Adsorption and Desorption Kinetics of Boron in Kashmir Soils

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(2010-322-D)

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Faculty of Postgraduate Studies

Sher-e-Kashmir University of Agricultural Sciences

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Thesis

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in partial fulfilment of requirement for the award of the degree of

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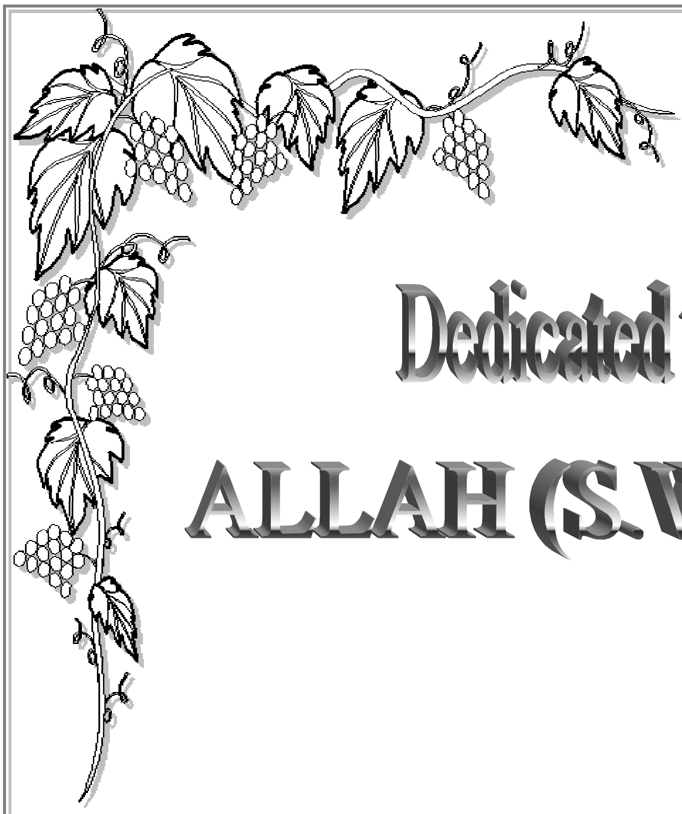

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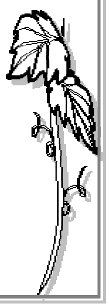
ALLAH (S.W.T)



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Certificate – I

This is to certify that the thesis entitled **“Adsorption and Desorption Kinetics of Boron in Kashmir Soils”** submitted in partial fulfilment of the requirements for the award of the degree of **Doctor of Philosophy in Agriculture (Soil Science)**, to the **Faculty of Postgraduate Studies, Sher-e-Kashmir University of Agricultural Sciences and Technology of Kashmir**is a record of bonafide research work carried out by **Ms. Shaista Nazir (Regd. No. 2010-322-D)** under my supervision and guidance. No part of the thesis has been submitted for any other degree or diploma.

It is further certified that any help or information received during the course of investigation have duly been acknowledged.

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Certificate – II

We, the members of the Advisory committee of **Ms. Shaista Nazir (Regd. No. 2010-322-D)**, a candidate for the degree of **Doctor of Philosophy in Agriculture (Soil Science)**, have gone through the manuscript of the thesis entitled, **“Adsorption and Desorption Kinetics of Boron in Kashmir Soils”** and recommend that it may be submitted by the student in partial fulfilment of the requirements for the award of degree.

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Certificate – III

This is to certify that the thesis, **“Adsorption and Desorption Kinetics of Boron in Kashmir Soils”** submitted by **Ms. Shaista Nazir (Regd. No. 2010-322-D) to the Faculty of Postgraduate Studies, Sher-e-Kashmir University of Agricultural Sciences and Technology of Kashmir**in partial fulfilment of the requirements for the award of the degree of **Doctor of Philosophy in Agriculture (Soil Science)** was examined and approved by her Advisory Committee and external examiner on ………………..

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Title of the Thesis	:	**Adsorption and Desorption Kinetics of Boron in Kashmir Soils**

ABSTRACT

Distribution of different forms of boron, adsorption-desorption Kinetics and its availability to berseem were investigated through laboratory and green house experiments. Bulk soil samples from ten different locations of Kashmir were collected. The mean content of water soluble, hot water soluble, calcium chloride, HCl, leachable, AB-DTPA extractable and total boron was 0.35, 0.46, 0.63, 0.64, 0.93, 1.13, and 45.46, respectively. All the forms of boron were correlated significantly with each other. Total boron was non-significantly correlated with other forms of boron. All the forms of boron were positively and significantly correlated with pH, EC, CEC, clay and silt content, and negatively with organic carbon and sand content. 50 % of the soils were deficient in available boron.

Boron adsorption was positively and significantly correlated with clay content. Langmuir adsorption isotherms showed two sites of adsorption, in most of the soils. Soils of Khag, Bandipora and Sagipora confirmed well to Langmuir equation. Freundlich adsorption equation was applicable to all the soils over the concentration range of 1-100 mg ml^{-1}. Clay content was the prime factor governing boron adsorption. Boron desorption was less than boron adsorption. The per cent desorbed boron was higher at higher levels of pre-sorbed boron. Boron desorption obeyed the Langmuir equation over the entire concentration and desorption maxima (Dm) was higher in fine textured soils. Adsorption reaction was initially fast followed by slow processes and was complete after 48 hours in almost all soils. The parabolic diffusion kinetic model was best in describing the rate of boron adsorption, followed by Elovich and zero order while as first order, second order and power function equation failed in describing the boron adsorption kinetics. Desorption kinetics showed that it was desorbed from two separate sites. The total desorbable boron was higher and faster in initial stage and then slower, latter on. Power function kinetic model described best the boron desorption, followed by Elovich kinetic model.

Dry matter, boron concentration and boron uptake in berseem increased with increased boron application. All extractants used for assessing boron-availability were significantly correlated with each other except AB-DTPA. Boron extracted with water gave highly significant correlation with Bray's per cent yield (0.884**) and boron uptake (0.710**) at 60 days growth and (0.913**)and(0.695**) at 90 days growth, respectively. The critical levels of boron in soils estimated by hot water were 0.48 and 0.49 mg kg^{-1} and by 0.01M $CaCl_2$ were 0.70 and 0.71 mg kg^{-1} soil at 60 and 90 days growth, respectively. The critical levels of boron in berseem plant at first and second cutting were 23 and 19 µg g^{-1}, respectively.

Keywords: Adsorption, Berseem, Boron, Desorption, Kinetics

Signature of Student	Signature of Major Advisor
Dated: ___________	Dated: ________________

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Place: Srinagar ***Shaista Nazir***
Dated:

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INTRODUCTION

Boron (B) is an important micronutrient element in crop production. The B concentration range between plant deficiency and toxicity symptoms is narrow (Reisenauer *et al.,* 1973), and poses difficulty to maintain appropriate boron in soil solution. Boron is unique among the essential mineral elements because it is the only element that is normally present in soil solution as a non-ionized molecule over the pH range suitable for the plant growth. Total boron content in soils is between 7 to 80 μgg^{-1} of soil. It is released by weathering of the minerals in the form of H_3BO_3 and its concentration is usually $< 1x10^{-4}$ M, which equals 0.1 mg/l (Krauskoph, 1973), a very small amount. Concentration of 1-2 mg B/kg of soil is perhaps more representative for surface soils. Compared with other nutrient elements, the chemistry of B in soils is very simple. Boron does not undergo oxidation-reduction reactions or volatilisation reactions in soils. Boric acid is a very weak, monobasic acid that acts as a Lewis acid by accepting a hydroxyl to form the borate anion. Boron containing minerals are either very insoluble (tourmaline) or very soluble (hydrated B minerals) and generally do not control the solubility of B in soil solution (Goldberg, 1993). The B concentration in the soil solution is generally controlled by B adsorption reactions; as is the amount of water soluble B available for plant uptake.

Boron is an essential nutrient element for the plant growth. It is needed for cell division, hence for the growth of young shoots. It is essential in sugar translocation and in the synthesis of hormones and proteins in plants. The normal B concentration in plant tissue is reported to be 20 and 100 $\mu g\ g^{-1}$ dry matter of mature leaves. A boron content of $<15\ \mu g\ g^{-1}$ indicates boron deficiency, whereas a boron concentration $> 200\ \mu gg^{-1}$ indicates boron toxicity. Boron deficiency is usually manifested in formation of white and rolled leaves

(FAO, 2007).Boron uptake by plants is controlled by the boron level in soil solution rather than the total boron content in soil. Boron uptake is a passive (non-metabolic) process. It moves with water in plant's tissues and accumulates in the leaves; therefore, boron uptake and accumulation are directly dependent on the rate of transpiration. Boron mobility in the phloem is now known to be plant-specie dependent.

Boron can occur naturally in the environment due to release into the air, soil and water by the weather. It may also occur in groundwater in very small amounts. Concentrations of boron added by humans are smaller than the concentrations added naturally by natural weathering. Plants absorb boron from the plant floor and the animals consuming it, may end up in food chains. Boron has also been found in animal tissues and human body (approximately 0.7 ppm).

Boron is found in soils in various forms and is distinguished in many categories (Hou *et al.,* 1994; 1996). However, only a few forms are available to plants and their determination is important for estimation of its availability to plants.

Boron is soils can be categorized into 3 groups:

1. Boron as a mineral component.
2. Boron adsorbed to soil particles, such as clay minerals, iron or aluminium oxides and organic matter.
3. Boron in soil solution as boric acid (H_3BO_3) and borate ions (BO_3^-). The boron in soil solution is available to plants (mainly as H_3BO_3).

The ratio between the boron concentration in the soil solution and the boron adsorbed to soil particles is affected by the components of the soil (clay minerals, free oxides and organic matter) and also by other factors such as type and concentration of salts in the soil, pH and temperature. Most of the boron in soil is adsorbed to organic matter, acting as a pool of boron from which the boron can be readily released into the soil solutionand this explains the high available B-contents in surface horizons (Evans & Sparks, 1983).Boron adsorption is highly influenced by pH, increases as the pH increases. The agricultural practice that is most often used to raise soil pH is liming. It is expected that after liming, there will be an increase in soil B-adsorption, especially in soils that contain higher amounts of iron and aluminum oxides. Soil characteristics and fertilizer/manure application influence the boron availability to crops and cropping sequences (Gupta, 1993). The supply of soil boron to plants depends upon relative abundance of different forms and equilibrium conditions, soil management practices and physico-chemical properties of soils. It is, therefore, desirable to study different forms and transformation of Boron and their relationship with soil characteristics.

The critical concentration of available boron for soybean plant grown on acid sedentary soils in Chotanagpur region (Bihar) was found to be 0.46 and 21.5 mg kg^{-1} (Datta *et al.,* 1994) while for cauliflower grown on Maharashtra soils was 0.52 and 21.0 mg kg^{-1}, respectively (Malewar *et al.,* 1999). The critical limit of B in plant refers to a level at or below which plant either develops deficiency symptoms or cause significant reduction in crop yield as compared to optimum.

Berseem (*Trifolium alexandrinum*) is an important fodder legume crop which responds well to B deficiency. A number of extractants have been used for predicting the B availability status of soils. Often a method found useful for one area has proved less satisfactory for other areas, suggesting that the difficulty in assessing boron availability in soils is a consequence of diverse soil physical and chemical characteristics. There is an urgent need to establish the critical level of soil and plant to demarcate boron responsive and non-responsive soils and select a suitable soil test method for assessing boron availability to berseem in soils of Kashmir. Boron content in plants can further help in diagnosing its deficiency and apparent soil testing for boron fertilization.

Understanding the mechanism of adsorption-desorption of boron on/from soil materials is vital to understand as plants respond primarily to the B-activity in soil solution. Boron adsorption-desorption is one of the most important phenomenon in soil that regulates its supply from soils, determining the release and fixation of applied boron and thus deciding on the efficiency of boron fertilization (Arora and Chahal, 2009) for plant growth. The dissolved boron remains in dynamic equilibrium with sorbed forms hence cannot be readily moved through leaching. Boron can be physically/chemisorbed as an unionized hydrated borate or chemisorbed by hydroxides of Al, Fe and Mg and its adsorption has been reported to follow Langmuir adsorption equation over a limited range (Hatcher and Bower, 1958).The studies ascertaining the pattern of B-release, kinetics of its desorption may be helpful in evolving empirical relationship predicting boron availability to plants. The kinetics of boron reactions in soils and on soil constituents has not been extensively investigated. Very little is known about boron reaction rates and mechanisms. There are number of studies on the kinetics of K and P reactions in soils (Sparks, 1985), but information on the adsorption-desorption kinetics of boron in Indian soils is very limited, especially in Kashmir Soils, no information on adsorption-desorption kinetics of Boron is available.

Considering these aspects, the investigation was conducted with the following objectives:

a) Distribution of different forms of Boron in soil, and their relationship with different soil characteristics.
b) Kinetics of Boron adsorption-desorption studies in soils of Kashmir.
c) Establishment of Critical limit of available Boron for berseem (*Trifolium alexandrinum*)

Chapter – 2

REVIEW OF LITERATURE

Boron is a vital micronutrient for plants, and they vary in their boron requirement, but the range between deficient and toxic B concentration is smaller than for any other nutrient element. Plants retort directly to the activity of boron in soil solution and only indirectly to boron adsorbed on soil constituents. Both deficient and toxic levels of B in the soil solution can occur during a single growing season. Some of the prose relevant to the present study is reviewed under the following heads:

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2.1 Physico-chemical properties of boron in Nature

In 1824, Sir Jons Jakob Berzelius identified boron as an element and the first American chemist W. Weintruab in 1909 produced pure boron (Angew, 1970; Dunitz, 1971). Two foremost boron substances, branded as boric acid (H_3BO_3) and borax (sodium pentaborate decahydrate) were accessible to the researchers and farmers in the 1930's and all the previous information on B utilization relates to them (Shorrocks, 1991; 1995; 1997; Borax, 2002). In nature, boron symbolized as (B) never exists in the elemental nature in environment. It survives as amalgamation of the B^{10} (19.78%) and B^{11} (80.22%) isotopes

(Budavari*et al.*,1989). The primary source of both boron and borates is the mining of boron-containing minerals such as colemanite, ulexite, tincal, and kernite. Only certain deposits can be mined economically. These are located in arid regions of Turkey and the USA, and also in Argentina, Chile, Russia, China, and Peru. Boronchemistryisexceptionallycomplexandissimilartosilicon(Evansand Sparks,1983;CottonandWilkinson,1988;LoomisandDurst,1992).At roomtemperature(25^{0}C),elementalboronpersistsasasolid form.Thecrystallineandamorphousstructuresofboronhavespecificgravitiesof2.34a nd2.37,respectively.Itisa moderatelyinert metalloidinabsenceofstrongoxidizingassociates. Hydrolytically unstablesodiumperboratesofB–O–ObondsreactwithH$_2$OtoformulateH$_2$O$_2$and sodiummetaborate ($NaBO_2 \cdot nH2O$). Veryweakacidofboricacid (H_3BO_3;pKa of9.15) andsodium borateswhichoriginategenerallyasundissociatedboricacid[$B(OH)_3$]insolutionwhen pHislessthan7whereasmetaborateanionB(OH)$_4$speciesproducedinsolutionatpH> 10.The toxicologicalandchemicalpropertiesof borax($Na_2B_4O_7.10H_2O$),boricacid(H_3BO_3),boraxpentahydrate($Na_2B_4O_7.5H_2O$)a ndotherboratesarelikelytobeidenticalonamolarBequivalentbasiswhendissolvedin water(Budavari*et al.*, 1989;USGS,2004;Wikipedia, 2007).

Boron was first used as a fertilizer about 400 years ago when borax (then called Tincal or Tincar) was shipped from Central Asia to Europe. Not until 1915, however, was boron suggested as an essential element for plant growth, when P. Maze of France made this suggestion as a result of his work with corn grown in nutrient solutions. Katherine Warington, at the Rothamsted Experimental Station in England, provided the first proof in 1923 that boron was an essential element.

2.2 Reactions and Chemistry of boron in soils

A great amount of comparatively recent work has established the importance of the dual role of boron as an essential and a toxic element in plant nutrition.

Goldberg(1997)revealedacomprehensivestudyregardingboronreactionsinsoils.Accordingto her,boronisavitalplantmicroelement.Conversely,thechemistryofothermacroandmicroelements,thereisanexceptionaboutboron,forthereasonthatthedeficientandtoxicboronconcentrationrangesaremuch narrowed.Alargeamountofboroninsoilsolutiondirectlyinfluencesplantsgrowthand merelyindirectlyto boron adsorbed ondifferentsoilcomponents.Alotofsoilfactorsincludingtexture,moisture,pH, temperature,claymineralogy and organic matter exaggerated plant B availability (Albion, 2003).Diverse boron adsorbingsurfacesinsoils comprisedclayminerals,organic matter,FeandAl-oxides,calcium carbonateand magnesiumhydroxide. Shealsoconductedexperimentsonchemicalmodelssuchasthe Triplelayermodel,ConstantCapacitancemodelandtheStern VSC-VSPmodelanddescribedboron adsorptionundervaryingpHandboronconcentrations.

Differentboronadsorptionreactionswerealsoreportedbyusingthe Freundlich,Langmuir adsorptionisothermequationandthephenomenologicalKerenmodel. Borondesorptionratewasillustratedbytheuseof Elovichreaction,powerfunctionandfirstorderrateequations.Shealsoprovedthatborondesorptionreactionsfrequentlyshowedindicationofhysteresis.Likewise,otherstudiesalsoshowedvariouschemical reactionsofboroninsoil(Harder,1961;1970;EvansandSparks,1983;Keren,1984;Hingston,1986). Krauskopf (1972) reported that micronutrients especially boron has diverse kind of reactionsinsoilsandthebiologyandchemistryof boroninsoilis entirelydifferentthanothermicronutrients (LoomisandDurst,1992).

Boron had an imperative relationship with soil salinity and higher saltsconcentrations alongwithboronsignificantlyloweredtheplantgrowth.Yermiyahu*et al.*(2008)revealedthatbothboronandsalinityintandemaffectedplantgrowtheitherthrough soilorirrigationwater. Theytested bell pepper (*Capsicum annuum*L.) at dissimilarsalinityandboronlevelsingreenhouse.Theresults showedthatminimizedboron uptakewasobtainedinthepresenceof chloride(Cl^-)andviceversa. Chaudhary (2005) studied the boron equilibrium in soil.Adsorption and desorption reactions are likely to be major factors in regulating boron concentration in solution and ultimately availability to plants. Besides the concentration of boron in soil solution, boron adsorption and desorption is also influenced by soil characteristics. Boron adsorption reactions on soils are described by various adsorption equations.

2.3 Worldwide Status of Boron in soils

Clarke and Washington (1924) reported the relative abundance of boron in igneous rocks as 0.001 percent, and Wells (1937)has estimated 0.01 percent (100 ppm) in the 10- mile crust of the earth. Schalscha *et al.*(1973)has listed 56 known boron minerals. Natural deposits of borates occur in arid regions and boric acid is present in fumaroles in Tuscany. Tourmaline, a resistant borosilicate containing about 3 percent of boron, is widely distributed in rocks and soils. Boron is common as an impurity in many minerals and rocks,as Goldschmidt and Peters (1932) have demonstrated by spectroscopic analyses. They reported from 30 to 300 ppm in shales, iron ores, and corals—all rocks of marine origin. A variety of igneous rocks contained only about 3 ppm. The boron content of chalk, limestone, and dolomite was also low.

Warington(1923)provedwithacknowledgedresultsfortheveryfirsttimethatboronwasanessentialplantnutrientin1923;hesuggestedthatfortheregenerationofthese plants,boronwas indispensableelement(Anonymous 1935; 1936). The resultsofMaze(1915)revealedthatBoron(likewiseAluminium,fluorineandiodine) wasneededfortheutmostgrowthofmaizeinsolutionculture. Then again, hedidnotcertifytheiressentialitybutfew ancientstudiesshowedits essentialrolesincropnutrition(ArnonandStout,1939).After thatera,fewotherstudies showeditsimportanceinmanycrops (Dregne and Powers,1942).

