-B and OR-B through OX-B are also negative indicating reversion of soluble B to oxide bound B either through adsorption or occlusion.

The content of boron in grains was positively and significantly correlated with all the fractions of B in soil whereas the content of B in straw was correlated with only RS-B. This could be due to translocation of boron from the source to sink at the reproductive stages of growth.

The content of B in grains is directly influenced by specifically adsorbed B followed by RS-B as indicated by the direct effect of both by path coefficients in table 56. The dominant role of SA-B over RS-B on the content of boron in grains mean that at later stages of growth particularly in short duration crops SA-B plays major role as RS-B get depleted. This is further supported by the path coefficient of SA-B to RS-B. The direct effect of SA-B on the content of B in grain was very high as indicated by the path coefficient of 1.0513 and the indirect effect of RS-B (0.7544), OX-B (0.8745), OR-B (1.0014) and RES-B (0.7495) through SA-B was also high. The direct effect of RS-B on the content of B in grains was high while the indirect effect of SA-B, OX-B, OR-B and RES-B through RS-B was moderate to high. The direct effect of OX-B on RS-B was low and the indirect effect of other four fractions through OX-B was also low. The direct effect of organically bound B on RS-B was very high and negative (-1.0850) and indirect effect of OR-B, SA-B, OX-B and RES-B through OR-B was also high and negative.

Grain yield was found to correlate significantly with RS-B and the content of B in straw and grain which mean that RS-B reflect very well in the content of B in straw, grain and ultimately in the yield.

Though the available B (hot water extractable) and readily soluble boron (0.01M$CaCl_2$ extractable) are found to be used synonymously in literature, the data in this experiment firmly ascertain that 0.01M$CaCl_2$ extractable and hot water extractable B are not one and same. The comparison of values on available B and RS-B in this experiment as well as in the fractionation study (experiment 2) show that hot water over extracts B probably from SA-B, a portion from oxide bound boron and organically bound boron. This could be due to the boiling of soil for five minutes that might have disturbed specifically adsorbed boron and solubilised some amount of OX-B, OR-B. Though available boron significantly correlated with fractions of boron it did not show any significant correlation with the content of boron in straw, grain and with the yield also. Instead readily soluble boron significantly correlated with all the fractions of B and the content of B in straw, grain and with yield also. These findings are further supported by the reports of Sims and Johnson (1991) who opined that though hot water extractable B has been regarded as a suitable index of plant available B but in some studies, the levels of hot water extractable B have not been correlated with plant response however this may vary with plant species. Since hot water is suspected to extract some portion of specifically adsorbed and oxide bound B, hot water extractable B may give a reproducible index of boron availability with respect to long duration annual crops, biennial crops and plantation crops. This definitely requires crop specific investigations.

Dynamics and management of boron in tropical soils of Kerala

In brief the status, chemistry, dynamics and fertility together with respect to boron in soils of Kerala are discussed hereunder:

Among the 65 soils characterized in the present study, 89 percent of the samples have the real problem of acidity with pH less than 5.5. With respect to organic matter status, 17 per cent of the samples were critically poor, another 30 per cent of samples are in the medium range with the risk of becoming low under tropical climate if not properly managed. The low organic matter status were reported in high rainfall areas and also in sandy soils. High levels of available P were noticed in 42 per cent of the soil samples which may cause induced deficiency of zinc and boron. Almost 60 per cent of samples were low to medium in K fertility, 82 per cent of soil samples were critically deficient in calcium, and 100 per cent samples were deficient in Mg. Only less than 18 per cent soils were deficient in S, 14 per cent in Cu, 5 per cent in Zn and 18 per cent were deficient in boron. However high levels of phosphorus in soils with sufficient levels of Zn and boron might be affected by P induced deficiencies of these elements. Zinc and B deficiency symptoms in soils with high P status can be corrected only by foliar application of these nutrients. Deficient levels of boron were found to be associated with coarse texture (AEUs 1, 2 and 3), low organic matter (AEUs 1 and 2) and high rainfall areas. The availability of boron was found to increase with decrease in pH and the increase in electrical conductivity as noticed in saline soils of *Pokkali* and *Kaipad*. The higher levels of boron in acid sulphate/saline soils of *Kuttanad* , *Pokkali* and *Kaipad* lands (AEUs 4, 5 and 7) is a consequence of sea water inundation to these areas.