IndifferentRussianstates(likeLatvia,Belarus,EstoniaandRussia),mostofthesoilshadlowestboronlevels.Pieve(1959)quotedwatersoluble boronvalues(mgkg^{-1})of(0.08–0.38)inPodzoluvisols,(0.30–0.90)inKastanozemsand(0.38–1.58)inChernozems.While, Gembarzewski(1987),demonstratedthat>50%ofthecentral andeasternPolandsoils in 11 counties were acknowledged as extremelysmall in boron (characteristicallyPodzols).InLatvia,almost40%ofsoilswereborondeficientandthesesoilsweretypicallyPodzoluvisols(AnspoksandLiepins,1987).Likewise,fewresearchersreportedthatthe majorityofsouthernFinlandispronetohold<0.50mgBL^{-1}hotwatersolubleboron (HWSB),moreoverhealsoinvestigatedthatsoilboroncontentsweremoreinsoilswith elevatedpHandenhanced base exchangecapacity(Kiviniemi, 1946;Kurki,1982; Wikner, 1983;Veijalainen, 1983). Sobrinho and Freire (1980) recognized that several boron responsivesoils in theSaoPaulodistrictofBrazilarerecognizedaslatosols(Ferralsols),podzolicsoil,LuvisolsandAcrisolswhilewatersolubleBoronlevelsarenormally <0.50mgkg^{-1}.InUSA,althoughborondeficithasbeenreportedinabove40statesbutinAtlanticand GulfofMexico,GreatLakesvicinityandthePacificNorthwesternprovinces,borondeficitismoreprominentowingtothefrequencyofAcrisols,Podzolsand Andosols (Berger,1962;Bingham*et al.*,1971; Anon, 1936).

Sillanpaa(1982)performedanesteemedintercontinentalestimationregardingmicronutrient levels on the basis of soil chemical analysis in nearly 30 countries. Afterward,healsoworkedonboronstatusinwheat-sownareasofFinlandandtropical andMediterraneanregionsoftheworld (Veijalainen,1983; SillanpaaandVlek,1985;).Eight yearsafterthatresearch,Sillanpaa(1990), conductedfieldinvestigationin14 participatingnationsincludingPakistantoendorsethedemandformicronutrientsonthe maincerealcropslikewheat(*TriticumaestivumL.*),rice(*Oryzasativa*)andmaize(*Zea maysL.*).He reportedthatoutof14countries,thesoilsandcropsofelevencountries showed goodresponses toboronapplication. An underlyingand severe borondeficitwasacknowledgedin21and10%research investigations,respectively(Sillanpaa,1990).

Sillanpaa(1982)furtherrevealedthatborontoxicityanddeficitintenselybegun inPakistan,Mexico,IraqandTurkey.Thiswasparticularlyoccurredatirrigatedplaces.According to this study, low boron soils comprised of calcareous material (Rendzinas), thoroughly weathered soils (Podzols, Ferralsols, Acrisols), coarse textured soils(Arenosols),volcanicashsoils(Andosols)andshallowsoils(Lithosols).Categorically, coarsetexturedsoilsandsturdilyweatheredsoilsequesterorseizethe negligiblequantityofplant availableboronfraction.

Cultivatedsoils ineastandsouthChinaassemblethedistinctforemostboronscarcearea oftheplanet(Zheng*et al.*,1980;1982a; 1982b;1989).Especiallysouth ofYangtzeandseveralsoilsinnortheasternChinaareidentifiedduetotheproofofboronresponsesandsoilanalysis.ThesoilmapsofChinademonstratevastareasofsoilskeepingreally lowhotwatersolubleBlevels(<0.25mgkg^{-1}).InnorthoftheYangtze,soilsdeveloped fromcalcareousandloessalluviumoriginatedfromYellowriver,thereforeborondeficiency iscommonlyintrinsic(Chang*et al.*,1983;Chang,1993).Conversely,thearidregionssoilsofwesternChinaareboron loadedandtypicallycategorizedas*LithicYermosols*and*LithicKastanozems*(Zheng*et al.*,1983).WhereasinIndia,investigationsonsoilBoronstatusandcropresponsestoboronapplicationillustratedthatoutstanding boron deficit observed in various states.

In Egypt and Syria, widespread boron deficiencies were reported by many researchers (Elseewi, 1974; Elseewi and Elmalky, 1979) and it varied spatially (Ryan *et al.*, 1998). Moreover, they measured concentrations of boron in waters and soils of Egypt. Some studies showed that fly ash had significant consequences on physico-chemical properties of soils as well as yield, and concentration in plants (Gutenmann *et al.*, 1979; Elseewi *et al.*, 1980a; 1980b).

Boron deficiency occurred in soils of New Zealand and especially this was noted in the forest of pine (Will, 1971). Sakal and Singh (1995) identified Bihar, Orissa, Meghalaya, Karnataka, West Bengal, Assam and Gujarat as predominantly boron deficient areas in India. They further reported that in Maharashtra most of soils rarely pointed out boron deficiency as these soils were created from the basalts of the *Deccan Trap*. Likewise, other Indian researchers also reported boron deficiency in soils of India and responses of different crops to boron application (Singh *et al.*, 1976; Prasad, 1978; Sarkar, 2006; Sarkar *et al.*, 2006).

The prevalence of boron deficiency on cotton *(Gossypium hirsutum)* has been acknowledged for many years in African countries like Cameroon, Benin, Chad, Ivory Coast and Nigeria (Smithson, 1972; Heathecote and Smithson, 1974; Smithson and Heathcote, 1976; Lombin, 1985). Whereas the information about soil boron in Nigeria is entirely missing. Odunze *et al.* (1992) established 0.32–0.49 mg B kg^{-1} in Luvisols in savannah whilst Lombin (1985) accounted lowest boron levels in Nigeria. In case of Europe, Northern European and Scandinavia (Sweden, Denmark, Norway) some Cambisols, Podzols and Luvisols restrain greatly of the boron responsive areas especially in Sweden, Finland, Germany, Poland and Denmark (Moller, 1983; Wikner, 1983). The reported data from European part of the USSR stated that soil boron deficiency also occurred in these areas (Zyrin and Zborishchuk, 1975).

In Finland and Sweden, the soil parent materials are almost exclusively metamorphic and acid igneousrocks (Kiviniemi,1946;Moller,1983;Wikner,1983;Veijalainen,1983).InCanada, borondeficiencymostprevalentespeciallyintheprovinceofBritish Columbia ondifferent soils includesLuvisols,Podzols, Kastanozems andOkanaganvalley(Gupta,1983, 1984b).Similarly,boronadsorption caused by ashedsoilsfromvolcanicactivityinSouthernChilewasalsoreportedbysomescientists(Schalscha*et al.*,1973).

2.4 Sources of Boron

Boron enters the environment mainly through natural processes and, to a lesser extent, from human activities.

Natural processes lead to boron releases:

- from boron-containing rocks through weathering;
- from seawater, as boric acid vapor; and
- from volcanic activity and other geothermal releases such as geothermal steam.

Human activities mainly release boron through:

- agricultural use, mainly from the use of borate-containing fertilizers and herbicides;
- burning of domestic waste, crop residues and wood fuel, as boron is present in many plants being necessary for their growth;
- power generation using fossil fuels such as coal and oil;
- Waste from borate mining and processing, including the manufacture of glass products. The use of glass products does not release boron, however, as the boron is tightly bound within the glass itself;
- the use of borates and perborates in the home and industry;
- leaching from treated wood or paper; and
- disposal of sewage and sewage sludge. IPCS (1998)

It is however difficult to determine the exact amount of boron which enters the air, soil, or water from many of these sources. Manyboronsourcesareeasilyavailableinthemarketsandthesecanbe usedasboronfertilizer.Thesearewell-refinedandabsolutelysolublecompoundsofboron. Theseincludeboricacid{H_3BO_3, 17%B},Na-tetraborate(21.4%B),solubor(20.8%B),boraxorsodiumtetraboratedecahydrate(11.3%B),B-frits(8-10%B),colemanite (6-8% B,variable),ulexite,hydroboracite,aschariteanddatolite ores alsocontainedboronbutinvariableamounts(Shorrocks,1997).Manyresearchersusedvariousboron sourcesforboron fertilizationdependinguponthesolubilityofthematerial(Sherrell,1983).H3BO3 and boraxareeasilydissolvedinsoilsandarequicklyavailableforplantuptake,butatthesametime there is aproblemofleachingifboronisnot adsorbedoruptaken.

2.5 Forms of soil Boron

Compared with other nutrient elements, the chemistry of boron in soils is very simple. Boron does not undergo oxidation-reduction reactions or volatilisation reactions in soils. 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, 1993). The Boron concentration in soil solution is generally controlled by boron adsorption reactions, as is amount of water soluble boron available for plant uptake. Plants respond only to the boron activity in soil solution; boron adsorbed by the soil surfaces is not perceived as toxic by plants.

Malave Acuna (2005) studied the different soils as potential boron sources for plants. It was shown that the boron concentration of soil solution is generally controlled by reactions with boron adsorbing surfaces involving aluminum and iron oxides, magnesium hydroxide, clay minerals, calcium carbonate and organic matter. Cummunar and Keren (2005) studied the equilibrium and non-equilibrium transport of boron in soils, and concluded that boron transport in soils was strongly controlled by the pH-dependent and rate limited adsorption. Chaudary *et al.*(2005) reviewed the boron equilibrium in soils. The studies suggested that the adsorption and desorption reactions are likely to be major factors in regulation of boron concentration in solution and ultimately for availability to plants. Besides the concentration of boron in soil solution, boron adsorption and desorption is also influenced by soil characteristics.

Concentration of boron in the soil solution has been reported to be influenced by soil pH (Wojcik and Wojcik, 2003), sesquioxide, clay content , organic matter and ionic strength of the supporting electrolytes.In soil solution, boron mainly exists as undissociated acid H_3BO_3. Boric acid (also written as $B(OH)_3$) and H_2BO_3 are the most common geologic forms of boron, with boric acid being the predominant form in soils as reviewed by Evans and Sparks(1983). They further reported that boric acid is the major form of boron in soils with H_2BO_3 being predominant only above pH 9.2. In their review, they stated that boron occurs in aqueous solution as boric acid $B(OH)_3$, which is a weak monobasic acid that acts as an electron acceptor or as a Lewis acid.

Boron fractionation was studied in relation to its availability to corn in 14 soils (Jin *et al.*, 1987). Up to 0.34% of the total boron was in a water-soluble form, 0 to 0.23% was nonspecifically adsorbed (exchangeable), and 0.05 to 0.30% was specifically adsorbed. Jin *et al.* (1987) reported that most of the boron available to corn was in these three forms and that boron in non-crystalline and crystalline aluminum and iron oxyhydroxides and in silicates was relatively unavailable for plant uptake. For the identification of different pools of boron in soils, Hou *et al.* (1994) proposed a fractionation scheme, which indicated that readily soluble and specifically adsorbed boron accounted for2% of the total boron. Various oxides-hydroxides, and organically bound forms constituted 2.3 and 8.6%, respectively. Most soil boron existed in residual or occluded form. Studies by Zerrari *et al.* (1999) showed that the residual boron constituted the most important fraction at 78.75%.

2.5.1 Water soluble Boron

Available boron, measured by various extraction methods, in agricultural soils varies from 0.5 to 5 mg kg^{-1}. Most of the available boron in soil is believed to be derived from sediments and plant material. Gupta (1968) reported that available boron on Podzol soils from eastern Canada ranged from 0.38 to 4.67 mg kg^{-1}. Few studies have been conducted that attempt to identify solid-phase controls on boron solubility in soils. Most of the common boron minerals are too much soluble for such purposes (Lindsay *et al.*, 1991).

Kang *et al.* (2002) evaluated the boron behaviour in some specific soils of Japan. The investigators found that about 70 % of the added boron was found water soluble and exchangeable forms indicating that the added boron (boron fertilizer) easily leaches from soil, and may impact the water systems.

2.5.2 Hot water soluble Boron

Hot water soluble boron (HWSB) content was less in ignored soil than finely supervised soils(Rahmatullah *et al.*,1999). They also revealed that soil OM and HWSB were significantly correlated (at $P < 0.01$) with total B. The maximum HWSB amounts were witnessed in *Caribou* silt loam, *Acadia* silty clay loam and silt loam to *Interval* loam soil series while it was relatively minimum in *Permo-carboniferous* rocks derived soils (Gupta, 1969; Ho and Houng, 1991). Similarly, he developed an important correlation between hot water extractable boron and total soil boron together with fixation of supplemental boron. He reported that hot-water soluble and total boron content of soils respectively fluctuated from 0.38-4.67 and 45-124 mg kg^{-1}. Usually the boron content was uppermost in heavy textured and slightest in light textured sandy soils. Hot water soluble fraction changed from 0.44 to 4.69 % of total soil boron, with the negligible proportion in the coarser soils and greatest in the finer soils. Likewise, some other researchers also reported HWSB content in Taiwanese soils (Yang, 1960a ; Ho and Houng 1991; Lee, 1995).

Hot water and pressurized hot water extractions on 40 untreated arid soils and observed less predictable linear relationships (R^2 = 0.68). In general, hot water extracted the least boron and pressurized hot water the most regardless of soil type, rate of boron application or duration of incubation.Kang *et al.* (2002) evaluated the boron behaviour in some specific soils of Japan. Concentration of hot water soluble boron was extremely low in some soils, around 0.2 mg/kg. A positive correlation was found between concentration of hot water soluble boron and organic matter, suggesting that this fraction has some organic boron.

Shiffler*et al.* (2005) studied the variations in extractable boron using three extraction methods on boron treated incubated soils. The amount of boron extracted increased as the rate of boron application increased with different soil extraction methods. Regression coefficients associated with regression of extractable boron and rate of boron application were high with all three procedures. R^2 values ranged from 0.955 to 0.998 for hot water extraction, from 0.988 to 0.997 for pressurized hot water and from 0.991 to 0.998 for DTPA-Sorbitol.

Levels of hot-water soluble boron (HWS-B) in different soils in northern and north eastern Thailand show a close correlation with the incidence of hollow heart in peanut. The disorder was higher in soils with low levels of clay and organic matter. Hollow heart symptoms were found in peanut on soils with HWS-B values below 0.14 mg B/kg. A reduction in seed yield of 40-50% as the result of boron deficiency was common in soils with HWS-B 0.12-0.14 mg B/ kg (Rerkasem *et al.,* 1988). Nazif *et al.* (2006) studied the Status of Micronutrients in Soils of District Bhimber (Azad Jammu & Kashmir). Hot water soluble (HWS) boron ranged from 0.02-0.84mg kg^{-1} and was found low in 80% and medium in 20% of sites.

Sharma and Katyal (2006) studied the water soluble boron in benchmark soils of India and its affiliation with soil properties. The concentration of hot water soluble-boron (HWSB) in the surface horizons of fifty-seven benchmark soils of India was investigated. The content of hot water soluble boron increased linearly with an increase in EC and pH. With a change in soil moisture regimes from aquic through ustic to aridic/torric, the EC, pH and lime content increased, whereas organic matter and clay content decreased. The hot water soluble levels of boron availability increased as the soils became aridic.

2.5.3 Calcium chloride soluble Boron

Hot-$CaCl_2$ extractable boron (HCB) was significantly correlated with clay content (r = 0.69*), specific surface area (r = 0.68*), CEC (r = 0.63*) and total aluminum oxides (r = 0.70*) in all the soils under study. In addition, there was a correlation between HCB and organic carbon (r = 0.75*) in the four Oxisols. The correlation coefficient between the product (carbon x clay) and soluble boron contents was also highly significant (r = 0.78**). Multiple regression analysis showed that total aluminum oxide, as well as exchangeable calcium and aluminum, were correlated with HCB, explaining 85% of the variation. The product (carbon x clay) took into account the effect of textural gradient and showed high positive correlation with hot-$CaCl_2$ 0.01 mol/l extractable boron. Among the other chemical attributes, only total CEC presented a positive correlation with soluble boron (r = 0.63*).

Maze(1915) studied effect of some soil properties on extractable boron content in Argentine pampas soils. Two hundred soil samples were taken in order to characterize their 0.02 *M* $CaCl_2$ extractable boron content and studied the boron behavior with regard to other soil properties and environmental conditions. The amount of extracted boron on all samples had a significant correlation with soil organic carbon (positive), and soil pH (negative). Since solubility in hot $CaCl_2$, 0.02 *M* is considered an availability index; these results support the hypothesis that organic carbon content is the main boron reserve for plants. When a multiple regression was calculated, both variables organic carbon and pH explained 57% of variation in extractable boron. The exchangeable calcium content had a light influence especially in the sub superficial layer. Chaudhary and Shukla (2003) studied the availability of soil boron fractions to mustard (*Brassica juncea*) in arid soils of Rajasthan (India)**.** The relationships of different Boron fractions with hot 0.01 M $CaCl_2$ extractable boron suggest it to be a better extractant for available boron in soils for mustard crop grown on arid soils of Rajasthan (India).

2.5.4 Acid soluble Boron

Acid soluble boron was highly and significantly correlated with calcium carbonate content of soils (Elseewi and Elmalky, 1979).

2.5.5 Leachable Boron

The leachate boron concentration data suggested that slowly soluble boron dominates the leachate after only 12 to 15 minutes of leaching of the different soils under study. One of the soils under study contained very little leachable boron. Furthermore, the isotopic data suggest that the soil fractions that are sources of slowly soluble boron are, in decreasing order of contribution, the carbonate, organic, and free iron portions(Swihart *et al.*,1986).Kang *et al.* (2002) evaluated the boron behaviour in some specific soils of Japan. It was seen that in about 34 days, 1.4 to 17.4 % of the total water soluble boron in the fertilizers leached out, when applied to celery (highly boron demanding crop).

2.5.6 Total Boron

The total boron content of most agricultural soils ranges from 1 to 467 mg kg^{-1}, with an average content of 9 to 85 mg kg^{-1}. Gupta (1968) reported that total boron on Podzol soils from eastern Canada ranged from 45 to 124 mg kg^{-1}. Total boron in major soil orders, Inceptisol and Alfisol, in India ranged from 8 to 18 mg kg^{-1} (Borkakati and Takkar, 1996). Such wide variations among soils in the total boron content are mainly ascribed to the parent rock types and soil types falling under divergent geographical and climatic zones. Boron is generally high in soils derived from marine sediments.

Rahmatullah *et al.* (1999) conducted field and greenhouse experiments to assess the importance of boron distribution in calcareous soils as it influenced its bioavailability and discharge for plant utilization. Total boron content ranged from 31-41 mg kg^{-1} while non-specifically adsorbed boron (extracted by $CaCl_2$), specifically adsorbed boron (extracted by mannitol), boron occluded in Mn hydroxides (extracted by $HCl-NH_2OH$) and boron 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 boron, respectively.Xu *et al.*(2001) studied the soil boron fractions and their relationship to soil properties and found that non-specifically adsorbed Boron (NSA-B) and specifically adsorbed B comprised < 1% of total Boron. In contrast, Boron occluded in Mn oxyhydroxide (MOH-B), in amorphous Fe and Al oxides (AMO-B) and in crystalline Fe and Al oxides (CRO-B) comprised from 0.01 to 7.6% of Total Boron. The content of the NSA-B fraction significantly decreased with increasing mean annual rainfall on the site and increased with increasing soil pH and exchangeable calcium. The MOH-B fraction was positively correlated with soil pH and cation-exchange capacity, and negatively with rainfall and temperature. The AMO-B fraction was significantly related to amorphous Fe_2O_3 and rainfall. The CRO-B fraction was positively correlated with pH and exchangeable Calcium, but not with crystalline Fe_2O_3. These results emphasize that the forms of boron in Chinese soils were distinctly different from those in soils of southeast USA and Greece.

In different soils while studying the Boron isotopic mass balance in boron affected agricultural soils the individualfractions arranged from highest tolowest boron concentration were carbonate,free iron, organic, clay, silt and non-magnetic sand. Because of the large weight proportionof the clay size fractions in the soils, thelargest proportion of the total boron in bothsoils is held in this fraction, which consistsof clay minerals, mica, and quartz(Swihart *et al.*,1986).Kang *et al.* (2002) evaluated the boron behaviour in some specific soils of Japan. The total boron content of the different soils under study was found to be in the range of 20.2 to 77.1 mg/kg, which hold within the range of values that compare with the natural abundance of boron (2 to 100 mg/kg).Chaudhary and Shukla (2003) studied the availability of soil boron fractions to mustard (*Brassica juncea*) in arid soils of Rajasthan (India). The readily soluble, specifically adsorbed, oxide bound and organically bound boron constituted only 2.29 to 8.86 per cent of total boron. The major portion of boron in soils existed as residual or occluded forms, which accounted for 91.14 to 97.71 per cent of total boron, with a mean of 95.16 per cent.

Total average boron content in Indian soils differed from 3.80-630 mg B kg^{-1} and this total boron content had no any significance to plant availability(Katyal *et al.,*1982). They analyzed 36825 soil samples, and reported that 33 % were deficient in available boron. According to them, many crops responded to boron application in different agro ecological provinces of India (Sarkar, 2006).

2.5.7 Relationship among forms of soil Boron

Methods of assessing boron availability to kiwifruit plants growing on high boron soils were studied(Tsadilas *et al.,*1997). Different methods were used for extracting various forms of boron in soils like hot water soluble (Hws-B), 0.05M mannitol in 0.01M calcium chloride ($CaCl_2$ extractable (Man-B), 0.05M hydrochloride acid (HCl) soluble (HC1-B), resin extractable (Resin-B), and saturation extract (Sat-B). The amounts of boron recovered by the first four methods investigated were strongly correlated with each other, the highest correlation was obtained being between Hws-B and HC1-B. Plant boron was highly correlated to the boron recovered by the first four extractants and poorly correlated to the boron determined by the saturation method.

Niaz *et al.* (2011) studied the relative efficiency of different extractants for available boron estimation in alkaline calcareous soils. Significant correlation was found for available boron among all the extractants tested, the strongest correlation ($r = 0.99^{**}$ at $P < 0.01$) was observed between Hot water soluble boron and 0.05 M HCl-extractable B.

2.6 Factors affecting Boron availability in soils

Plantobtainsalltheessentialnutrientsfromsoilmediumthroughtheirroots,consequentlyall the soil properties are directlyassociated with the availability ofinfluentialnutrientsparticularlyboron.Theavailabilityofboronisinfluencedbydynamicsoil propertiesincludingorganicmatter,texture,cultivation,drought,andmicrobialactivity (Mezuman and Keren,1981).Similarly,theresultsofotherresearchersrevealedthatthere wasanappreciablerelationshipamongstSAR,salinityandborononthericeseedlingsandtheirgermination(PaliwalandAnjaneyulu,1967).Boronmovesinalldirectionsinthesoilby mass flowof water.Boronavailabilitydecreasedwith increasingpH andmostof the totalsoilboronis unavailabletoplants(Borax,1998).

Indiversesoils,asmallquantityofboronisgraduallycomplexedwithinorganicmatter(GuandLowe,1990; Yermiyaho*et al.*,1995)adsorbedonclays(Hingston,1964; Bingham1971)andtosomeextentitisprecipitatedwith$CaCO_3$andisquite unavailableforplantgrowth(Shorrocks,1997).Sandysoil(coarsetexture)thatiswell drained ismost likelytobeborondeficient becauseofleaching (Ouellette,1958; Rashid, 1995;1996b).

2.6.1 Effect of pH on Boron availability in soils

One of the most important factors affecting the availability of B in soils is pH. With increasing soil solution pH, boron becomes less available to plants. Soluble boron content in soils was highly and significantly correlated with solution pH (Elrashidi and O’Connor, 1982). Boron uptake by plants at identical water soluble boron content was greater at lower soil solution pH (Wear and Patterson, 1962). Soil pH affects plant growth and nutrient availability, therefore boron at high pH is less available to plant. Some studies showed that pyrophyllitic soils and different ions played a significant role in boron adsorption in relation to pH (Keren and Sparks, 1994a; Communar and Keren, 2006). Moreover, boron adsorption-desorption kinetics and equilibrium in soil solution in association with pyrophyllitic soils, has also been discovered by researchers (Keren *et al.*, 1994b). Similarly Keren *et al.* (1981) revealed that pH had a specific role in adsorption of Boron in sodium montmorilonitic clay soils.

In a most recent study, few researchers revealed that calcite is typically utilized to raise pH of soil however it maximized soil boron fixation (Chen *et al.,* 2009). They further investigated that adsorption of boron straight forwardly amplified with elevation 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 boron removal in de-salination and reverse-osmosis reactions or processes. Some researchers revealed that Boron retention by hydroxy Al and Fe was absolutely pH reliant and greatest retention was occurred at alkaline pH (Sims and Bingham, 1968a). Moreover, aging considerably decreased boron retention by these materials (Evans, 1987). It was accomplished that the hydroxyl ions in these solutions encouraged hydrolysis of the precipitates of hydroxy-Al and -Fe, consequentially boron (as borate ions) released from the precipitates. Boron availability decreased with increasing pH and most of the total soil boron is unavailable to plants (Kubota *et al.,* 1948; Borax, 1998).

Application of lime increases boron fixation by soils because it raises the soil solution pH. In addition to its effect on soil pH, calcium carbonate also acts as an important boron adsorbing surface in calcareous soils (Goldberg and Forster, 1991).Adsorption of boron 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, 2006 studied the effect of soil texture and solution pH on boron transport in soils and found the retardation in boron transport in soils increased with the increase of clay content and solution pH. The impact of the rate-limited adsorption on boron transport was dependent on water flux and was controlled by mass-transfer processes. The boron breakthrough curves (BTCs) for the loamy sand and sandy loam soils (where B transport was ideal) were simulated using the ideal-transport-based (local equilibrium-non equilibrium [LE-NE]) model. This model successfully described boron transport at different water fluxes and pH values when using the adsorption parameters derived from batch equilibrium experiments. The adsorption rate coefficient values obtained from BTCs were smaller than those obtained from the batch kinetic data.

2.6.2 Effect of Organic matter on Boron availability in soils

Organic matter is an important soil constituent affecting the availability of boron. Native soil boron and hot water soluble boron were highly significantly correlated with organic carbon content (Miljkovic *et al.,* 1966). Organic matter is an important soil constituent affecting the availability of boron. This is considered as the leading source of reserve boron because it complexes with boron to remove it from the soil solution when the levels are high after boron fertilization (Borax, 1998). It then re-supplies the soil solution to sustain ample levels when boron is removed by crops or leaching occurred.In diverse soils, a small quantity of boron is gradually complexed within organic matter (Gu and Lowe, 1990; Yermiyaho *et al.,* 1995; 1988) adsorbed on clays (Frederickson and Reynolds, 1959; Hingston, 1964; Bingham 1971) and to some extent it is precipitated with $CaCO_3$ and is quite unavailable for plant growth (Shorrocks, 1997). Soil organic matter adsorbs more boron than mineral soil constituents on a weight basis (Gu and Lowe, 1990). Boron adsorption on an organic and composted organic matter increased with increasing pH (Yermiyahu *et al.,* 1995). Communar and Keren (2008) studied different impacts of dissolved organic matter (DOM) and treated sewage effluents on boron 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 boron were more than that of DOM. Moreover, DOM formed various complexes with free soil solution-boron.

Consequently, soil boron concentration significantly reduced as the total DOM concentration increased. Many researchers conducted experiments on organic matter (OM) in relation to available boron fraction and they concluded that organic matters straightforwardly bestow an imperative responsibility in controlling the soil solution boron concentration and there was a significant role of OM in desorption or adsorption of boron in soils (Marzadori *et al.*, 1991). Furthermore, OM had a significant outcome on dropping boron removal by plants (Yermiyahu, 2001). Yermiyaho *et al.* (1988) conducted an experiment on boron sorption on composted organic matter and their results showed that at pH 8.0, the extent of sorbed boron enhanced by almost 57 %. They also determined the sorption isotherms of boron on organic matter at three pH levels of soil 7.0, 7.9, and 8.9. The sorption improved with high pH and growing boron 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 boron increased by about 57 %. The sorption of boron nutrient enhanced with increasing its concentration in solution and pH. Datta and Bhadoria (1999) found while studying the acid soils of West Bengal that organic carbon, pH and cation exchange capacity (CEC) positively influenced the adsorption of boron while free Fe_2O_3, organic carbon and clay retarded release of boron from these soils.

Likewise, Yermiyahu (2001) studied the functions of soil organic matter content on boron uptake by bell pepper along with soil solution boron concentration. He revealed that OM significantly affected boron uptake by plants. Moreover he reported that uptake of boron by plant is relatively controlled by soil solution boron levels than total soil boron content. The organic matter was primed from the solid proportion of alienated straw-containing livestock dung. He categorized it as mature compost (COM). On the commencement of the trial, boron concentration in the soil solution diminished with improving rates of COM and ultimately growing levels of COM guided to smaller amount of boron in the leaf tissues. This decline in boron concentration was more at elevated levels of boron application. Similarly, the consequences of COM level on plant boron concentration were too enormous at highest boron application levels. Adjusted soil solution boron concentration was positively correlated with the leaf boron concentration.

Chaudhary and Shukla (2003) studied the availability of soil boron fractions to mustard (*Brassica juncea*) in arid soils of Rajasthan (India).The soil characteristics that influenced the Boron concentration and its uptake in mustard plants were pH, EC and organic carbon. Nazif *et al.* (2006) studied the Status of Micronutrients in Soils of District Bhimber (Azad Jammu & Kashmir).The correlation coefficient (r) obtained between hot water soluble Boron and soil pH was -0.056. The result was negative non-significant. The r-value recorded between hot water soluble boron was 0.638. It means hot water soluble boron was positively and significantly correlated with organic matter. These findings were in agreement with Perveen *et al.* (1993) and Goldberg *et al.* (2002) who reported positive significant correlation between hot water soluble boron and organic matter content. The correlation value calculated between hot water soluble boron and lime content was -0.164. Hot water soluble boron was negative non-significant correlated with lime content.

A significant positive correlation was found among available boron contents and EC, pH and organic carbon while studying the relationship and distribution of various forms of boron with different physico chemical properties of soil in Bikaner district (Mathur *et al.*,2011). Raza *et al.* (2002) studied boron fractionation in some Saskatchewan soils. Cation exchange capacity (CEC) appeared to be an important characteristic to predict the boron pools. No significant correlation was found between soil organic carbon content and the different boron pools, except for hot water soluble (HWS) Boron.

2.6.3 Effect of $CaCo_3$ on Boron availability

While studying the boron fractionation in some Saskatchewan soils, investigators found that correlation coefficients between the boron pools and particle size distribution were poor and correlation between carbonates and boron pools were insignificant(Raza *et al.,* 2002). Goldberg *et al.* (2002) found that the magnitudes of the boron 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 boron adsorption in calcareous soils (Tanaka, 1967; Goldberg and Forster, 1991). Boron adsorption on reference calcites increased with increasing solution pH from pH 6 to 9, exhibited a maximum at pH 9.5, and decreased with increasing solution pH from pH 10 to 11 (Goldberg and Forster, 1991). Communar *et al.* (2004) found that application of lime increases boron fixation by soils because it raises the soil solution pH (Elseewi, 1974, Elseewi and Elmalky 1979; Mandal *et al.,* 1993; Lehto and Malkonen, 1994). In addition to its effect on soil pH, calcium carbonate also acts as an important boron 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 (Elseewi, 1974; Elrashidi and O’Connor, 1982).

2.6.4 Effect of Soil texture on Boron availability

Negative correlation was observed between hot water soluble boron and lime content(Sudhir *et al.,*1997). The r-value obtained between hot water soluble boron and sand was -0.407. The results were negative and significantly correlated between hot water soluble boron and sand content. These results were supported by Yu and Bell (2002). The correlation coefficient (r) between hot water soluble boron and silt was 0.342. The results were positive and non-significant. Similar results were studied by Yu and Bell (2002) who found positive correlation between hot water soluble boron and silt content. The correlation value (r) between hot water soluble boron and clay was 0.274. The result was positive non-significant between hot water soluble boron and clay content. This result was in agreement with the findings of Goldberg *et al.* (2002) and Nuttall *et al.* (2003) who reported positive correlation between hot water soluble Boron and clay content. Communar and Keren (2006) studied the effect of soil texture and solution pH on boron transport in soils and found the retardation in boron transport in soils increased with the increase of clay content and solution pH.

2.7 Kinetics of B-adsorption

2.7.1 Boron adsorption

Some of the studies showed that adsorption of boron by clay-minerals were a two-step progression in which boron adsorbs primarily onto the particle borders (Couch and Grim, 1968; Keren *et al.*,1985b), consequently move about, and integrate compositionally into tetrahedral locations by substituting Al and Si (Harder, 1961;Fleet, 1965). The configuration of adsorption of boron is supposed as ligand replacement with exterior OH groups on the clay particle margins (Couch and Grim, 1968; Keren and Talpaz, 1984; Goldberg *et al.*, 1993b; Keren *et al.*, 1994; Keren and Sparks, 1994).

Adsorbed boron is dependent on soil texture, and increases with increasing clay content (Bhatnager *et al.*, 1979; Wild and Mazaheri, 1979; Mezuman and Keren, 1981; Elrashidi and O'Connor, 1982). Boron adsorption maxima increased with increasing clay content (Biggar and Fireman, 1960; Singh and Sinha, 1976; Nicholaichuk *et al.*, 1988; Communar and Keren, 2006).Boron adsorption on soils is very dependent on solution pH. Boron adsorption by soils increased as a function of solution pH in the range of pH 3 to 9 (Bingham *et al.*, 1971; Schalscha *et al.*, 1973; Mezuman and Keren, 1981; Keren *et al.*, 1985a; Barrow, 1989; Lehto, 1994) and decreased in the range of pH 10 to 11.5 (Goldberg and Glaubig, 1986a). Boron adsorption maxima were significantly positively correlated with solution pH (Evans, 1987) Because coarse textured soils often contain less available boron than fine textured soils, boron deficiency often occurs in plants growing in sandy soils (Fleming, 1980).

Native boron was significantly positively correlated with soil clay content (Elrashidi and O'Connor, 1982). At identical water soluble boron content, plant boron uptake was greatest for the coarsest textured soil (Wear and Patterson, 1962).

A highly significant correlation was found between soil content of the clay minerals kaolinite, montmorillonite, and chlorite and the B adsorption maximum. Aluminium and iron oxides play an important role in B adsorption behaviour on soils (Bingham *et al.,* 1971; Elrashidi and O'Connor, 1982). Boron adsorption is highly and significantly correlated with the aluminium oxide content of soils (Bingham *et al.,* 1971). Numerous studies have investigated boron adsorption by various aluminium and iron oxides both crystalline and amorphous (Hatcher *et al.,* 1967; Keren and Gast, 1983; Goldberg and Glaubig, 1985, 1988; Bloesch *et al.,* 1987; Goldberg et al., 1993a, 1993b, 1996; de Bussetti *et al.,* 1995).

Boron adsorption on both crystalline and amorphous aluminium and iron oxides increased with increasing pH up to an adsorption maximum at pH 6 to 8 for aluminium oxides and pH 7 to 9 for iron oxide (Goldberg and Glaubig, 1985; Bloesch *et al.,* 1987). Above the maximum, boron 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; Sims and Bingham, 1968a). Boron adsorption per gram was greater for aluminium than iron oxides (Goldberg and Glaubig, 1985). This is likely due to the higher surface area of aluminium oxides, since adsorption per square metre was similar in magnitude for aluminium and iron oxides (Goldberg and Glaubig, 1985). Boron adsorption on oxide minerals occurred rapidly, being virtually complete after one day of reaction time. Competing ions such as silicate, sulfate, phosphate, and oxalate decreased the magnitude of Boron adsorption on oxides (Bloesch *et al.,* 1987; de Bussetti *et al.,* 1995). The effect of competing ions on boron adsorption can be slight, in the case of sulfate, or substantial in the case of phosphate (Bloesch *et al.,* 1987). The ability of competing anions to leach adsorbed boron from oxides increased in the order: chloride < sulfate < arsenate < phosphate. Significant silicate adsorption produced only a slight decrease in boron adsorption by aluminium oxide suggesting that some boron sorption sites show boron preference (Goldberg and Glaubig, 1985).

Magnesium hydroxide can remove appreciable amounts of boron from solution (Rhoades *et al.,* 1970a). Due to magnesium hydroxide coatings, silicate minerals containing mainly magnesium in their chemical formulas adsorbed more boron than a silicate without magnesium in its chemical formula (Rhoades *et al.,* 1970a). Layer silicate clay minerals are important boron adsorbing surfaces in soils (Harder, 1961; Hingston, 1964; Sims and Bingham, 1967; Singh, 1971; Keren and Mezuman, 1981; Keren and Gast, 1981; Keren and Talpaz, 1984).

Clay minerals exhibit increasing boron adsorption with increasing solution pH with adsorption maxima occurring at pH 8 to 10 (Hingston, 1964); boron adsorption decreases with increasing pH above the maximum for clay minerals, the order of Boron adsorption per gram is: kaolinite < montmorillonite < illite (Harder, 1961; Hingston, 1964; Sims and Bingham, 1967; Keren and Mezuman, 1981;). The rate of boron adsorption on clay minerals consists of a fast adsorption reaction and a slow fixation reaction. Short term experiments have shown that boron adsorption reaches equilibrium in less than one day (Hingston, 1964; Kerren *et al.,* 1981). Long term experiments have shown that fixation of boron increased even after six months of reaction time (Harder, 1961). The effect of temperature on boron adsorption by clays has been investigated (Harder, 1961; Couch and Grim, 1968; Singh, 1971; Goldberg *et al.,* 1993a). For a very short reaction time of two hours, boron adsorption in the pH range of 5.5 – 9.5 decreased with increasing temperature (Goldberg *et al.,* 1993a).

Boron adsorption for longer reaction times of twelve hours to sixty days increased with increasing temperature (Couch and Grim, 1968; Singh, 1971;

Jasmund and Lindner, 1973). Boron adsorption on clays increased with increasing ionic strength of the solution (Fleet, 1965; Couch and Grim, 1968; Keren and O'Connor, 1982; Goldberg *et al.*, 1993b; Keren and Sparks, 1994). Decreases in water content decreased boron adsorption on clays (Keren and Mezuman, 1981). Wetting and drying cycles increased boron fixation with the greatest increase occurring during the first wetting and drying cycle (Keren and Mezuman, 1981). Competing anions affect the magnitude of boron adsorption on clays (Goldberg and Glaubig, 1986a; Goldberg *et al.*, 1996). The presence of chloride, nitrate, and sulphate had little effect on boron adsorption on clays; the presence of phosphate, however, appreciably reduced boron adsorption.

The magnitude of boron adsorption on kaolinite was affected slightly while boron adsorption on montmorillonite was completely unaffected by substantial silicate adsorption suggesting that the majority of boron adsorbing sites are specific to boron (Goldberg and Glaubig, 1986a). The magnitude of boron adsorption on clay minerals is affected by the exchangeable cation (Keren and Gast, 1981; Keren and Mezuman, 1981; Keren and, O'Connor, 1982). Calcium clays adsorbed more boron than sodium and potassium clays (Keren and Gast, 1981; Keren and O'Connor, 1982). On per gram basis clay minerals adsorb significantly less boron than do most oxide minerals. It may be more appropriate to compare boron adsorption capacity on a surface area basis. However, since boron adsorbs on the edges of clay minerals and edge surface areas of clays are difficult to determine, this comparison is not readily available (Su *et al.* 1994). Boron adsorption was greater on soils having higher calcium carbonate content (Elrashidi and O'Connor, 1982; Elseewi, 1974).

Metwally *et al.* (1974) studied the boron fixation by amorphous oxides and found that Sorption of boron was greater by amorphous oxides, prepared in the laboratory, than by samples of Ca- or Na-saturated alluvial soils or clay minerals. The fixing capacity of the oxides followed the order Fe $(OH)_3$> Al $(OH)_3$> Si-gel suspensions. Molecular adsorption of B $(OH)_3$ and exchange of B(OH)- for the OH groups in the hydroxide suspensions, or H bonding between

Si and the OH groups of the borate ions in the Si-gel, are suggested as the main mechanisms of boron fixation. Fixation of boron by the hydroxides, and bonding energies of the fixed boron, increased with increasing pH from 4 to 8.5, whereas boron fixation by Si-gel was only significant at pH > 8 and increased in the presence of calcium, possibly due to the formation of difficultly soluble Ca-B-silicate.

Goldberg *et al.* (2002) studied the influence of soil solution cation composition on boron adsorption by soils and found that boron adsorption increased with increasing solution pH, reached an adsorption maximum near pH 9, and decreased with further increases in pH. Boron adsorption as a function of solution pH was independent of solution cation composition from pH 4 to 8.5. At pH values greater than 8.5, increased Boron loss from solution was found for the magnesium systems.

2.7.2 Applicability of different Kinetic models to describe Boron adsorption

Adsorption increased with the increase in fineness and organic carbon content of soils. Clays had adsorptions almost of the order of loam soil with slightly higher content of montmorillonite at 22°C but at 45°C kaolinite adsorbed slightly higher amounts of boron. Generally it was higher at 45°C than at 22°C. Although both the Langmuir and Freundlich adsorption isotherms were valid within a wide range of boron concentration, the Freundlich isotherm fitted better than Langmuir's(Singh, 1971).Goldberg (1997) studied the various reactions of boron in soils and concluded that boron adsorption reactions can be described empirically using the Langmuir adsorption isotherm equation, the Freundlich adsorption isotherm equation, and the phenomenological Keren model. Chemical models such as the constant capacitance model, the triple layer model, and the Stern VSC-VSP model can describe B adsorption over changing conditions of solution pH and B concentration.