The fractionation of soil boron in 31 soil samples representing 23 agro ecological units varying in physico-chemical properties as well as in available B revealed the clear picture of different forms of soil boron associated with water soluble, clay, organic matter and sesquioxide. Quantitative dominance of different fractions was in following order

RES- B > OR -B > OX- B > SA-B > RS-B

All the fractions except RES-B have a significant negative correlation with pH, positive significant correlation with EC. Organic matter bound boron was positively and significantly correlated with OC. Oxide bound B was significantly correlated with sand, silt, clay, sesquioxide and AEC indicating its dominance in all the soil separates as well as its association with sesquioxide and positively charged sites of broken edges as well as the amorphous Fe and Al oxyhydroxide clay minerals. These results give an indication of the role of pH, soluble boron salts, organic matter, oxides and hydrous oxides dominated by amorphous clay minerals of tropical soils in retention and solubility of boron.

The pattern of adsorption studied in six soil types revealed that only two soils namely *Onattukara* and *Kayal* lands of *Kuttanad* were found to follow Langmuir pattern of adsorption and there was no appreciable adsorption in sandy soils of *Onattukara*. In sandy soil, adsorption was minimum to cover the surface of adsorption with constant binding energy. In organic matter rich *Kuttanad* soil, quantity desorbed immediately below equilibrium concentration might have been existed with constant binding energy.

The adsorption maxima in *Kayal* land soil was 17 mg kg^{-1} whereas it was 0.5 mg kg^{-1} in sandy soil. All the soils except *Onattukara* sandy soil followed Freundlich adsorption isotherm indicating the decrease in binding energy with increase in surface coverage in an exponential fashion that too at lower concentrations. The K_F (Freundlich K), which is the amount adsorbed at unit equilibrium concentration decreased with increase in temperature from 25 to 40^{0}C. The buffer power increased with temperature in laterititic and Chittoor black soils whereas it decreased in Elavampadam, *Kole* and *Kuttanad* soils suggesting the possibility of denaturing of sites of adsorption associated with OM which suggest that there will be less buffering of B in these soils in summer season when the soil temperature increases. The intercept of Q/I curve decreased to negative values with increase in temperature which is an indication of desorption of boron from the sites when the solution concentration fell below equilibrium concentration.

The thermodynamic parameters *ie.* free energy of adsorption (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS) revealed that free energy of adsorption decreased with temperature in Pattambi, Elavampadam, *Onattukara* and *Kole* soils. In black cotton soils of

Chittoor and *Kuttanad* soils it was slightly increasing. The decrease in free energy with a positive enthalpy and positive entropy in Pattambi, Elavampadam, *Onattukara* and *Kole* soils revealed that the adsorption of B in these soils are spontaneous and endothermic. The slight increase in free energy with negative enthalpy change and entropy change in black and *Kuttanad* soil is an indication of exothermic adsorption without any spontaneity. It can be summarized that adsorption increases with temperature in Pattambi, Elavampadam, *Onattukara* and *Kole* while it decreased with temperature in other two soils. In black cotton soil, the decrease in adsorption might be due to shrinkage of vermiculite clay at higher temperature while in *Kuttanad* soils adsorption might be due to sites associated with OM which are the major sites of adsorption. In brief, results of the adsorption experiment revealed the key points for management of B in the different soil types particularly in summer season.