Goldberg(1993) studied the chemical modelling of boron adsorption at the mineral-solution interface successfully using the constant capacitance model for oxides, clays, and soils, in these studies boron adsorption was described as forming a trigonal inner-sphere surface complex. Such a configuration is chemically reasonable over most of the pH range since boric acid is a very weak monobasic acid with a pKa of 9.2. The ability of the constant capacitance model to predict boron adsorption on soils using the surface complexation constants determined from the soil properties was evaluated.

Langmuir and Freundlich isotherms fitted well to the adsorbed data and highest values for maximum boron adsorption were found in clayey soils, which were significantly correlated with contents of total, free and amorphous iron and aluminum oxides, as well with the physical attributes. Ninety four percent of the variation in the maximum adsorption could be related to the free iron content(Loomis and Durst,1992).Datta and Bhadoria (1999) studied the adsorption and desorption of boron in acid soils of West Bengal and found that Freundlich isotherm proved more effective in describing boron adsorption in soils as compared to Langmuir equation. The split Langmuir isotherm demonstrated that any of the adsorption maxima, calculated from lower, upper or entire isotherm, could be of practical use. Contrary, bonding energy coefficient, calculated either at lower or higher equilibrium concentration failed to show any practical benefit. Regression models as a function of boron application rate and adsorption equation parameters to predict boron uptake from applied boron, demonstrated the utility of Langmuir and Freundlich equation parameters.

While studying the influence of soil solution salinity on boron adsorption by soils found that boron adsorption for different soils act as a function of solution boron concentration which conforms to the Langmuir adsorption isotherm equation. The boron adsorption maxima obtained with the Langmuir equation for both EC were not statistically and significantly different at the 95% level of confidence. The constant capacitance model, a surface complexation model, was able to describe boron adsorption as a function of solution boron concentration and solution pH(Goldberg et *al.,* 2002).Muhammad *et al.* (2008) compared Freundlich and Langmuir adsorption equations for boron adsorption on calcareous soils and concluded that Freundlich model showed better fit of sorption data than the Langmuir model as was evident from higher values of R^2 (0.97). The results suggested that for a particular soil, boron adsorption isotherm needs to be constructed for site specific boron fertilizer application. High clay contents ranging from 70 to 320 g/kg and more $CaCO_3$ (35 to 128 g/kg) increased the amount of adsorbed boron in these soils.

Chen *et al.* (2009) while studying the effect of pH on boron Adsorption-Desorption Hysteresis of Soils found that the sorption results were described well by the Freundlich equation. Boron adsorption markedly increased as pH increased. This increase was more pronounced when $Ca\ (OH)_2$, as opposed to NaOH, was used for pH adjustment.Angew (1970) compared different isotherm equations for boron adsorption and desorption on soils with fertilizer applications. Sorption processes were fitted to linear forms of the Freundlich, Langmuir and Temkin equations. Boron adsorption data were well described by Freundlich and Langmuir isotherms, while the Temkin showed a lowest fit. All fertilized plots showed higher intensity of adsorption (Freundlich 1/n range 0.617-0.765 L kg^{-1}), and applications of distiller's residue plus anaerobic digestate and organic-mineral fertilizer to soils increased the maximum adsorption and buffering capacity, with the Langmuir and Temkin models, respectively. The Freundlich intensity of adsorption 1/n was positively correlated with the Langmuir maximum adsorption Xm and Temkin buffering capacity b.

The boron adsorption was studied at two soil mass (ms) to solution volume (vs.) ratios, ms/vs. = 0.5 and 1, and the Langmuir, Eadie-Hofstee, Freundlich, and Temkin adsorption equations were fitted to the boron adsorption data. The proportion of adsorbed boron was gradually less in the more concentrated solutions, with differences in ms/vs. ratio and in treatments: the percentage of boron adsorbed was greater for ms/vs. = 0.5 and for distiller's residue and mineral fertilizer. The Freundlich isotherm represented the measured boron adsorption data well; at ms/vs. = 0.5, the values of Freundlich adsorption maxima Xm varied from 93.14 to 111.88 mg kg^{-1} (organo mineral fertilizer and distiller's residue, respectively; at ms/vs. = 0.5) and from 32.14 to 40.32 mg kg^{-1} (mineral fertilizer and control, respectively; at ms/vs. = 1). The adsorption isotherms were well explained by the lower soil mass to volume solution ratio in the order Freundlich > Temkin ≌ Langmuir > Headie-Hofstee(Das, 2000).

Arora and Chahal (2010) studied the effect of soil properties on boron adsorption and release in arid and semi-arid benchmark soils of India and found that the adsorption isotherms indicated that the adsorption of boron increased with its increasing concentration in the equilibrium solution. The Langmuir adsorption isotherm was curvilinear and it was significant when the curves were resolved into two linear parts. The maximum value of adsorption maxima (b1) was observed to be 7.968 mg B kg^{-1} in Garhi baghi soil and the bonding energy (k) constant was maximum at 0.509 L mg^{-1} in Jodhpur ramana soil. The Langmuir isotherm best explains the adsorption phenomenon at low concentrations of the adsorbent, which of course was different for different soils. There was significant correlation between b1 and clay (r = 0.905**), organic matter contents (r = 0.734*), and cation exchange capacity (CEC; r = 0.995**) of soils. A linear relationship was observed in all the soils at all concentration ranges between 0 and 100 mg B L^{-1}, indicating that boron adsorption data conform to the Freundlich equation.

2.8 Kinetics of B-desorption

2.8.1 Boron desorption

Boron desorption reactions in soils have been investigated less extensively than boron adsorption reactions. For some soils, the boron desorption isotherm corresponded closely to the boron adsorption isotherm (Wild and Mazaheri, 1979; Elrashidi and O’Connor, 1982). Other soils exhibited hysteresis that is the boron adsorption isotherm did not correspond to the boron adsorption isotherm (Okazaki and Chao, 1968; Rhoades *et al.*,1970b ;Elrashidi and O’Connor, 1982). Hysteresis was not significantly correlated with any of the following soil properties: clay, organic carbon, pH, electrical conductivity, cation exchange capacity, surface area, aluminium oxide content, and iron oxide content (Elrashidi and O’Connor, 1982). Adsorbed soil boron was completely desorbed after five sequential extractions (Okazaki and Chao, 1968). Boron desorption reactions on soil minerals have been found to be reversible in some studies (Keren and Gast, 1981; Bloesch *et al.*, 1987) and hysteretic in others (Harder, 1961). The pronounced hysteresis of boron desorption from composted organic matter is attributed to the formation of dihydroxy and hydroxy– carboxy bonds with B (Yermiyaho *et al.*, 1988).

Desorption occurred when boron concentration in the soil solution decreased, the amount of boron released being reduced by lime application or soil drying(Tanaka, 1967). Griffin and Burau (1974) studied the kinetics and equilibrium reactions of boron desorption from different soils of California and found that the desorption reactions at each postulated were independent. When the C versus t relationship was approximately linear, it was assumed that the faster reactions were complete and that the increase in boron concentration was due to a slow reaction. The data for $t > 20$ hours were fitted by regression analysis to the linear expression, the total boron concentration due to all the faster reactions, providing the rate of this slow reaction is constant at all t.

Elrashidi and Connor (1982) studied the boron sorption and desorption in some Mexico soils and found that two types of boron desorption reactions were present in the soils investigated (reversible and hysteretic).The tendency for desorption to be hysteretic was not significantly correlated to any soil property measured. Zerrari *et al.* (1999) studied the adsorption and desorption of boron on soils and the influence of application of manure. A comparison between the desorption and adsorption isotherms showed that there was a hysteric effect for all the substrates studied. However, this effect was more important for the soils than for the composted manures. The desorption index for the composted manures was 1.5183, indicating the reversibility of the desorption process. The mean desorption indices observed varied from 1.9711 to 4.7639 for soils. Significant relationships were observed between these indices and some of the soil characteristics, of which were organic matter content (r=0.7).

Boron was added to the untreated and the fly ash-treated soils, left in contact for 30 days, and its desorbability was studied. It was observed that although B sorption maximum of soils tended to increase upon fly ash addition, the affinity of B to sorption sites remained practically unaltered in most of the cases. Boron sorption was an exothermic reaction and the greatest part (more than 60%) of sorbed B in the fly ash-treated soils could be easily desorbed within 24 h, reaching 80% for the acid soils and 100% for the calcareous soil after 120 h of desorption time. It was concluded that although there was a tendency of an increase in B sorption capacity in most cases upon fly ash addition, this increase was not generally accompanied by an increase in strength of B retention by soil surfaces. A major part of added B in the fly ash-treated soils remained labile enough to be released in the soil solution in a short time(Malewar,1999).

Desorption was affected with Morgan's solution in three sequential extractions in similar conditions as for adsorption. B desorption increased, but the percentage of desorbed B was low and decreased as concentration increased, depicting moderate to strong hysteresis between B adsorption and desorption. Desorption was easier in the Bt2 horizon ($P < 0.05$) with the first extraction yielding 60% of total desorbed B than in the Ap horizon, where it yielded only 49% (Kparmwang, 2002).Wojcik (2003) studied the behaviour of soil boron and boron uptake by M.26 apple rootstock as affected by application of different forms and nitrogen rates. The results showed that nitrogen as calcium nitrate and ammonium nitrate increased boron both in soil solution and non-specifically adsorbed on soil surface and decreased boron concentration on Al and Fe oxides, indicating that N-NO_3 inhibited boron sorption on Fe and Al oxides. Maximum boron desorption from Fe and Al oxides were obtained within 1 day after N-NO_3 was supplied. Nitrogen application as calcium nitrate and ammonium nitrate increased availability and uptake of boron by plant roots.

Su *et al.* (1994) studied the boron release from weathering of illites, serpentine, shales, and illitic/palygorskitic soils. The objectives of the study was to identify source minerals contributing to the continued boron release after extraction of soluble boron and to estimate its release rate from weathering of B-containing minerals and soils. Illite and palygorskite soils were successively extracted 7 to 26 times following each 12-h equilibration in 0.1 and 0.01 M CaCl2 solution until the supernatant solutions contained less than the detection limit of 0.001 m mol B L^{-1}. Boron release rates decreased with time and increasing pH. Average boron release rates from 150 to 180 d ranged from 0.005 fmol $m^{-2}s^{-1}$ to 0.342 fmol m^{-2} s^{-1} at pH 5, 0.004 fmol m^{-2} s^{-1} to 0.060 fmol m^{-2} s^{-1} pH 7, and 0.002 fmol m^{-2} s^{-1} to 0.044 fmol m^{-2} s^{-1} at pH 9. Boron release from the two soils was accompanied with high magnesium release into the solution, suggesting palygorskite as a major source for boron.Chaudhary and Shukla (2004) studied the boron adsorption and desorption in arid soils of India and found that cation exchange capacity and clay content retarded the release of boron from soils. The degree of irreversibility (hysteresis) of boron adsorption/desorption increased with increase in pH, organic carbon, cation exchange capacity and clay content of soil.

While studying boron fixation and its release in soils and bark compost and found that bark compost showed a 10-fold higher fixation of boron (64.1 mg kg^{-1}) compared to greenhouse soil, indicating that bark compost displayed a significant capacity for boron trapping. In greenhouse soils, only around 9% of the adsorbed boron was released during a one month period of incubation. Bark compost showed the highest amount of release during the incubation period, accounting for 64% of the adsorbed boron. Moreover, the ratio of boron release increased to 77% in the case of the soil mixed with bark compost. These results, suggest that different kinds of fixation-releasing mechanisms operate in the soil and bark compost(Van *et al.,* 2005). Sharma *et al.* (1995) found that application of farmyard manure (FYM) did not change boron desorption capacities of soils corresponding to low boron concentration range significantly, however, it increased boron desorption capacity pertaining to high boron concentration in all soils, except in Alfisols and Entisols having pH of 9.8 and 5.1, respectively.

Application of FYM increased the desorption slope factor applicable to low concentration range in Inceptisols, but decreased it in Entisols. Thedesorption slope factor applicable to high concentration range decreased with FYM application in all soils except in Entisols, where it was increased. Boron desorption index slope decreased with FYM application in low boron concentration range, but increased in high concentration range for all soils except for Entisols pH 5.1, in which a reverse trend was observed. Application of FYM increased the retention of added boron in soils and may help reducing the leaching. Diana *et al.* (2006) studied the organic and mineral fertilization effects on physical characteristics and boron dynamic in an agricultural soil and found that the boron desorption was not modified by the variation on soil mechanical resistance; no correlation was found between boron desorption index and physical-mechanical parameters of the soil. The boron fractions, not readily available for plants, occluded in aluminium (Al) and iron (Fe) oxyhydroxides (Ox-B) and organically bound (OM-B), were negatively correlated with colloid index (Ic).

Apparent hysteresis was observed in that both derivational families of desorption isotherms deviated from the adsorption isotherm for the five soils at their original pH. Moreover, hysteresis coefficients, n_{des}/n_{ads} and λ_{trad} for the traditional approach, had a positive correlation with organic carbon content, but they had a negative correlation with free Fe_2O_3 and free Al_2O_3 content(Chen *et al.*,2009).Arora and Chahal (2010) studied the effect of soil properties on boron adsorption and release in arid and semi-arid benchmark soils of India and found that soils that have a higher affinity for boron adsorption, like Garhi baghi, tended to desorb less amount of boron, that is, 43.54%, whereas Ballowal saunkhari desorbed 48.00%, Jodhpur ramana 48.42%, and Naura soil 58.88% of the adsorbed boron. Boron desorption by these soils is positively and significantly correlated with the sand content (r = 0.714**) and negatively with clay content (r = -0.502*) and CEC (r = -0.623**). The maximum value of 37.59 mg kg^{-1} for desorption maxima (Dm) was observed in Garhi baghi soil and also a constant related to B mobility (Kd) was found to be maximum in Garhi baghi (0.222 L kg^{-1}).

Goldberg and Donald (2011) studied the release of native and amended boron from arid zone soils after varying incubation times. it was found by the investigators that boron desorption decreased as a function of time for at least some of the extractions and treatments for all the soils.this is consistent with published literature that added boron becomes less extractable with increased incubation time. comparison between the three extractants revealed no statistically significant differences in amounts of adsorbed boron for three of the soils. for the two other soils, the order of desorbed boron amount was hot water soluble < 0.1 *m* nacl extractable < diethylenetriaminepentaacetic acid-sorbitol extractable. the decrease in boron release with respect to incubation time approached zero for all five soils for most of the extractant solutions, as evidenced by slopes that were not statistically and significantly different from zero at the 95% level of confidence for almost all treatments of all three extractions.

2.8.2 Applicability of different kinetic models to describe Boron desorption

Boron desorption followed a 2 site analog of a linear form of the 1-site Langmuir expression. Langmuir adsorption maximum values for each site corroborated those calculated from the kinetic study and supported the multisite interpretation of the kinetic data.Elrashidi and Connor (1982) studied the boron sorption and desorption in some Mexico soils and found that boron sorption in seven of the 10 soils conformed to the Langmuir adsorption isotherm, but only over limited concentration ranges. On the other hand, the Freundlich adsorption isotherm was applicable over the entire Boron concentration range (0 to 100 mg/ml) for all 10 soils. Simple and multiple regression models allowed various boron sorption parameters to be predicted from selected soil properties. Boron desorption data could also be expressed by the Freundlich isotherm(Griffin and Burau, 1974).Sakal *et al.*(1994) studied the kinetics of boron desorption from calcareous soils. Five kinetic equations (second approximation or pseudo-first order, two constant rate, first order, parabolic diffusion and Elovich) were tested for their suitability in describing boron desorption from four calcareous soils. The comparison of coefficients of determination (R^2) and standard errors of estimate (SE) showed that the second approximation, two constant rate and first order equations followed by parabolic diffusion adequately described the boron release, whereas Elovich equation failed to describe it. It was further observed that two separate pseudo-first order reactions due to desorption from two independent boron retention sites were involved with a higher rate of boron release from site 1 and lower from site 2 in all the four soils.

Boron desorption reactions often exhibit hysteresis(Goldberg, 1997). The rate of boron desorption can be described using the first order rate equation, the Elovich reaction rate equation, and the power function equation. For non-hysteretic systems, boron desorption reactions can be described using the empirical and chemical boron adsorption models discussed above. The Langmuir equation was able to describe boron adsorption– desorption on soils (Hatcher and Bower, 1958), but due to hysteresis, was unable to describe boron leaching from soils (Rhoades *et al.*, 1970b). Zhu *et al.* (1998) studied the adsorption-desorption of boron in soils and its effect on boron uptake of plant. The experimental results were fitted to the Freundlich and Langmuir isotherm equations. There was a significant hysteretic desorption of boron in some of the tested soils. The adsorption curve was different from that of desorption curve, resulting from Ke' or n' of the desorption equation being larger than that of the adsorption equation. Therefore, the difference due to hysteretic desorption could be described qualitatively by the hysteretic coefficient (DELTAK + DELTAn). When DELTAK + DELTAn >0.25, the hysteretic desorption was more significant. The contents of amorphous Al and Mn oxyhydroxides were positively correlated with the hysteretic coefficient of the experiment (n=11, r=0.790, respectively). Rape shoot uptake of boron was significantly correlated with the value of DELTAK + DELTAn (r=-0.761, n=11). The application of boron reduced the hysteretic desorption effect on plant uptake, enabling the plant to absorb higher amounts of boron from the soil.

Analyses of B, K+, Mg^{2+}, $Ca^{2+,}$ Cl^{-} and pH infractions supposed that boron existed not only in a simple form of borate but also in ion-pair with cations partly in acidic soil, and borate was the primary form existing in the calcareous soil. In studying desorption kinetics with electro ultrafiltration, the boron content of some fractions was accumulated, and the accumulative quantities were fit to time factors in three kinetic equations: the zero-order, first-order, and parabolic diffusion equations. The parabolic diffusion equation had the best degree of fit, followed by the zero-order equation, and the first-order equation was the worst(Zhu *et al.*,2000).

Boron adsorption and boron desorption could be fit with the same Freundlich parameters for non-hysteretic soils, but different sets of Freundlich parameters were necessary to describe boron adsorption and boron desorption for hysteretic soils (Elrashidi and O’Connor, 1982). Chaudhary and Shukla (2005) studied the kinetics of boron desorption from arid soils of India. Eight kinetic models were tested to describe boron desorption in arid soils of Rajasthan varying in physical and chemical characteristics. The comparison of coefficient of determination (R^2) and standard error of estimate (SE) revealed that the order of application to describe boron desorption kinetics in these soils was as follow: second approximation>two-constant rate equation>Elovich rate equation>parabolic diffusion rate equation. This was further observed that the two separate pseudo first-order reactions due to desorption from two independent boron retention sites were involved with higher rate of boron release from site 1 and lower from site 2 in all the soils under study.

Metwally (2005) studied the kinetics of desorption reactions and leaching of boron from salt-affected soils of El-Tina Plain, North Sinai, and found that the first reaction is fast and its mechanism indicated to a desorption of boron from nonspecific retention sites where boron is weakly held by physical adsorption in outer-sphere complexes onto adsorbing surfaces in soils. The second reaction is slowest probably due to a release of boron from specific retention sites in which boron is more strongly bound via ligand exchange in inner-sphere surface complexes. Sparing dissolution of boron containing materials may be another mechanism for the slow reaction. The fast reaction was stopped after 6-8 hrs and desorbs 62 to 72% of total desorbable B. The desorption rate constants decreased from 0.306 and 0.032 in virgin soil to 0.210 and 0.024 mg kg^{-1} h^{-1} in cultivated soils, for fast and slow reactions, respectively. Considerable portions of water-soluble boron, specifically bound boron and non- specifically held boron were displaced from surface soil layers down to the subsurface and deep layers.

Boron desorption data was well expressed by the Freundlich isotherms for all the soils, that were able to continuously release boron. All fertilization treatments showed values of desorbed boron higher than that of the unfertilized control, and therefore there was a positive effect of fertilizers regard to boron release, particularly for organic mineral and integrated fertilizations. Correlations relating constants desorption and soil properties indicated that mostly the soil composition (clay, silt, and sand), and the iron and aluminium oxides would act on boron release (Diana, 2006).

2.9 Uptake of Boron by plants

Boron (B) is one essential micronutrient required by plants for their normal development and growth. However, throughout the history of this element research, it has been established that concentration ranges in the soil solution causing either deficiency or toxicity symptoms in plants are smaller than for any other element (MalaveAcuna, 2005). In addition to this situation, those ranges change according to the plant species; that is, a concentration interval of B can be normal for a specific type of plant, while for others can be either toxic or deficient, which has had a profound influence for a better knowledge of B behaviour in soils. Soil factors affecting availability of B to plants are pH, texture, moisture, temperature, content and quality of organic matter, and content and kind of clay. The B concentration of soil solution is generally controlled by reactions with B adsorbing surfaces involving aluminium and iron oxides, magnesium hydroxide, clay minerals, calcium carbonate, and organic matter. Rochester (2007) conducted an excellent study on uptake and export of different plant elements in Australia by using cotton as test crop. He reported that lint yields of seven cotton crops varied from 975-2725 kg ha^{-1}. He also estimated uptake of boron and other nutrients at initial to delayed boll formation stages.According to his findings cotton crops accumulated an average of 340 g B ha^{-1}.

Studies by Vlamis and Ulrich (1971) showed that young blades of sugar beets contained more boron than the mature and old blades of plants grown at low concentrations of boron in a nutrient solution. However, at higher boron concentrations in solution, no differences were found. The highest boron values in sugar beets occurred in the older leaves, but the lowest boron content occurred in the fibrous and storage roots (Vlamis and Ulrich, 1971). The boron concentration of corn leaves increased with age in seedling leaves. The uppermost corn leaves had higher concentrations than did leaves at positions below. Boron concentration in corn leaves and tassels of flowering corn plants increased with age, but boron in other plant parts remained low and relatively constant .Gorsline *et al.* (1968) noted that boron concentration in the whole corn plant decreased during initial growth, remained unchanged during most of the vegetative period, and then decreased after silking.

Boron level in leaf tissue of rutabaga was greater from early samplings than it was from late samplings(Gupta and Cutcliffe, 1972). Older cucumber (*Cucumis sativus* L.) leaves contained more boron than the younger leaves; and within the leaf, boron accumulated in the marginal parts. Boron accumulation was greater in the marginal section of corn leaves than in the midrib section. Generally, boron in plants has a tendency to accumulate in the margin of leaves (Kohl and Boswell, 1975). Results of Miller and Smith (1977) showed that alfalfa leaves had much higher boron content (75 to 98 mg kg^{-1}) than tips (47 mg kg^{-1}) or stems (22 to 27 mg kg^{-1}). In a field study conducted in Prince Edward Island, Canada, the highest boron concentrations were in leaves and upper halves of plants of most specie. The boron concentrations were lowest in the stems. The lowest boron concentration was in alfalfa and the highest in Brussels sprouts and rutabaga. In a separate experiment, where the effect of not applying boron was studied against applied boron, the trend in boron accumulation in the various plant parts was similar. The boron content of pistils and stamens, although very high, was lower than in leaves and sometimes of corollas.

Renan and Gupta,1991found that without added boron, the bottom third of the leaves of alfalfa and red clover contained significantly higher boron than did the upper leaves. In the case of stems the opposite was the case, i.e., the upper third of the stems contained more boron than the bottom third. This trend was similar for the unfertilized and boron-fertilized areas for leaves; however, in the presence of added boron, differences in the boron content in the upper and lower stems were not significant.

The general theory is that boron translocates readily in the xylem, but once in the leaves, it becomes one of the least mobile of the micronutrients. Thus the boron immobility in leaves in terms of localized cyclic movement prevents escape and transport of this element over long distances (Oertli, 1969). The results of Shelp (1989) have also shown that younger leaves contain less boron than mature leaves; the authors assumed that the boron supply for mature leaves is delivered principally via the xylem. The fact that boron deficiency exhibits in the younger leaves and not in the older leaves can be explained by the fact that the boron concentration is higher in the older leaves than in the younger leaves, as reported for alfalfa and red clover (Renan and Gupta, 1991) and for broccoli (Shelp,1989). Since the boron concentration in the upper leaves was easily increased with boron fertilization (Renan and Gupta, 1991), boron deficiency is controlled without much difficulty using boron applications.

Boron availability generally decreases as soils dry, making B deficiency in plants more likely (Fleming, 1980). This may be because plants encounter reduced amounts of available B when extracting moisture from lower depths during dry conditions (Fleming, 1980). Diffusivity of B decreased with decreasing water content because drying reduces soil solution mobility and increases the diffusion path length (Scott *et al.,* 1975). However, total diffusible B from repeated extractions was independent of water content (Sulaiman and Kay, 1972). Boron adsorption increases with increasing soil temperature. However, this may be due to an interactive effect of soil temperature with soil moisture since B deficiency is associated with dry summer conditions (Fleming, 1980). Tanaka (1970) studied the differences in boron requirement between crop plants and found that sunflower roots eluted with Na-borate/boric acid (pH 8.5) adsorbed about 30 mμ g B/g of root. The uptake of B by sunflower from culture solutions with a pH of 4.7 or 7.5 was studied. Plants grown at high pH accumulated more B in their roots and less in their leaves than those at low pH.Dicot roots had a greater B adsorption capacity than monocot roots

The higher the clay content of a soil, the lower is the B activity in solution for any given amount of B added. It was suggested that the soil adsorption sites act as a pool to which B can be stored or removed depending on the change in solution B concentration in soil. The B uptake by the plants is higher as the sand content increases, for any total amount of B added. However, the experimental results from all three soil-sand mixtures lie on the same line when the B content in the shoot is plotted against B activity in soil ($R^2 = 0.9695$). The dry matter of the plants was decreased with both an increase in total amount of B added and an increase in the sand content for any given amount of total B. As found for B uptake, the relative dry matter weight and the relative yield values lie on the same linear line when they are plotted against B activity in soil solution from all three soil systems. This indicates that the yield responds to B activity in soil solution only(Keren *et al.*,1985).

Keren *et al.* (1985a) studied the plant uptake of boron as affected by boron distribution between liquid and solid phases in soil. Experimental results of boron in soil solution as a function of total boron content in soil were compared with values computed using a competitive adsorption model. The agreement between the calculated and the experimental results indicates that models can be used to predict boron activity in soil solution at water content lower than that of the saturated paste. Boron uptake by the plants was linearly correlated with the boron content in the soil for both soil systems. The boron content in the leaf tissue of the plants grown in the soil-sand mixture was significantly higher than that of the plants growing in the soil system at any level of boron added. However, when boron content in the leaf tissue was related to boron activity in soil solution, the experimental points for both soil systems lay on the same straight line, indicating that boron uptake by plants and boron activity in soil solution were highly correlated. It is evident that the dry leaf weight is linear correlated with the boron content in the leaf tissue, and, therefore, is linearly correlated with boron activity in soil solution. It is concluded that boron in soil solution, rather than adsorbed boron, influenced boron uptake by plants.

Boron uptake by plants is controlled by the B level in soil solution rather than the total B content in soil. The affinity of organic matter for B can affect B uptake by plants because of changing B concentration in soil solution. Boron concentration in the soil solution at the beginning of the experiment decreased with increasing levels of compost. This decrease was most prominent at high levels of B application. The effect of the compost level on leaf B concentration was also prominent at high B application rates, with increasing levels of compost resulting in less B in the leaf tissues. Boron concentration in the leaves was highly significantly correlated (r^2=0.88) with the B concentration adjusted in the soil solution. This correlation coefficient was further improved (r^2=0.98) when B concentration in the soil solution was calculated using a B adsorption model. The results presented herein indicate that organic matter plays an important role in controlling B concentration in the soil solution, and that it has a prominent effect on reducing B uptake by plants(Yermiyahu *et al.*,2001).

Because boron (B) and calcium ($Ca^{2+)}$ seem to have a strong effect on legume nodulation and nitrogen fixation, rhizobial symbiosis with leguminous plants, grown under varying concentrations of both nutrients, was investigated. The study of early pre-infection events included the capacity of root exudates to induce nod genes, and the degree of adsorption of bacteria to the root surface. Both phenomena were inhibited by B deficiency, and increased by addition of Ca^{2+}, resulting in an increase of the number of nodules. The infection and invasion steps were investigated in pea nodules harbouring a *Rhizobium leguminosarum* strain that constitutively expresses green fluorescent protein. High Ca^{2+} enhanced cell and tissue invasion by Rhizobium, which was highly inhibited after boron deficiency. This was combined with an increased boron concentration in nodules of plants grown on boron-free medium and supplemented with high Ca^{2+} concentrations, and that can be attributed to an increased boron import to the nodules. Histological examination of indeterminate (pea) and determinate (bean) nodules showed an altered nodule anatomy at low boron content of the tissue. The moderate increase in nodular boron due to additional Ca^{2+} was not sufficient to prevent the abnormal cell wall structure and the aberrant distribution of pectin polysaccharides in B-deficient treatments. Overall results indicate that the development of the symbiosis depends of the concentration of B and Ca^{2+}, and that both nutrients are essential for nodule structure and function(Reid*et al.*, 2004).

Inplants,excessiveBconcentrationproducesmanyabnormalitiesinthemaingrowthstream (Reid*et al.*,2004)andthiswasduetotoxicBlevels.Borontoxicitysymptomsdepicted theBbuildupatthelastpartofthetranspirationstreamandfictitious Bdistributioninthemajorityofspecies.The distinctive apparentsignofBtoxicityinnumerousplantspeciesofteninitiatedaschloroticpatches onolderleafmarginsandtipsofleaves,whichleadstoburningandnecrosis(Eaton,1944 ; Crisp*et al.*,1976;Cartwright*et al.*,1986;Bergmann,1992;Bennett,1993;Miwa*et al.*,2007).SomestudiesshowedthatthenecroticorchloroticleafsegmentshaveextremelyhighBcontentsthenadjoiningleaf tissues and barleyexhibiteddistinctivesketches forvariouscultivars (OertliandRoth,1969).

Recently Nable *et al.* (1997) and Miwa *et al.* (2007) performed research on toxic effect of B on different crops and his findings revealed that B affluent soils are more significant because these soils produce B toxicity in the field. Miwa *et al.* (2007) reported that in Australia, about 17 % of the barley yield declined owing to B toxicity. They further reported that toxic soil B levels reduced the yield outputs in many crops and this toxicity was an international tragedy in foodstuff production. The findings of Miwa *et al.* (2007) provided the fundamental information regarding crop productivity in soils containing excess B, which are distributed in arid areas of the world.

2.10 Critical limits of Boron in soils and plants

Boron requirements vary considerably among crops. The optimum range in leaf tissue of most crops is from 20 to 100 ppm. Some crops are particularly sensitive to boron and can be injured when the leaf boron level is too high. For example, boron levels in excess of 50 ppm have been associated with boron toxicity in peaches. The boron critical level for corn is about 4 ppm, while alfalfa, cotton, peanut, and soybeans have critical levels of 20 ppm. Corn, having a fairly low boron requirement, is also sensitive to excess boron. Toxicities may occur when the boron level in young corn leaf tissue exceeds 25 ppm (Yermiyahu*et al.*,2001). Members of the Papilionaceae and Cruciferae have fairly high boron requirements with critical levels being about 25 to 30 ppm boron in the leaf tissue. Those plants which have fairly high boron requirements are also ones with fairly good tolerance to excessive boron. Boron is not a very mobile element and deficiency symptoms occur in the newly emerging tissue. The boron concentration in leaves remains constant during the growth cycle. Boron deficiencies result in various physiological diseases in plants, such as "hollow heart" in peanuts, pitting and cracking in apples, "Hen & Chick" disorder in grapes, blossom blast in pear, gummy nuts in almond etc.

2.11 Various techniques for determination of Boron in soils and plants

Boron (B) is a non-metal, in contrast to the other micronutrient elements. It is present in diminutive amounts in igneous, sedimentary and metamorphic rocks. In areas with geothermal activity, gases flowing from inner earth contain B. Different scientists around the world have developed various proceduresfor boron determination andtheir implementationtotheanalysisofsoilandplantsamples(Wolf,1974; ParkerandGardner,1981;SimsandJohnson,1991;Spouncer*et al.*,1992; Keren,1996;SahandBrown,1997). Currently, B concentration has been evaluated by employing absorption spectrometry,flameatomicemission, neutron scattering testvianeutronradiographyalongwithprompt-activationanalysis,potentiometry,ICP-OEC(inductivelycoupledplasma- optical emission spectrophotometery, chromatography, MS (mass spectrometry) and spectrophotometry.Spectrophotometricprocedure implicatedacolorimetricreactionof Azomethane-HwithBhasbeentheforemostacceptableBestimationtechniqueforplant, soilandwatersamples(Bingham,1982; Wolf,1974; ISO,1996;WHO,2003). Colorimetricprocedures,ordinarily,gothroughfromseveralhindrancesandcomprisereducedperfectionandsensitivity.Inmodernera,theuseofICP–MSandICP–OESforBassessment insoilandplantsampleshaveintensifiesterrifically.Otherstudies alsoshowed thecolorimetricdeterminationsofboronbyusingAzomethane-Hascolourdevelopingreagent(BergerandTruog,1945; Berger, 1949; Ho*et al.*,1991;1986;1988;RenanandGupta,1991). Few researchers investigated variousconcentrationsofBwithinthesoilsolutionbyusingthiscolourdeveloping reagent(Jame*et al.*,1982).

Chapter – 3

MATERIALS AND METHODS

To study the distribution of different forms of Boron, kinetics of its Adsorption-Desorption and its availability, composite soil samples were collected from ten locations representing almost all the districts of Lesser Himalayas (Kashmir Valley). The study area lies between latitude 33^{0}22′12.0″ to 34^{0}49′5.6″ N and longitude 73^{0}46′40.0″ to 75^{0}35′35.0″ E at an elevation ranging from 1582 to 2115 m mean average soil level. The study area comprises of three distinct physiographic zones viz. high altitude zone (HAZ), mid altitude zone (MAZ) and low altitude zone (LAZ). There is a considerable variation in temperature with monthly mean temperature of 18^{0}C and maximum of 33° C in June/July and minimum of – 3^{0}C in January. Soil temperature regime is mesic and moisture regime is udic.

The present investigation entitled, **“Adsorption and Desorption Kinetics of Boron in Kashmir Soils”**, was carried out at SKUAST-K, Shalimar, Srinagar, during 2011-12. The details of the techniques followed and materials used during the course of this investigation are presented as;

3.1 Materials

For investigating the “Adsorption and Desorption Kinetics of Boron in Kashmir Soils”, composite surface soil samples (0-20 cm) were collected from the following locations in Kashmir, differing in their properties. Bulk surface soil samples were also collected from all these locations. The exact locations of these sites and classification according to criteria of soil taxonomy are presented in Table 3.1 and figure 1.

Table 3.1: Taxonomical Classification and Location of soil samples

Sample Code	Location	District	Latitude	Longitude	Elevation (m)	Physiography	Taxonomy*
S_1	Tangmarg	Baramulla	34° 4'3.03"	74°25'56.07"	2107	High Altitude	Fluventic Eutrochrepts
S_2	Khag	Budgam	34° 2'9.90"	74°32'51.84"	1806	Mid Altitude	Fluventic Eutrochrepts
S_3	Anantnag	Anantnag	33°45'5.26"	75°11'38.63"	1623	Low Altitude	Typic Eutrochrepts
S_4	Kulgam	Kulgam	33°39'0.54"	75° 0'17.09"	1763	Mid Altitude	Typic Eutrochrepts
S_5	Tral	Pulwama	33°57'0.22"	75° 7'43.68"	1791	Mid Altitude	Typic Hapludalfs
S_6	Shalimar	Srinagar	34° 9'49.99"	74°51'35.52"	1586	Low Altitude	Typic udifluvent
S_7	Bandipora	Bandipora	34°11'34.43"	74°39'57.70"	1582	Low Altitude	Typic Haplaquepts
S_8	Kangan	Ganderbal	34°15'31.57"	75° 5'43.49"	2115	High Altitude	Typic Udorthents
S_9	Sagipora	Kupwara	34°23'54.89"	74°21'28.37"	1593	Low Altitude	Typic Eutrochrepts
S_{10}	Shopian	Shopian	33°42'33.85"	74°49'33.19"	2088	High Altitude	Dystric Eutrochrepts

***Soil Map NBSS & LUP**

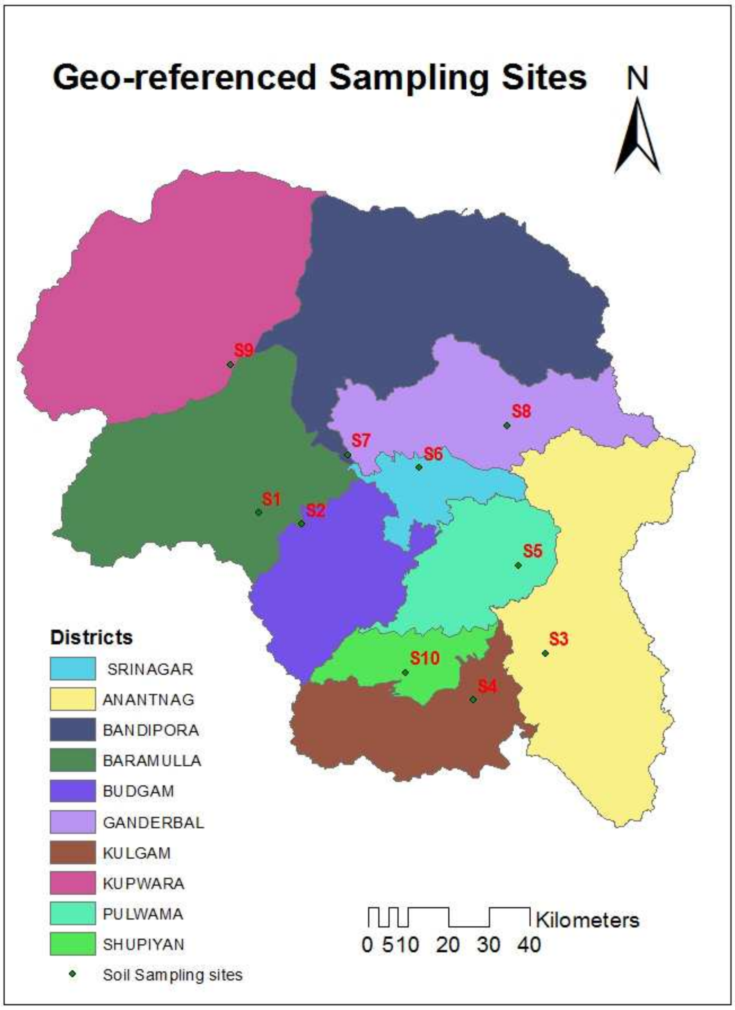


Figure 1: Exact locations of the Soil Sampling Sites

3.2 Preparation of soil samples

The soil samples were air dried in shade, ground with wooden mallet and passed through a 2 mm plastic sieve. For organic carbon determination, the soil was passed through 0.2 mm sieve. After mixing thoroughly, the processed soil samples were stored in polythene bags for laboratory studies.

3.3 Chemical characteristics of soil

3.3.1 Soil reaction (pH)

Soil pH was determined in 1: 2.5 soil: water suspension with digital glass electrode pH meter (Jackson, 1967).

3.3.2Electrical conductivity (EC)

Electrical conductivity of the suspension liquid of 1: 2.5 soil: water suspension was determined with the help of Solu bridge conductivity meter at 25°C (Jackson, 1967).

3.3.3 Cation Exchange Capacity (CEC)

Cation exchange capacity of soil was determined according to the procedure outlined by Rhoades (1982).

3.3.4 Calcium Carbonate ($CaCO_3$)

Calcium carbonate was determined by the method given by Puri (1930). 10 gram of soil in 200 ml distilled water was titrated with 0.5 N ammonium sulphate in presence of bromothymol blue and bromocresol green indicators.

3.3.5 Organic Carbon (OC)

Organic carbon was determined by Walkley and Black’s rapid titration method. 1.0 gram soil was digested with a mixture of potassium dichromate (10 ml) and concentrated sulphuric acid (20ml). The excess of potassium dichromate not reduced by the organic matter of the soil was determined by titration using standard ferrous ammonium sulphate solution in the presence of ortho-phosphoric acid using diphenylamine as an indicator.

3.4 Mechanical analysis

The mechanical analysis of the soil sample was done by following the Hydrometer method (Moodie*et al.,* 1959).

3.5 Extraction of different forms of boron

Boron free polyethylene centrifuge tubes, glassware, and distilled and deionized water was used throughout the study. All the chemicals used were of the Analytical Grade.