The incubation experiment aimed to study the effect of added OM in three different soils *ie.* sandy, lateritic and low land soils of Elavampadm with different levels of borax and organic matter. This experiment opened up the role of organic matter in deciding the boron supplying power of different soils. Though different in magnitude it was observed that either organic matter or borax independently could increase available boron substantially after one month of incubation and maintained almost a constant level during the further course of incubation up to three months. However, higher levels of organic matter reduced the available boron after one month incubation indicating the adsorption of applied boron by OM and maintained almost a constant level. Substantially higher amount of B than initial level could be maintained throughout the period of incubation while the combined application of borax and organic matter explaining the existence of adsorption desorption equilibrium between OM and soluble boron. These results focus the importance of added OM in governing the boron supplying power of low organic matter, low pH soil as that of *Onattukara* sandy and lateritic soils.

In the field experiment conducted to optimise the level of boron for rice nutrition, treatments with different levels of borax produced significant difference in productivity of tillers, no of grains per panicle, thousand grains weight and ultimately grain yield and so also in the uptake of boron. The maximum grain yield of 8.07 Mg ha^{-1} was produced in the treatment with 6 borax ha^{-1} which is almost a one tone increase over control. Soil analysis at panicle initiation stage showed that difference in levels of borax application significantly influenced the status of available P and sulphur in soil. The available boron in soil significantly increased with the levels of borax application. Among the different fractions of boron in soils at PI and harvest, both RS-B and SA-B increased from control and were highest in treatment which produced maximum grain yield and reduced at higher levels of borax. Oxide bound-B and organically bound-B and residual boron significantly increased linearly with these levels of borax application. Borax being a soluble material first contributes to RS-B which later might have gone to SA-B as equilibrium exists between these fractions. Increase in borax beyond 6 kg resulted in shifting equilibrium from RS-B and SA-B towards OX-B and OR-B fractions.

Specifically adsorbed boron had high direct effect on RS-B. The direct effect of RS-B and OR-B on the content of boron in shoot was high at PI, also indirect effect of SA-B through RS-B was also high indicating that plant absorption at PI was mainly from RS-B & SA- B. Path coefficients clearly indicate the high direct effect of OR-B (1.0569) on the available B at harvest stage while SA-B produced high direct influence on RS-B. The indirect effect of OX-B, OR-B and RES-B through SA-B on RS-B was high. Straw and grain analysis showed that maximum content of B is in straw (17.33 mg kg^{-1}) as well as was in grain (5.7 mg kg^{-1}). This was recorded in treatment with 6 kg borax ha^{-1} and it was significantly superior to all the treatments. Boron content in grain was significantly and positively correlated with all the fractions of B in soil. Path analysis clearly indicated that RS-B, SA-B had high direct effect than the content of boron in grain while all other fractions produced high indirect effect through RS-B and SA-B on the content of B in grains.

The soil characterisation experiment revealed the clear picture on nutrient status of soils of different AEUs of the state, the light of which could be thrown into management of nutrient elements in the soils of the state. The most critical nutrient elements in the soils are calcium and magnesium. The acute deficiency of these two elements, if not managed immediately by suitable resources would lead to drastic reduction in crop production in soils of the state. Boron deficiency is reported in 18 per cent of soils and would also be expected in another 50 per cent of soils as the status of boron in these soils is close to critical limit (0.5 mg kg^{-1}). The fractionation of soil boron revealed the different forms of boron, and their close association with different organic and inorganic constituents in soil. The dynamic equilibrium existing among different fractions of boron governed by soil pH gave an insight to the information on solubilisation and release of boron associated with organic matter, sesquioxide, oxide and hydrous oxide dominated amorphous clay minerals in tropical soils of the state.

The results of adsorption study with six unique soil types of the state throw light into the fate of applied boron at different soil temperatures. The buffer power increased with temperature in lateritic and Chittoor black soils indicate the greater capacity of these soils to replenish the depletion of boron in soil solution and in all the soils when the solution boron fell below a minimum level, desorption was observed. In the summer season, applied boron will be subjected to adsorption in sandy, *Kole* and lateritic soils temporarily limiting the plant availability. Cultural practices to reduce soil temperature should be adopted in these soils prior to the application of boron fertilizers. The results of incubation experiment point fingers to the fact that either borax or organic matter alone could improve the available boron status of soils substantially and care should be taken while the combined application of heavy doses of organic matter and borax as it may restrict the release of applied boron due to retention by organic matter. Though it is not available for a short period it will be preserved as organically bound boron preventing it from leaching losses which would be later released for plant absorption.