3.5.1 Water Soluble Boron

Water soluble boron (WS-B) was extracted by shaking 20 g of soil with 20 ml of deionized water in a 75 ml polyethylene centrifuge tube for two hours (Hatcher & Wilcox, 1950). The contents were centrifuged and the supernatant was preserved in refrigerator for B estimation.

3.5.2 Hot Water soluble Boron

Hot Water soluble Boron (HWS-B) was extracted by the method described by Wear (1965). 20 g of soil was taken in a 250 ml (B-free) Erlenmeyer flask, 40 ml of deionized water and 0.4 g of activated charcoal were added and reflux condenser (water cooled) was attached to the flask. The flask was heated on the hot plate to first sign of boiling, followed by refluxing of the contents exactly for 5 minutes. The contents were allowed to cool and then filtered using Whatman No. 42 (B-free) filter paper.

3.5.3 $CaCl_2$ soluble Boron

$CaCl_2$ soluble Boron was extracted by adding 20 ml of 0.01 M $CaCl_2$and 0.4 g of activated charcoal to 10 g of soil in a 250 ml (B-free) Erlenmeyer flask (Wear, 1965). Reflux condenser was attached to the flask. The mixture was heated on a hot plate for 5 minutes and refluxed thereafter for 5 minutes. When still warm, contents of the flask were filtered through Whatman No. 42 filter paper to get clear extract.

3.5.4 Acid soluble Boron

Acid soluble Boron was determined by extracting10 g of soil with 20 ml of 0.05 N HCl in 50 ml polyethylene centrifuge tube. The contents were shaken on a horizontal shaker for five minutes followed by centrifuging and supernatant solution was preserved for boron estimation (Ponnamperuma *et al.*, 1981).

3.5.5 Leachable Boron

Leachable Boron (adsorbed plus soluble B) was extracted by the method of Rhoades *et al.* (1970b). Five grams of soil was taken in 50 ml polyethylene centrifuge tube and shaken for 16 hours with 25 ml each of 0.01 M Manitol-0.01 $CaCl_2$solution. After centrifuging, the clear supernatant solution was kept in refrigerator for B determination.

3.5.6 AB-DTPA-Boron

AB-DTPA Boron was extracted by adding 20 ml each of 1.0 M NH_4 HCO_3 and 0.005 M DTPA adjusted to pH 7.6 to 10 ml of soil. (Gestring and Soltanpour, 1984).

3.5.7 Total Boron

For extraction of total boron, one gram of soil was fused with 6 g of Na_2CO_3 at 1000^oC in a platinum crucible of 30 ml capacity. The residue was dissolved in 50 ml of 6N HCl according to the modified procedure developed by Gupta (1966). The final volume was made up to 100 ml and subsequently used for analysis of total boron by Azomethane-H method.

3.6 Adsorption-Desorption of Boron

Surface soil samples representing 10 different locations of the valley were selected varying in physical and chemical characteristics for adsorption-desorption study. Boron free centrifuge tubes, glassware and deionized water were used during adsorption-desorption investigation.

3.6.1 Boron Adsorption Study

Adsorbed Boron acts as a buffer pool between solid and solution phase. Solubility of Boron in soil is mainly governed by adsorption process to soil surfaces. To determine adsorbed boron, 20 g of soil sample (in duplicate) was equilibrated with 20 ml of 0.01 M $CaCl_2$ containing 1,2,5,10,20,40,60,80 and 100 mg ml^{-1} of boron (using Boric acid) in 50 ml polyethylene centrifuge tubes, in incubator for 24 hours at 25± 1°C with intermittent shaking. After equilibration, the suspension was centrifuged for 10 minutes, and the supernatant solution was filtered through Whatman No 42 filter paper, following procedure outlined by Erashidi and O'Connor (1982). The boron concentration in the filtrate was determined by the Azomethane–H method (Wolf, 1974), using Spectrophotometer. The amount of boron adsorbed was calculated from the difference between the initial boron and equilibrium boron concentrations.

The data of boron sorption were fitted to the following adsorption equations.

Langmuir equation: $\mathbf{C/(x/m) = 1/b\ (C) + 1/b\ K}$

Freundlich equation: $\mathbf{Log\ (x/m) = 1/n\ Log\ C + Log\ K}$

Where,

C= equilibrium concentration (μg B ml^{-1})

x/m= adsorbed B (μg B g^{-1} soil)

b= adsorption maxima (μg B g^{-1} soil)

k= a constant related to bonding energy (mlμg^{-1})

1/n= slope of the regression line, and

K & n= empirical constants

3.6.2 Boron Desorption Study

The boron desorption was studied by adding 20 ml of Boron free 0.01 M $CaCl_2$ to each soil sample after the adsorption study. The mixture was re-suspended by vigorous agitation and equilibrated for 24 hours at 25± 1° C, with intermittent shaking on rotary shaker. The suspension was centrifuged for 10 minutes and the supernatant was removed for B analysis. The process was repeated for three more times, resulting in a total of four desorptions for each adsorption sample. The boron concentration in the filtrate was determined through Azomethane –H method, using Spectrophotometer. The amount of boron desorbed was calculated as the difference between equilibrium boron concentrations at each desorption step and the equilibrium concentration previous to each desorption step.

The amount of boron retained (x/m) by soil during desorption was calculated as the difference between amount of boron retained in previous step and boron desorbed in the present step. The data obtained pertaining to the retained boron (x/m) by the soil during desorption at the corresponding equilibrium concentrations were fitted into Langmuir's equation, given below;

$$\mathbf{De/S = 1/\,Kd\,Dm + De/Dm}$$

Where,

S = Boron adsorbed (μg g^{-1})

De = Boron desorbed (μg g^{-1})

Dm= desorption maxima (μg g^{-1})

Kd = constant related to mobility of boron (ml g^{-1})

Dm (desorption maxima) and Kd (constant related to mobility of solid phase) were worked out from the linear plots of De vs. De/S according to the Langmuir desorption relationship.

3.7. Kinetics of Boron Adsorption-Desorption

Adsorption-desorption kinetics of boron was studied on the surface soil samples representing ten soils of Kashmir, varying in physical and chemical properties.

3.7.1. Adsorption Kinetics

Adsorption reactions of boron in soils are important for retention and release of boron for plant nutrition. For adsorption kinetic study, 10 g of soil sample in triplicate was taken in 50 ml polyethylene centrifuge tubes, and 10 ml of 0.01 M $CaCl_2$ solution containing 40 μg B ml^{-1} was added to each tube. The samples were equilibrated at 25± 1° C for 0, 1, 2, 4, 8, 16, 24, 48 and 72 hours on a reciprocating shaker. At the end of reaction time, the suspension was centrifuged for 20 minutes. The samples were filtered using Whatman's No.42

filter paper. The boron concentration was determined using Azomethane –H method as per the procedure outlined by Wolf (1974). The amount of Boron adsorbed was calculated from the difference between the amount initially added and the quantity remaining in solution after equilibration.

3.7.2. Desorption Kinetics

The soil samples used for adsorption kinetics after 48 hours were equilibrated with 0.05M mannitol in the same centrifuge tube. The mixture was equilibrated at 25± 1° C for 0, 1, 2, 4, 8, 16, 24, 48 and 72 hours on end to end shaker, followed by centrifugation for 10 minutes. The samples were filtered using No. 42 Whatman's filter paper and kept in refrigerator for B analysis. The boron concentration in the filtrate was determined using Azomethane –H method (Wolf, 1974).

3.8. Rate of Adsorption and Desorption Reaction

To find out the rate of adsorption-desorption reaction, the following integrated rate equation was used;

$$\mathbf{Log\ (B_0\text{-}C) = Log\ B_0\text{-}\ (K/2.303)t}$$

Where,

B_0 = Total adsorable /desorable B (µg B g^{-1} soil)

C= Concentration of adsorbed/desorbed B (µg B g^{-1} soil)

t = Time of adsorption/ desorption.

K = Rate constant

In case the plot of Log (B_0-C) versus time (t) follows a linear relationship, then the reaction is pseudo-first order with respect to B concentration. The slope of the line will be K/2.303 and intercept will be the log of total B concentration of the solid phase at the start of the particular reaction.

The various other kinetic models used to describe Boron adsorption/ desorption from soils were tested for goodness of fit by least square regression analysis. These are;

1) Zero order

$qt = q_0 + K_0t$

Where $K_0$is the zero order rate constant [(mg B kg^{-1}) S^{-1}]

2) First order

$Lnqt = lnq_0 + K_1t$

Where $K_1$is the first order rate constant [S^{-1}]

3) Second order

$1/qt = 1/q_0 - K_2t$

Where $K_2$is the second order rate constant [(mg B Kg^{-1}) S^{-1}]

4) Parabolic Diffusion

$q = \alpha + Kdt^{½}$

WhereKd is the Diffusion rate constant [(mg B Kg^{-1}) $S^{-1/2}$]

5) Elovich

$q_t = q_0 + (1/B)ln - (\alpha B) + (1/\beta) lnt$

Whereα is the initial B adsorption rate (mg B Kg^{-1} h^{-1}) and β is B desorption constant (mg B Kg^{-1} h^{-1})

6) Power function

$lny = ln a + b ln t$

Where y is the quantity of boron adsorbed/desorbed at time ‘t’ and a & b are constants (Dalal, 1974).

In all equations, q_0 and q_t are the amount of Boron adsorbed (mg B Kg^{-1}) at time zero and t, respectively. To determine the equation that best described the adsorption of boron in soils, a standard Error of estimate was calculated for each equation. A relatively high value of the coefficient of determination (R^2) and low standard error (SE) was used as criteria for the best fit (Chien and Clayton, 1980). The Standard Error was calculated as follows;

$$SE = [\Sigma (q-q')^2 / (N-2)]^{0.5}$$

Where q & q' are the measured and calculated amounts of B in soil, respectively at time‘t’ and N is the number of measurements (Steel and Torrie, 1960).

3.9. Estimation of boron in soil extract

Boron in soil extract was estimated calorimetrically using Azomethane-H method, originally given by Shanina *et al.* (1967) and later on modified by Wolf (1974), John *et al.* (1975) and Gupta (1979b).

For this purpose, 1.0 ml of the extract was taken in a 10 ml polyethylene tube. To that 2 ml of buffer solution (EDTA-disodium salt) and 2 ml of Azomethane-H solution was added. The contents were mixed by inverting the tubes three times and were allowed to stand for one hour after which absorbance was read at 420 nm using spectrophotometer. The amount of boron in the extract was calculated from the standard curve prepared by taking standard solutions containing 0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0 and 4.0 ppm boron.

3.10. Pot Culture Experiment

A pot culture experiment was conducted using bulk surface (0-15 cm) soil samples collected from 10 sites varying in physical and chemical characteristics to know the response of Boron application to Berseem (*Trifolium alexandrium*) crop and also to estimate the critical level of Boron to separate boron deficient soils from non-deficient soils. Soils were air dried ground and sieved through 2 mm plastic sieve and mixed thoroughly.

Polyethylene lined pots were filled with 4-5 kg of soil after giving the treatments and thoroughly mixing them. Treatments comprised of 0, 1 and 2 mg B kg^{-1} soil using borax. The basal dose of nitrogen, phosphorus and potassium was applied through urea, DAP and MOP, respectively. Each treatment was replicated thrice. The pots were watered to bring the soil to 100 % saturation. Twenty five healthy seeds of berseem (cv. Multicut) were sown in each pot on 4^{rth} of October, 2011. Thinning was done after one week of germination to maintain twenty plants per pot. Uprooted plants were buried in the same pots and pots were irrigated as and when required with de-ionized water.

The above ground part of the crop was harvested at 60 days of growth for first cutting, followed by the second cut at 30 days after first cut. Fresh weight was recorded at both cuttings. The plant samples were successively and thoroughly washed with tap water, 0.1 N HCl, distill water and finally with de ionized water. The samples were dried in oven at 65°C, and dry weight was also recorded. The samples were ground and finally stored for analysis.

3.11. Estimation of boron in plant samples

Total boron content of the plant was determined by dry ashing according to the method outlined by Gains & Mitchell, 1979. In a silica crucible, 0.5 g of dried plant sample was placed and ashed at 550°C in a muffle furnace. The grey white ash was dissolved in 10 ml of 6 N HCl and heated to 80°C on hot plate to evaporate to dryness. The residue was dissolved in de-ionized water and was transferred to 25 ml volumetric flask and volume was made to mark with de ionized water. The solution was then filtered through Whatman No.42 filter paper. The boron in the extract was determined by using Azomethane-H method as proposed by Gupta (1979b).

3.12. Establishment of Critical Level

To determine critical level of boron in soil and berseem crop, Bray’s percent yield and percent uptake were computed as described by Bray (1948) method as under;

$$\text{Bray's \% yield} = \frac{\text{Yield without B treatment}}{\text{Yield with optimum Btreatment}} \times 100$$

$$\text{Bray's \% Buptake} = \frac{\text{B-uptake without B treatment}}{\text{B-uptake with optimum B treatment}} \times 100$$

The plant and soil critical concentration of boron was established by graphical procedure (Cate & Nelson, 1965). Average per cent yield response of Berseem to B-application was also determined.

Statistical Analysis

Statistical analysis including simple and multiple correlation coefficients were worked out between various soil properties, forms of Boron and adsorption/desorption parameters as per the details described by Cochran and Cox (1957).

Statistical analysis of soil, plant composition and yield were done according to the methods outlined by Panse and Sukhatme (1967).

Chapter – 4

EXPERIMENTAL FINDINGS

The results of different experiments carried out in the present investigation are presented under the following heads:

- 4.1 Distribution of different forms of boron in soils.
- 4.2 Boron adsorption-desorption by soils
- 4.3 Kinetics of boron adsorption-desorption
- 4.4 Response of Berseem to boron and its critical limits in soils and plants

The physico-chemical characteristics of different soils investigated, varied widely (Table 4.1) in texture (silt loam to silty clay loam), pH (5.6 to 7.8), EC (0.11 to 0.36 dS m^{-1}), organic carbon (0.98 to 3.93 per cent), calcium carbonate (0.01 to 1.28 %) and cation exchange capacity (10.48 to 18.17 $cmol_c$ kg^{-1}).

4.1 Distribution of different forms of boron in soils

The distribution of different forms of boron in the soils of Kashmir was studied in ten soils representing major areas of Kashmir (Table 3.1and Fig 1).

4.1.1 Water Soluble Boron

The concentration of water soluble boron in the soil samples ranged from 0.07 to 0.95 mg kg^{-1} with a mean value of 0.35 mg kg^{-1} (Table 4.2). There was no specific distribution pattern in water soluble boron concentration.

Table-4.1Physico-chemical characteristics of different soils of Kashmir

Parameters	**Locations**									
	(S_1)	**(S_2)**	**(S_3)**	**(S_4)**	**(S_5)**	**(S_6)**	**(S_7)**	**(S_8)**	**(S_9)**	**(S_{10})**
pH (1:2.5)	6.1	6.5	7.8	5.9	6.4	5.6	6.2	6.2	7.2	5.8
EC (dSm^{-1})	0.12	0.21	0.36	0.15	0.19	0.13	0.11	0.19	0.22	0.19
OC (%)	3.93	1.17	0.98	2.80	1.33	2.57	1.72	1.76	1.01	2.69
$CaCO_3$ (%)	1.28	0.68	0.03	0.12	0.85	0.01	0.58	0.66	0.72	1.20
CEC [$cmol_c\ kg^{-1}$]	15.32	16.20	18.17	11.85	17.30	16.11	14.63	11.63	17.64	10.48
Coarse sand (%)	1.12	0.96	1.23	0.98	1.18	1.15	1.10	0.95	1.47	1.36
Fine sand (%)	19.08	26.64	15.77	28.02	18.62	34.05	32.20	27.65	14.53	40.64
Silt (%)	45.20	42.45	46.64	52.55	44.30	30.20	39.20	51.40	47.50	27.00
Clay (%)	34.60	29.95	36.36	18.45	35.90	34.60	27.50	20.00	36.50	31.00
Textural class	Silty clay loam	Clay loam	Silty clay loam	Silt loam	Silty clay loam	Clay loam	Clay loam	Silt loam	Silty clay loam	Clay loam

The concentration of water soluble boron was considerably higher in the soil of Sagipora, 0.95 mg kg^{-1}), followed by Anantnag soil (0.86 mg kg^{-1}), Tangmarg soil (0.34 mg kg^{-1}), Tral soils (0.34 mg kg^{-1}), Kulgam soil (0.25 mg kg^{-1}), Khag soil (0.22 mg kg^{-1}), Shopian soils (0.22 mg kg^{-1}), Kangan soil (0.15 mg kg^{-1}), Shalimar soil (0.10 mg kg^{-1}) and Bandipora soil (0.07 mg kg^{-1}) in descending order. The average concentration of water soluble boron was maximum in Sagipora soils (0.95 mg kg^{-1}) and minimum in Bandipora soil (0.07 mg kg^{-1}). It was seen that the percent contribution of water soluble boron to total boron is 0.74 (Table 4.3).

Clay and silt contents were positively and significantly correlated with water soluble boron content with coefficient values of r = 0.572** and 0.374**, respectively, whereas relationship of water soluble boron with sand content was negatively significant (r=-0.813**) (Table 4.4).

Water soluble boron content was also found to be significantly related with pH (r=0.860**) and EC (r=0.609**). There was a negative but significant correlation between water soluble content and organic carbon content (r= -0.451*). Calcium carbonate content was non-significantly related to water soluble boron content (r=0.030). The cation exchange capacity showed positive and significant correlation to water soluble boron (r = 0.602**).

The regression equation of water soluble boron (Equation 1, Table 4.6) clearly indicates the eighty two (82) percent variation in water soluble boron content, was due to soil properties like pH, EC, Organic Carbon, CEC, $CaCO_3$, sand and silt content of the soils.

Table - 4.2 Different forms of boron in different soils of Kashmir under investigation

Soils	Water soluble	Hot Water soluble	$CaCl_2$ extractable	Acid extractable	Leachable	AB-DTPA extractable	Total
				mg kg^{-1}			
S_1	0.34	0.41	0.58	0.63	0.88	1.08	48.52
S_2	0.22	0.47	0.64	0.51	0.94	1.14	44.84
S_3	0.86	0.78	0.95	1.15	1.25	1.45	49.36
S_4	0.25	0.29	0.46	0.54	0.76	0.96	45.64
S_5	0.34	0.48	0.65	0.63	0.95	1.15	47.82
S_6	0.10	0.18	0.35	0.39	0.65	0.85	43.78
S_7	0.07	0.10	0.27	0.36	0.57	0.77	42.46
S_8	0.15	0.13	0.30	0.44	0.60	0.80	41.86
S_9	0.95	1.27	1.44	1.24	1.74	1.94	50.55
S_{10}	0.22	0.47	0.69	0.51	0.94	1.19	40.72
Mean	**0.35**	**0.46**	**0.63**	**0.64**	**0.93**	**1.13**	**45.46**

Table - 4.3 Per cent contribution of different forms of boron to total boron

Soils	Water soluble	Hot water soluble	$CaCl_2$ extractable	Acid extractable	Leachable	AB-DTPA extractable
S_1	0.70	0.85	1.20	1.30	1.81	2.23
S_2	0.49	1.05	1.43	1.14	2.10	2.54
S_3	1.74	1.58	1.92	2.33	2.53	2.94
S_4	0.55	0.64	1.01	1.18	1.67	2.10
S_5	0.71	1.00	1.36	1.32	1.99	2.40
S_6	0.23	0.41	0.80	0.89	1.48	1.94
S_7	0.16	0.24	0.64	0.85	1.34	1.81
S_8	0.36	0.31	0.72	1.05	1.43	1.91
S_9	1.88	2.51	2.85	2.45	3.44	3.84
S_{10}	0.54	1.15	1.69	1.25	2.31	2.92
Mean	0.74	0.97	1.36	1.38	2.01	2.46

4.1.2 Hot Water Soluble Boron

Results on hot water soluble boron in different soils (Table 4.2) showed that it varied from 0.10 to 1.27 mg kg^{-1} soil, with a mean value of 0.46 mg kg^{-1} soil. Higher content of hot water soluble boron (1.27 mg kg^{-1}) was found in Sagipora soil, followed by Anantnag soil (0.78 mg kg^{-1}), Tral soil (0.48 mg kg^{-1}), Khag soil (0.47 mg kg^{-1}), Shopian soil (0.47 mg kg^{-1}), Tangmarg soil (0.41 mg kg^{-1}), Kulgam soil (0.29 mg kg^{-1}), Shalimar soil (0.18 mg kg^{-1}), Kangan soil (0.13 mg kg^{-1}), and Bandipora soil (0.10 mg kg^{-1}). Per cent contribution of hot water soluble boron to total boron was found to be 0.97 (Table 4.3).

The clay content was positively and significantly correlated (r = 0.477*) with hot water soluble boron content of soil. The relationship between organic carbon and hot water soluble boron was negatively and significantly correlated with each other (r = -0.362*) (Table 4.4). Calcium carbonate content of soil showed non-significant negative correlation (r= -0.095) with hot water soluble boron. The silt content showed positive and significant correlation with hot water soluble boron (r= 0.419*) whereas relationship with sand content was negatively significant (r= -0.783**). Cation exchange capacity also showed positive and significant correlation (r= 0.492*) with hot water soluble boron. Hot water soluble boron showed positive and highly significant correlation with pH and EC of the soil (r=773** and 0.589**, respectively).

The hot water soluble boron content in the soils investigated was largely controlled by soil properties. It is evident from the regression equation 2 (Table 4.6) that 70 per cent variations in hot water soluble boron was due to soil properties studied and significant effect was of pH, EC and CEC.

Table - 4.4Coefficient of Correlation between different forms of Boron and physico-chemical characteristics of soils

Forms of Boron	pH	EC	CEC	Organic carbon	$CaCO_3$	sand	Silt	Clay
Water soluble	0.860**	0.609**	0.620*	-0.451*	0.030	-0.813**	0.374*	0.572**
Hot water soluble	0.773**	0.589**	0.492*	-0.362*	-0.095	-0.783**	0.419*	0.477*
$CaCl_2$extractable	0.742**	0.593**	0.510*	-0.432*	0.110	-0.608**	0.163	0.576**
Acid extractable	0.637**	0.520**	0.359	-0.148	0.460*	-0.677**	0.242	0.564**
Leachable-B	0.576**	0.610**	0.140	-0.140	0.327	-0.486*	0.203	0.362
AB-DTPA extractable	0.874**	0.684**	0.663**	-0.436*	0.043	-0.463**	0.399*	0.580**
Total	0.686**	0.421*	0.766**	-0.219	-0.080	-0.928**	0.498*	0.563*

* Significant at 5 % level of significance

** Significant at 1 % level of significance

Table -4.5 Coefficient of Correlation among different forms of boron

Forms of Boron	Water soluble	Hot water soluble	$CaCl_2$ extractable	Acid extractable	Leachable	AB-DTPA extractable
Total	0.220	0.051	0.246	0.093	0.295	0.170
AB-DTPA extractable	0.995**	0.958**	0.903**	0.833**	0.762**	
Leachable	0.795**	0.811**	0.842**	0.893**		
Acid extractable	0.847**	0.881**	0.803**			
$CaCl_2$ extractable	0.913**	0.897**				
Hot water soluble	0.952**					

* Significant at 5 % level of significance

** Significant at 1 % level of significance

Table - 4.6 Regression equations between different forms of Boron and physico-chemical characteristics of soils

		Regression equation	**R^2**
Water soluble	=	5.89+0.361(pH) –1.76 (EC)-0.161(CEC)-0.040(OC)-0.324($CaCO_3$)-0.085(sand)-0.0521(silt)	82%
Hot water soluble	=	8.69+0.221(pH) –2.18 (EC)-0.197(CEC)-0.118(OC)-0.311($CaCO_3$)-0.0969(sand)-0.0559(silt)	70%
$CaCl_2$extractable	=	8.1+0.417(pH) –2.71 (EC)-0.206(CEC)-0.139(OC)-0.290($CaCO_3$)-0.0988(sand)-0.0689(silt)	77%
Acid extractable	=	5.63+0.0713(pH) –0.106 (EC)-0.108(CEC)-0.0300(OC)+0.0115($CaCO_3$)-0.0584(sand)-0.0336(silt)	97%
Leachable	=	4.54+0.032(pH) +0.58 (EC)-0.0923(CEC)-0.0187(OC)-0.025($CaCO_3$)-0.0418(sand)-0.0245(silt)	85%
AB-DTPA extractable	=	4.54+0.032(pH) +0.58(EC)-0.0923(CEC)-0.0187(OC)-0.025($CaCO_3$)-0.0634(sand)-0.0376(silt)	84%

4.1.3 Calcium Chloride extractableBoron

Perusal of data presented in Table 4.2 showed that 0.01 M $CaCl_2$ extractable boron in different soils range between 0.27 to 1.44 mg kg^{-1} with an average value of 0.63 mg kg^{-1} soil. The $CaCl_2$ extractable boron content in the soils investigated was in the order of Sagipora>Anantnag>Shopian> Tral>Khag>Tangmarg>Kulgam>Shalimar>Kangan>Bandipora with the values of 1.44, 0.95, 0.69, 0.65, 0.64, 0.58, 0.46, 0.35, 0.30, and 0.27 mg kg^{-1} soil, respectively. Calcium chloride boron contributed 1.36 per cent to total boron content (Table 4.3).

Calcium chloride extractable boron was positively and significantly correlated with pH (r= 0.742**) and EC (r= 0.593**) of the soil. The clay content was positively and significantly correlated (r= 0.576**) with calcium chloride soluble boron while as silt content was positively and non-significantly correlated (r= 0.163) with calcium chloride soluble boron. Significant negative correlation (r= -0.432*) was observed between $CaCl_2$-soluble boron and organic carbon content of soils. Calcium Carbonate showed non-significant relationship (r= 0.110) with $CaCl_2$ extractable boron. Positive and significant correlation (r= 510*) between cation exchange capacity and $CaCl_2$ extractable boron was observed (Table 4.4) while as significant and negative relationship was observed between $CaCl_2$ extractable boron and sand content of soils (r= -0.608**).

The regression equation 3 (Table 4.6) indicated that 77 per cent variation in the $CaCl_2$ extractable boron was largely controlled by the soil factors given in the equation. Organic carbon showed significant effect.

4.1.4 Acid extractableBoron

The content of boron extracted in 0.05 N HCl varied from 1.24 to 0.36 mg kg^{-1} soil with an average value of 0.64 mg kg^{-1} soil (Table 4.2). The acid soluble boron was higher than water soluble, hot water soluble and calcium chloride extractable boron. The data in table 4.2 showed that there was wide variation in acid soluble boron concentrations in different soils. Acid soluble boron was maximum in the soils of Sagipora (1.24 mg kg^{-1} soil) while minimum in Bandipora soils (0.36 mg kg^{-1}).

On an average the acid soluble boron content of the soils were 0.63, 0.51, 1.15, 0.54, 0.63, 0.39, 0.36, 0.44, 1.24 and 0.51 mg kg^{-1} soil in Tangmarg, Khag, Anantnag, Kulgam, Tral, Shalimar, Bandipora, Kangan, Sagipora and Shopian soils, respectively. Acid soluble boron fraction of the soils contributed 1.38 per cent to the total boron fraction of the soils (Table 4.3).

There was a significant positive curvilinear correlation between 0.05 N HCl extractable boron and clay (r= 0.564**), pH (r= 0.637**) and EC (r= 0.520**) of the soils (Table 4.4). The acid extractable boron was positively and significantly related with calcium carbonate content of the soils (r= 0.460*). Organic carbon content of the soils was negatively and non-significantly correlated (r= -0.148) with acid extractable boron. There was positive and non-significant correlation (r= 0.359) between cation exchange capacity and acid soluble boron. A negative but significant correlation (r= -0.677**) was observed between acid soluble boron and sand content of the soils under study. The results clearly revealed that available forms of boron (water soluble, hot water soluble, calcium chloride extractable and acid extractable) were mainly associated with clay fraction followed by pH and EC of the soils studied.

The water soluble, hot water soluble, calcium chloride extractable and 0.05 N HCl extractable boron were found to be highly and significantly correlated with each other (Table 4.5).

The regression equation 4 (Table 4.6) clearly indicates that 97 per cent variation in 0.05 N HCl extracted boron was due to soil properties like pH, EC, $CaCO_3$, CEC, sand, and silt content of the soil. The clay content was highly related to the variation.

4.1.5 Leachable Boron

The leachable boron consists of “adsorbed plus soluble boron” (Rhoades *et al.*, 1970b). It ranged from 0.57 to 1.74 mg kg^{-1} soil with a mean value of 0.93 mg kg^{-1} soil (Table 4.2). The content of leachable boron was maximum in soils of Sagipora (1.74 mg kg^{-1}), followed by Anantnag (1.25 mg kg^{-1}), Tral (0.95 mg kg^{-1}), Khag (0.94 mg kg^{-1}), Shopian (0.94 mg kg^{-1}), Tangmarg (0.88 mg kg^{-1}), Kulgam (0.76 mg kg^{-1}), Shalimar (0.65 mg kg^{-1}), Kangan (0.60 mg kg^{-1}) and Bandipora (0.57 mg kg^{-1}) in descending order. Per cent contribution of leachable boron fraction to the total boron fraction of soils was found to be 2.01 (Table 4.3).

Leachable boron was significantly and positively correlated with pH (r= 0.576**) and EC (0.610**) following curvilinear relationships with these parameters (Table 4.4). Non-significant but negative correlation was found between organic carbon (r= -0.140) and leachable Boron. There was also a significant and negative correlation between sand (r= -0.486*) and leachable boron. A positive but non-significant correlation was also observed between CEC (r= 0.140), $CaCO_3$ (r= 0.327), silt (r= 0.203) and clay (r= 0.362) and leachable boron.

There were highly positive relationships of leachable boron with water soluble, hot water soluble, $CaCl_2$extractable, 0.05 N HCl extractable forms of boron (Table 4.5).

The regression equation 5 (Table 4.6) showed that 85 per cent variation in leachable boron was controlled by soil factors given in the equation.

4.1.6 Ammonium Bicarbonate-DTPA Extractable Boron

The recently developed AB-DTPA (Ammonium bicarbonate-diethylenetriaminepenta acetic acid) extractant has proven to be effective for boron on alkali soils (Gupta, 1993). The extractant consists of 1.0 M

$NH_4HCO_3$and 0.005 M DTPA, maintaining the pH to 7.6 (Soltanpour and Workman, 1979).

In the soil samples, the concentration of AB-DTPA extractable boron ranged from 0.77 to 1.94 mg kg^{-1} soil with a mean value of 1.13 mg kg^{-1}soil (Table 4.2).The concentration of AB-DTPA extractable boron in the soils was in the order of Sagipora> Anantnag> Shopian> Tral> Khag> Tangmarg> Kulgam> Shalimar> Kangan> Bandipora, where it was found as, 1.94, 1.45, 1.19, 1.15, 1.14, 1.08, 0.96, 0.85, 0.80 and 0.77 mg kg^{-1} soil, respectively. AB-DTPA soluble boron fraction contributed 2.46 per cent to the total boron fraction of the soils (Table 4.3).

pH and EC were significantly and positively correlated with coefficient values of r= 0.874** and r= 0.684**, respectively (Table 4.4). Positive and significant correlation was observed between silt (r= 0.399**) and AB-DTPA boron, while as clay content observed highly significant and positive correlation (r= 0.580**) with AB-DTPA boron. Organic carbon was significantly and negatively correlated (r= -0.436*) with AB-DTPA boron. This form was also positively and significantly correlated with cation exchange capacity (r= 0.663**) of the soils. The sand fraction was also significantly and negatively correlated with AB-DTPA boron (r= -0.463*). It was interesting to note that this form of boron was also significantly correlated with other forms of boron (Table 4.5).

The regression equation 6 (Table 4.6) revealed that 84 per cent of variation in AB-DTPA boron was largely controlled by the soil properties studied.

4.1.7 Total Boron

Although total boron does not affect the plant growth and its concentration is low as compared to other forms of boron, but it helps in knowing its potential reserve in the soil. The data in Table 4.2 show that total boron content ranged from 40.72 to 50.55 mg kg^{-1} soil with an average value of

45.46 mg kg^{-1} soil (Table 4.2). The higher content of total boron (50.55 mg kg^{-1}) was observed in Sagipora soil, followed by 49.36 mg kg^{-1} in Anantnag soil, 48.52 mg kg^{-1} in Tangmarg soil, 47.82 mg kg^{-1} in Tral soil, 45.64 mg kg^{-1} in Kulgam soil, 44.84 mg kg^{-1} in Khag soil , 43.78 mg kg^{-1} in Shalimar soil, 42.46 mg kg^{-1} in Bandipora soil, 41.86 mg kg^{-1} in Kangan soil and 40.72 mg kg^{-1} in Shopian soil.

Total boron content of soils depends upon the parent material (Aubert and Pinta, 1977). Soils derived from sedimentary rocks contain higher content of boron. The perusal of Table 4.4 showed that total boron content was significantly correlated with pH (r= 0.686**), EC (r= 0.421*), CEC (r= 0.766**), silt (r= 0.498*) and clay (r= 0.563**) of the soil. There is negative and significant correlation between total boron and sand (r= -0.928**) and non-significant negative correlation with organic carbon (r= -0.219) and $CaCO_3$ (r= -0.080).

The total boron content was non-significantly correlated with all the forms of boron (Table 4.4). The relationships among various forms of boron extracted with different extractants are shown in Table 4.5. All forms of boron were well correlated with each other. Generally higher correlations were found when most commonly used hot water soluble boron was correlated with water soluble boron (r= 0.952**), 0.01 M $CaCl_2$ soluble boron (r= 0.897**), leachable boron (r= 0.811**), 0.05 N HCl soluble boron (r= 0.881**) and AB-DTPA boron (r= 0.958**).

The 0.01 M $CaCl_2$ soluble form of boron was highly and significantly correlated with water soluble boron (r= 0.913**), AB-DTPA boron (r= 0.903**), leachable boron (r= 0.842**) and 0.01N HCl soluble boron (r= 0.803**).

Acid soluble form of boron was also significantly correlated with leachable boron (r= 0.893**), water soluble boron (r= 0.847**), hot water soluble boron (r= 0.881**), AB-DTPA boron (r= 0.833**).

Leachable boron showed significantly higher correlation with water soluble boron (r= 0.795**) and AB-DTPA boron (r= 0.762**).

4.2 Boron adsorption-desorption by soils

4.2.1 Adsorption of boron by soils

Surface samples representing ten soils of Kashmir were used for the study of boron adsorption. The results of boron adsorption by these soils are shown in Table 4.7 and Fig. 2. The results of boron adsorption clearly showed that all the soils have affinity for boron adsorption. The amount of boron adsorbed for all the soils were plotted against the equilibrium boron concentration to obtain the adsorption isotherms, indicating the effect of boron concentration on boron adsorption. The adsorption isotherms indicated that though the adsorption of boron increased with increasing concentration in equilibrium solution, yet the percentage adsorbed boron decreased (Fig 2) the amount of boron adsorbed is different for different soils. The adsorption isotherms were L-shaped in the soils studied.

The data on boron adsorption by different soils is presented in Table 4.7 showed that the adsorption capacity of different soils for boron was different and behaviour of adsorption of boron by different soils was not uniform in whole concentration range.

Adsorption of boron was found to be maximum in the Sagipora soils, and Khag soils have the least adsorption capacity for boron. The data of boron adsorption (Table 4.7) when analysed statistically showed that adsorption of boron by these soils were positively and significantly correlated with clay content (r=0.906**), CEC (r=0.726**) and negatively and non-significantly with organic carbon (r=-0.222) of the soils.

Table - 4.7 Amount of boron adsorbed (µg g^{-1} soil) in different soils treated with different concentrations of boron

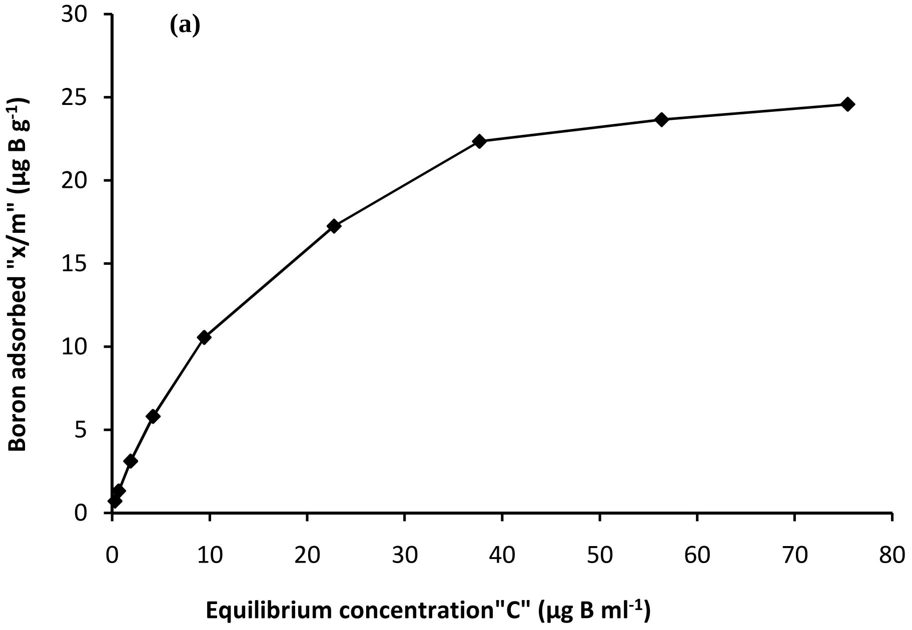
Initial B added (µg B mL^{-1})	Equilibrium Concentration (C)	B adsorbed (x/m)	% B adsorbed
S_1			
1	0.37	0.77	77.00
2	0.48	1.52	76.00
5	1.32	3.68	73.60
10	3.54	6.46	64.60
20	7.56	12.44	62.20
40	20.12	19.88	49.70
60	35.8	24.2	40.33
80	52.7	27.3	34.13
100	71.25	28.75	28.75
S_2			
1	0.29	0.71	71.00
2	0.65	1.35	67.50
5	1.89	3.11	62.20
10	4.2	5.8	58.00
20	10.1	9.9	49.50
40	23.87	16.13	40.33
60	40.78	19.22	32.03
80	59.4	20.6	25.75
100	78.65	21.35	21.35

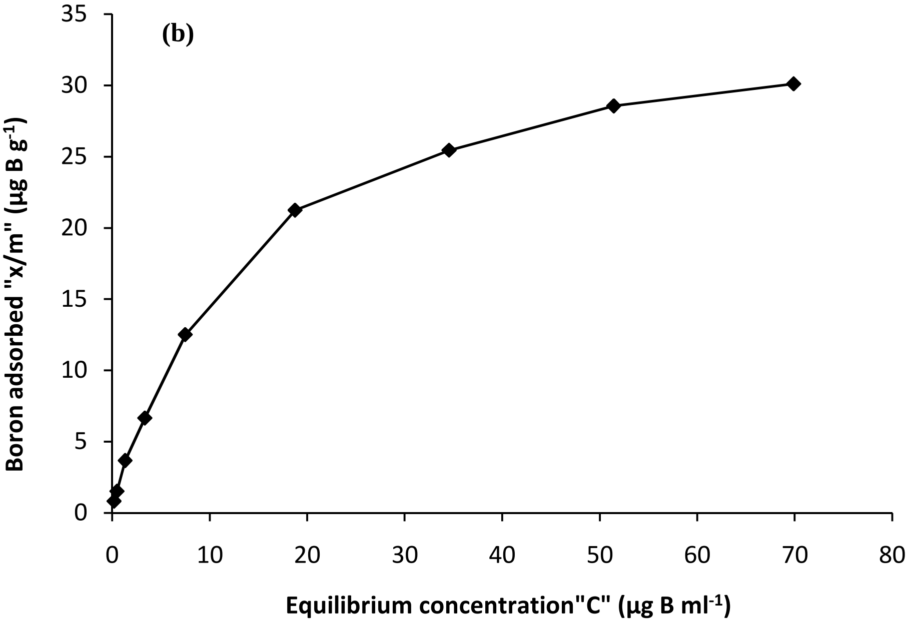
S_3			
1	0.22	0.78	78.00
2	0.498	1.502	75.10
5	1.48	3.52	70.40
10	3.76	6.24	62.40
20	7.82	12.18	60.90
40	20.89	19.11	47.78
60	37.2	22.8	38.00
80	53.9	26.1	32.63
100	71.7	28.3	28.30
S_4			
1	0.33	0.67	67.00
2	0.72	1.28	64.00
5	1.98	3.02	60.40
10	4.5	5.5	55.00
20	9.8	10.2	51.00
40	21.1	18.9	47.25
60	36.34	23.66	39.43
80	54.8	25.2	31.50
100	73.54	26.46	26.46