Though the application of boron fertilizers was not found to influence tillering in rice, it improved the grain production indicating the major requirement of boron in the reproductive stage. The path analysis of different fractions of soil boron to the content of boron in plant samples revealed that plant absorb boron from readily soluble fraction initially and at later stages it absorb from specifically adsorbed and organically bound B which emphasizes the need for organic matter addition in crop culture.

Summary

Summary

Representative soil samples from 23 agro ecological units under five agro ecological zones in Kerala have been collected and characterized for the study on "Chemistry and transformation of boron in soils of Kerala". Samples were characterized with respect to pH, EC, OC, available nutrients (P, K, Ca, Mg, S, Fe, Cu, Mn and Zn,), exchangeable cations, CEC, PBS and hot water extractable boron. Thirty one soil samples representing all the AEUs including one from the site of field experiment were selected from the 65 samples characterized based on their electrochemical properties and hot water extractable boron and subjected to fractionation experiment to quantify the boron that is associated with different inorganic and organic constituents in soil. The different fractions studied are RS-B, SA-B, OX-B, OR-B and residual boron

In the adsorption experiment, six soils *ie.* lateritic soil from Pattambi, wet land soil from Elavampadam, sandy soil from *Onattukara*, black cotton soil from Chittoor, *Kole* land soils from Thrissur and *Kayal* land soil from *Kuttanad* representing major soil types of the AEUs were selected for the study on the pattern and thermodynamics of boron adsorption at two temperatures as 25 and 40°C. The data obtained from these experiments were fitted to different adsorption isotherms *ie*. Langmuir and Freundlich isotherms. The thermodynamic parameters *ie.* free energy of adsorption (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS) have also been calculated.

An incubation experiment in the laboratory was conducted to study the effect of added organic matter in adsorption of boron and in turn the availability of boron. Three soil types lateritic upland soil from Pattambi, sandy soil from *Onattukara* and wet land soil from Elavampadam were selected for the study. Different doses of borax and organic matter were added to the soil and hot water extractable boron was analysed after 1, 2 and 3 months of incubation.

A field experiment was conducted to optimise the level of boron fertilizer for rice nutrition in the lateritic low land soils of Elavampadam. Boron was applied as different levels of borax *viz.* 0, 2, 4, 6, 8, 10 and 12 kg ha^{-1}. Borax was applied as two equal split doses as basal and the other at panicle initiation. Soil and plant samples were drawn at two stages as PI and harvest. The soil samples collected were analysed for pH, EC, OC available nutrients (P, K, Ca, Mg, S, Fe, Cu, Mn and Zn), exchangeable cations, CEC, PBS and hot water extractable boron and were also subjected to fractionation of soil boron. Shoot and root samples were analysed for B at panicle initiation stage. The total boron content in grain, straw and root were analysed at harvest. The salient results of the study are summarised and listed below.

- Eighty nine per cent of the samples under study were really confronted with the problems of soil acidity with pH less than 5.5.
- Seventeen per cent of the soils were poor in organic carbon status with content less than 0.76 per cent
- Soils from sandy plains and high rainfall areas were poor in organic carbon status.
- More than 40 per cent of the samples recorded high phosphorus status
- Sixty per cent soil samples were low to medium in potassium fertility
- Cent per cent of the samples were deficient in Mg and 82 per cent were deficient in Ca.
- Sulphur, Zn and Cu deficiency were comparatively less.
- Eighteen per cent of the soils from AEUs were deficient in available boron with content less than 0.5mg kg^{-1}.
- Soils of *Pokkali* and *Kaipad* recorded very high levels of boron due to direct entry of sea water
- More than 50 per cent of the soils of AEUs were sandy loam in texture
- Available boron was significantly and negatively correlated with soil acidity and positively with EC
- In the fractionation experiment, the total soil B is separated into different fractions as RS-B, SA-B, OX-B, OR-B and residual B and their relative dominance in soil is as follows.

  RES- B > OR -B > OX- B > SA-B > RS-B

- The most dominant fraction is residual B which constitute more than 90 per cent of soil boron
- OR-B was found to have high significant correlation with OC, while OX-B is highly significantly correlated with sesquioxide.
- Content of sesquioxide is the single most factor explaining 99 per cent variability in OX-B
- Regression analysis indicated that 51.4 per cent of variability in RES-B could be explained by sesquioxide
- The significant correlations among the fractions explain the existence of dynamic equilibrium between different fractions of B.
- Quantity – Intensity curves were fitted for all the six soils at 25^0C explaining more than 50 per cent variability
- Data of adsorption in *Onattukara* soil at 40^0C could not be fitted in Q/I plots
- The buffer power increased with temperature in lateritic and Chittoor black soils.
- Only two soils *viz* – *Onattukara* sandy soil and *Kayal* soil from *Kuttanad* followed Langmuir adsorption isotherms at 25^0C
- The adsorption maxima was high in *Kayal* land soil as compared to *Onattukara* sandy soils.
- All the six soils including the above two failed to follow Langmuir adsorption equation at 40^0C
- Data from all the soils except *Onattukara* sandy soils could be fitted into Freundlich adsorption isotherm.
- All the soils exhibited a negative intercept for Q/I curve at 40^0C due to desorption below equilibrium concentration, free energy of adsorption(ΔG^0) and entropy (ΔS^0) decreased with temperature in Pattambi, Elavampadam, *Onattukara* and *Kole* soil.

- The adsorption was found to increase with the temperature in Pattambi, Elavampadam, *Onattukara* and *Kole* while it decreased with temperature in other two soils.
- In the incubation experiment, the availability of boron increased substantially with the application of borax or organic matter after one month of incubation.
- At higher levels of organic matter, availability of applied boron reduced at two and three months after incubation.
- The combined application of organic matter and borax reduced the availability of applied boron due to adsorption by the added organic matter and it was much pronounced at higher levels of organic matter and borax.
- The treatments with different levels of borax could produce significant effect on number of productive tillers, number of grains per panicle, thousand grain weight, finally grain yield and boron uptake in rice.
- The maximum grain yield of 8.07 Mg ha^{-1} was recorded in the treatment with 6 kg borax ha^{-1}. However it was on par with the treatment 4 kg borax ha^{-1}.
- Among the different fractions of B estimated at PI and harvest, RS-B, SA-B increased linearly from control up to T_4 (6 kg borax ha^{-1}) and reduced with further increase in levels of borax, while OX-B and RES-B increased with increased doses of borax.
- The available boron increased linearly with the applied levels of borax both at PI and harvest.
- The content of boron in shoot at PI and harvest increased to a maximum value at T_4 and thereafter reduced.
- Maximum content of B in grain was recorded in the treatment with 6 kg borax ha^{-1}.
- The content of boron in shoot is highly correlated with RS-B, SA-B and OR-B fraction in soil indicating plant absorption from these fractions.

- Specifically bound boron had high direct influence on RS-B. OX-B and RES-B had high indirect effect on RS-B through SA-B.
- RS-B and OR-B had high direct effect on the content of boron in shoot at PI indicating absorption of these fractions by plants.
- At the harvest stage, specifically adsorbed boron had very high direct effect on readily soluble boron
- Oxide bound boron, organically bound boron and residual B produced high indirect effect through SA-B on the readily soluble boron but their direct effects were negative.

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CHEMISTRY AND TRANSFORMATION OF BORON IN SOILS OF KERALA

By

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ABSTRACT OF THE THESIS

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Abstract

Sixty five representative soil samples from 23 agro ecological units under five agro ecological zones of the state were collected and characterised with respect to the available boron status for the present study on “Chemistry and transformation of boron in soils of Kerala”. The samples were characterised for pH, EC, CEC, PBS, exchangeable cations, total sesquioxide and available nutrient status (organic carbon, P, K, Ca, Mg, S, Fe, Mn, Zn and Cu) along with available boron.. Among these soils 18 per cent of samples which included samples from southern and northern coastal sandy plains were deficient in boron (< 0.5 mg kg^{-1}) while the acid saline soils of *Pokkali* and *Kaipad* have recorded highest levels of available boron (> 3.0 mg kg^{-1}). The availability of boron was found to increase with soil acidity and electrical conductivity. Thirty one soil samples selected from 65 characterised samples representing all the AEUs and ensuring variability in physico-chemical properties and available boron were subjected to fractionation of soil boron.

The different fractions, readily soluble, specifically adsorbed, organically bound, oxide bound and residual boron accounted a mean status of 0.59, 0.86, 1.79, 2.31 and 94.45 per cent of total boron respectively in soils of different AEUs in Kerala. All the fractions except residual boron were significantly and negatively correlated with soil pH, and positively correlated with electrical conductivity. The oxide bound and residual boron were highly positively and significantly correlated with the content of sesquioxide and clay and the organically bound boron was significantly correlated with organic carbon content indicating the influence of organic matter, oxides and hydrous oxides dominated amorphous clay minerals of tropical soils in retention and solubility of boron.

Among the six soils included for adsorption studies (lateritic soil from Pattambi, wet land soil from Elavampadam, sandy soil from *Onattukara*, black cotton soil from chittoor, *Kole* land soils from Thrissur and *Kayal* land soil from *Kuttanad*), only two soils *ie. Onattukara* and *Kayal* land soils followed Langmuir adsorption isotherms at 25^0C. The adsorption data for all the soils except *Onattukara* sandy soil could be fitted in to Freundlich adsorption isotherm both at 25 and 40^0C. The amount of boron adsorbed at unit equilibrium concentration (Freundlich K: K_F)

decreased with increase in temperature from 25 to 40^0C. The intercept of Quantity-Intensity curve decreased to negative values at higher temperature indicating desorption of boron from the sites when solution concentration fell below equilibrium concentration. The decrease in free energy with a positive enthalpy and a positive entropy in Pattambi, Elavampadam, *Onattukara* and *Kole* soils revealed that the adsorption of boron were spontaneous and endothermic. The reverse was the case with black soils of Chittoor and *Kole* land soils where adsorption was exothermic and non spontaneous.

The incubation experiment conducted for a period of three months with different levels of organic matter and borax in three soils *ie. Onattukara* sandy, lateritic upland and low land of Elavampadam revealed the clear role of organic matter in adsorption, retention and release of boron. Either organic matter or borax independently could increase available boron substantially after one month of incubation and maintained almost a constant level during the further course of incubation. However higher levels of organic matter reduced the available boron after one month incubation as a result of adsorption by organic matter. At highest level of organic matter and borax (15 t and 12 kg ha^{-1} respectively), adsorption of boron was highest.

The field experiment to optimize the boron nutrition for rice in low land lateritic soils in central Palakkad plains (Elavampadam) revealed the clear role of boron in improving the productivity of tillers, number of grains per panicle, thousand grain weight and ultimately yield. The response curve fitted to find out the optimum dose of boron for grain yield showed that application of borax @ 5.5 kg ha^{-1} would result in yield improvement to the tune of 1 t ha^{-1}. The fractionation of soil boron at panicle initiation and harvest stage indicated that both readily soluble and specifically adsorbed boron in soil increased with the levels of borax up to 6 kg ha^{-1} while the other fractions increased linearly with the levels of borax up to 12 kg ha^{-1}. The correlation studies and path analysis clearly indicated that plant absorption of boron mainly take place from readily soluble, specifically adsorbed and organically bound boron in that order due to the existence of dynamic equilibrium between these fractions.