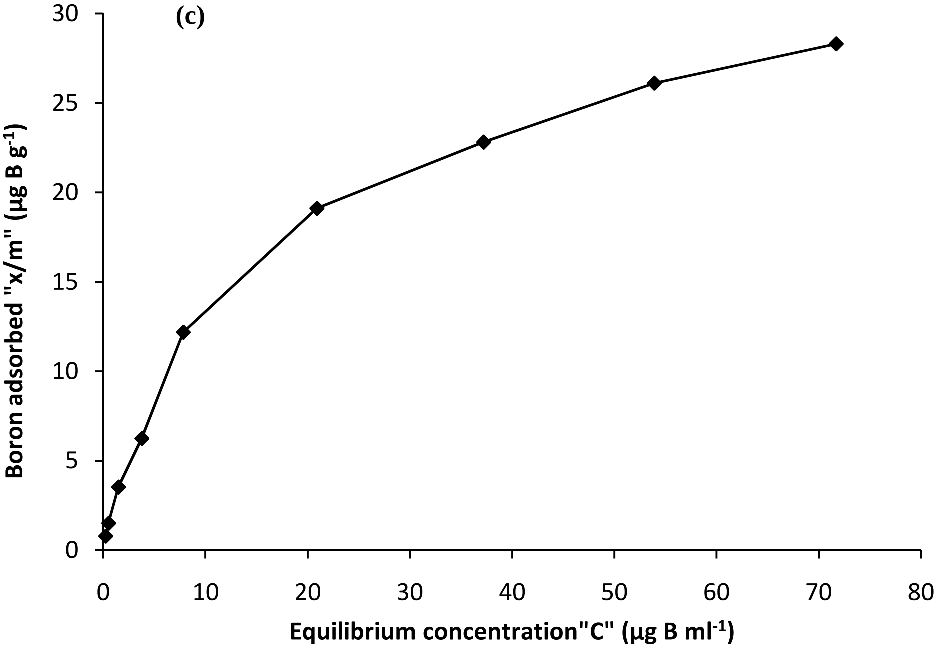
S_5			
1	0.23	0.77	77.00
2	0.49	1.51	75.50
5	1.352	3.648	72.96
10	3.49	6.51	65.10
20	8.2	11.8	59.00
40	19.87	20.13	50.33
60	35.5	24.5	40.83
80	53.3	26.7	33.38
100	73.1	26.9	26.90
S_6			
1	0.26	0.74	74.00
2	0.54	1.457	72.85
5	1.52	3.48	69.60
10	3.75	6.25	62.50
20	7.89	12.11	60.55
40	19.87	20.13	50.33
60	34.90	25.1	41.83
80	52.80	27.2	34.00
100	70.1	29.9	29.90

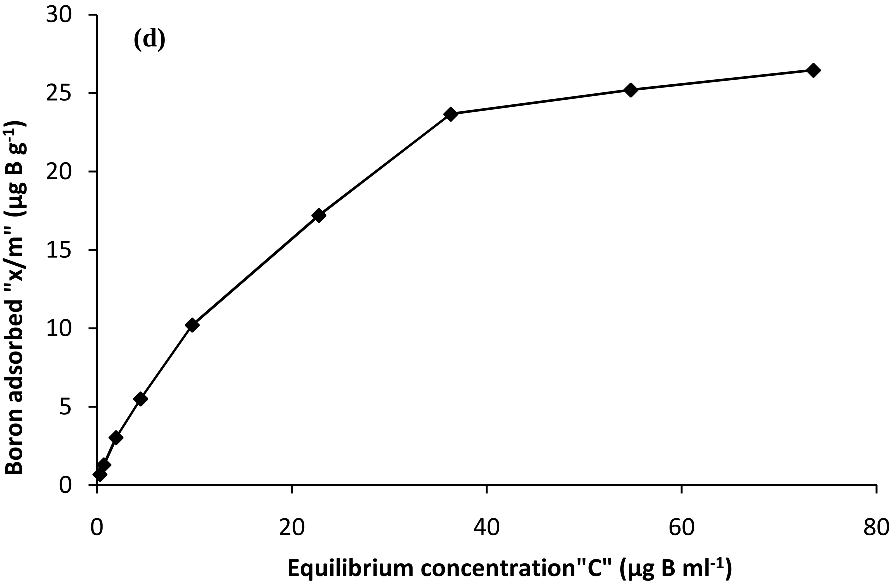
S_7			
1	0.3	0.7	70.00
2	0.68	1.32	66.00
5	1.9	3.1	62.00
10	4.2	5.8	58.00
20	9.45	10.55	52.75
40	22.76	17.24	43.10
60	37.67	22.33	37.22
80	56.35	23.65	29.56
100	75.43	24.57	24.57
S_8			
1	0.31	0.69	69.00
2	0.68	1.32	66.00
5	1.99	3.01	60.20
10	4.8	5.2	52.00
20	10.1	9.9	49.50
40	22.7	17.3	43.25
60	38.1	21.9	36.50
80	55.6	24.4	30.50
100	74.3	25.7	25.70

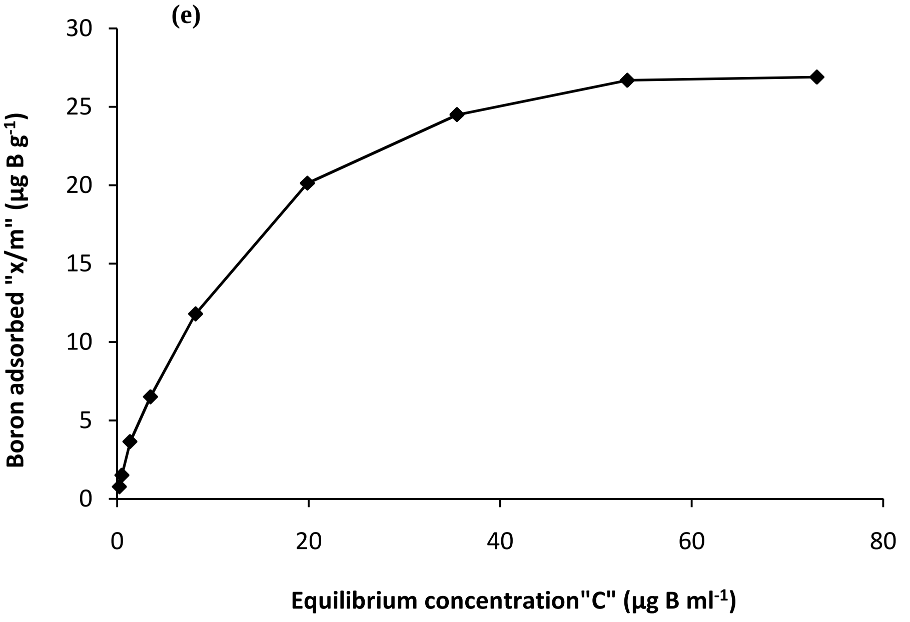
$\mathbf{S_9}$			
1	0.19	0.81	81.00
2	0.49	1.51	75.50
5	1.33	3.67	73.40
10	3.35	6.65	66.50
20	7.5	12.5	62.50
40	18.76	21.24	53.10
60	34.56	25.44	42.40
80	51.45	28.55	35.69
100	69.5	30.5	30.50
$\mathbf{S_{10}}$			
1	0.27	0.73	73.00
2	0.56	1.44	72.00
5	1.58	3.42	68.40
10	3.78	6.22	62.20
20	9.92	10.08	50.40
40	22.51	17.49	43.73
60	35.80	24.2	40.33
80	51.80	28.2	35.25
100	69.90	30.1	30.10

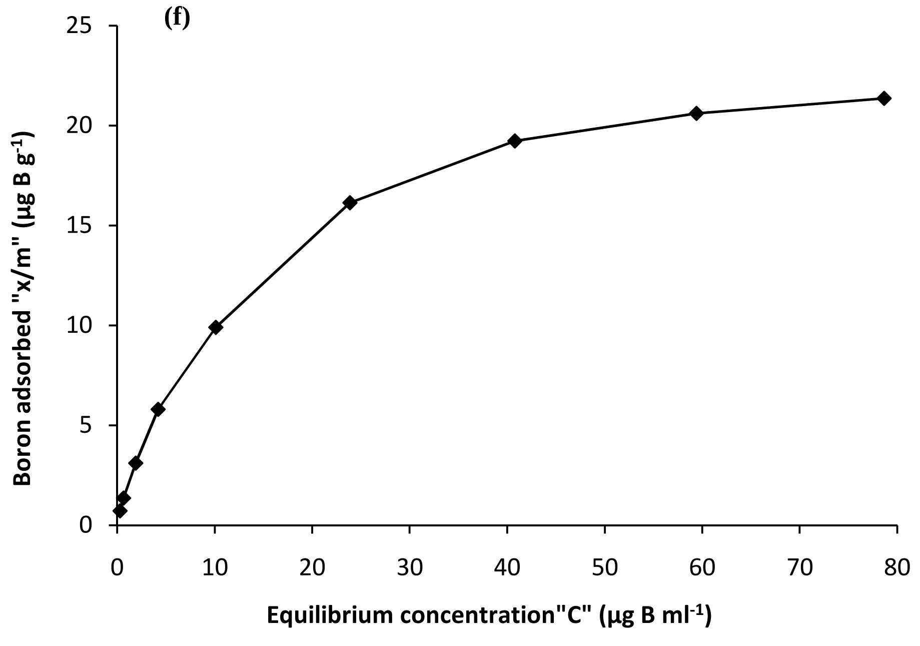

(a)
Boron adsorbed "x/m" (µg B g-1)
0
5
10
15
20
25
30
0
10
20
30
40
50
60
70
80
Equilibrium concentration"C" (µg B ml-1)

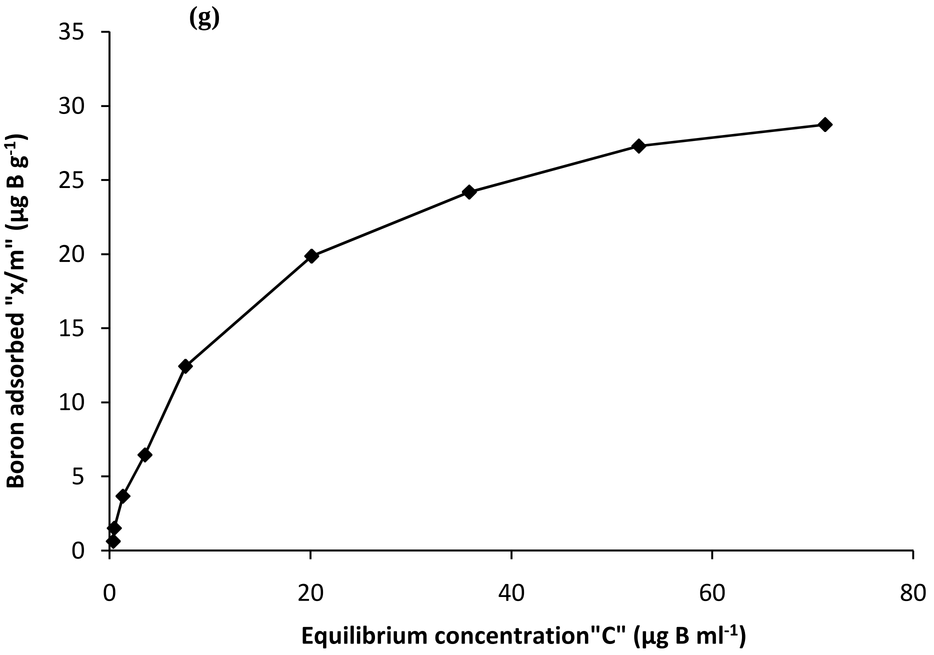

(b)
Boron adsorbed "x/m" (µg B g-1)
0
5
10
15
20
25
30
35
0
10
20
30
40
50
60
70
80
Equilibrium concentration"C" (µg B ml-1)

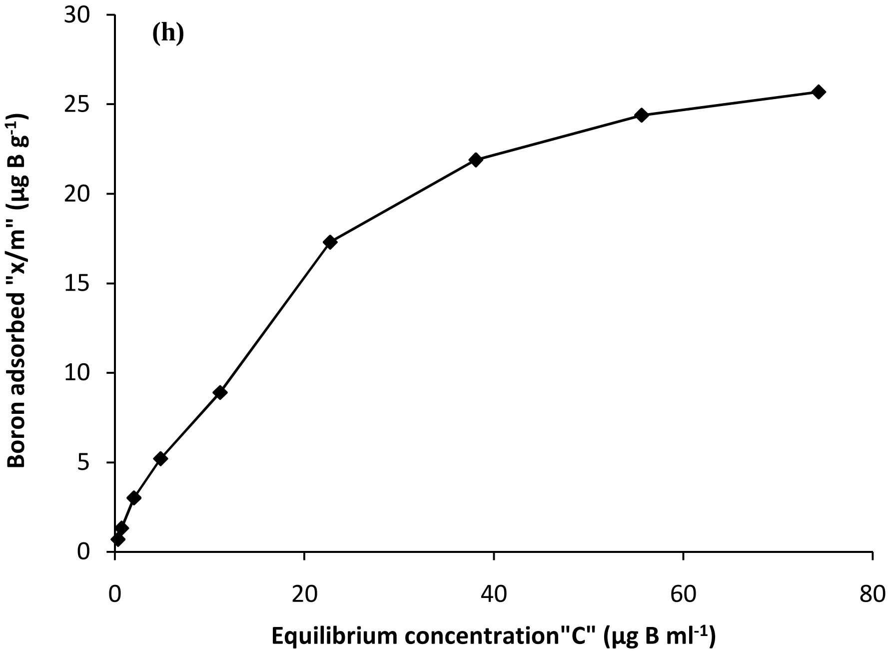

(c)
Boron adsorbed "x/m" (µg B g-1)
0
5
10
15
20
25
30
0
10
20
30
40
50
60
70
80
Equilibrium concentration"C" (µg B ml-1)

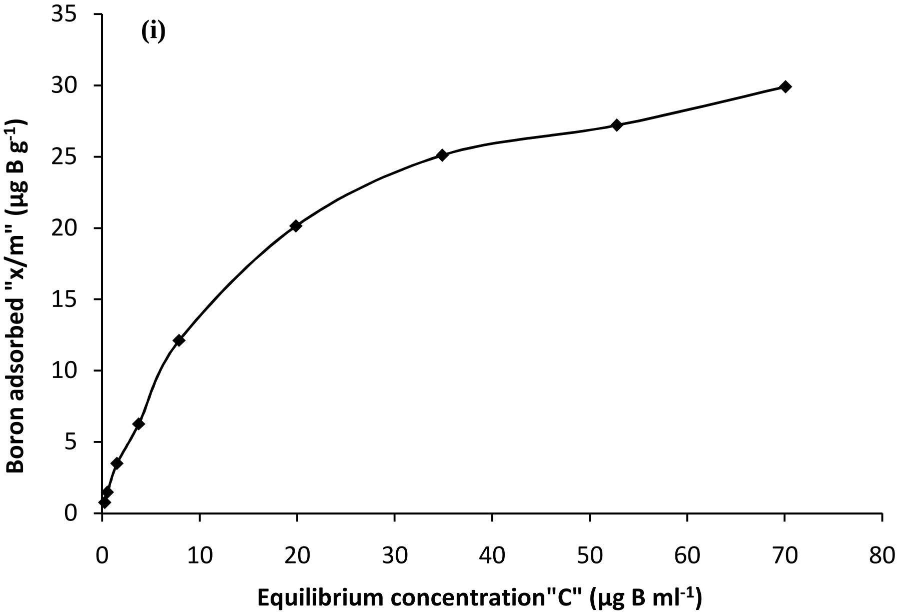

(d)
Boron adsorbed "x/m" (µg B g-1)
0
5
10
15
20
25
30
0
20
40
60
80
Equilibrium concentration"C" (µg B ml-1)


(e)
Boron adsorbed "x/m" (µg B g-1)
Equilibrium concentration"C" (µg B ml-1)
0
5
10
15
20
25
30
0
20
40
60
80


(f)
Boron adsorbed "x/m" (µg B g-1)
Equilibrium concentration"C" (µg B ml-1)
0
5
10
15
20
25
0
10
20
30
40
50
60
70
80


(g)
35
30
25
20
15
10
5
0
0
20
40
60
80
Boron adsorbed "x/m" (μg B g^{-1})
Equilibrium concentration"C" (μg B ml^{-1})


(h)
30
25
20
15
10
5
0
0
20
40
60
80
Boron adsorbed "x/m" (μg B g^{-1})
Equilibrium concentration"C" (μg B ml^{-1})



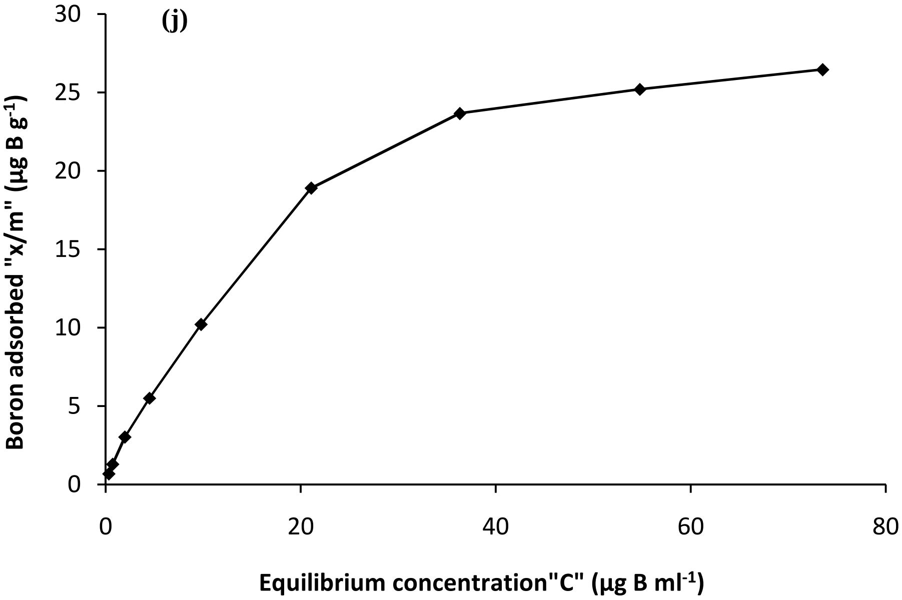


Figure 2: Boron Adsorption isotherms for a)Tangmarg soil b) Khag soil c) Anantnag soil d) Kulgam soil e) Tral soil f) Shalimar soil g) Bandipora soil h) Kangan soil i) Sagipora soil and j) Shopian soil

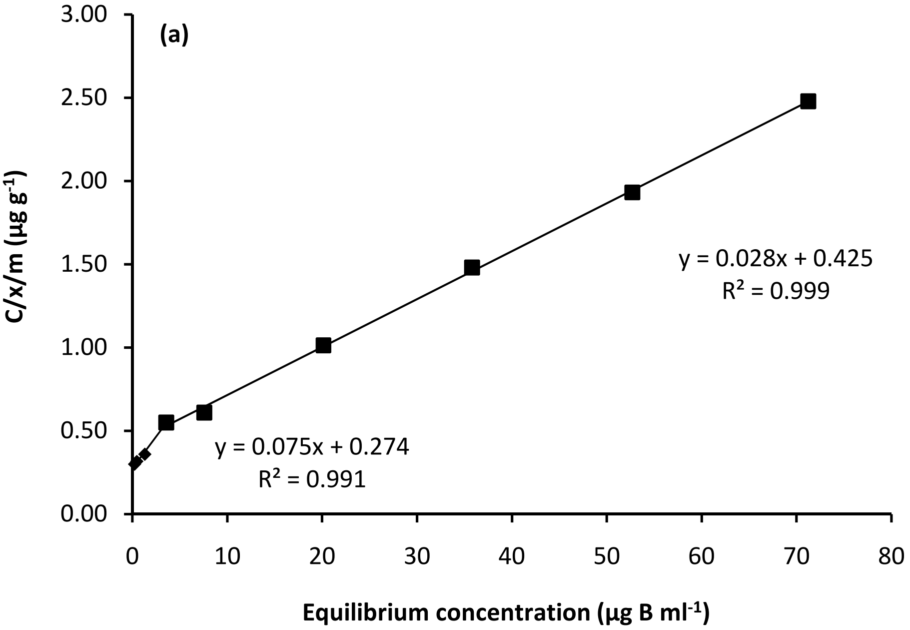
4.2.1.1 Langmuir Adsorption Isotherms.

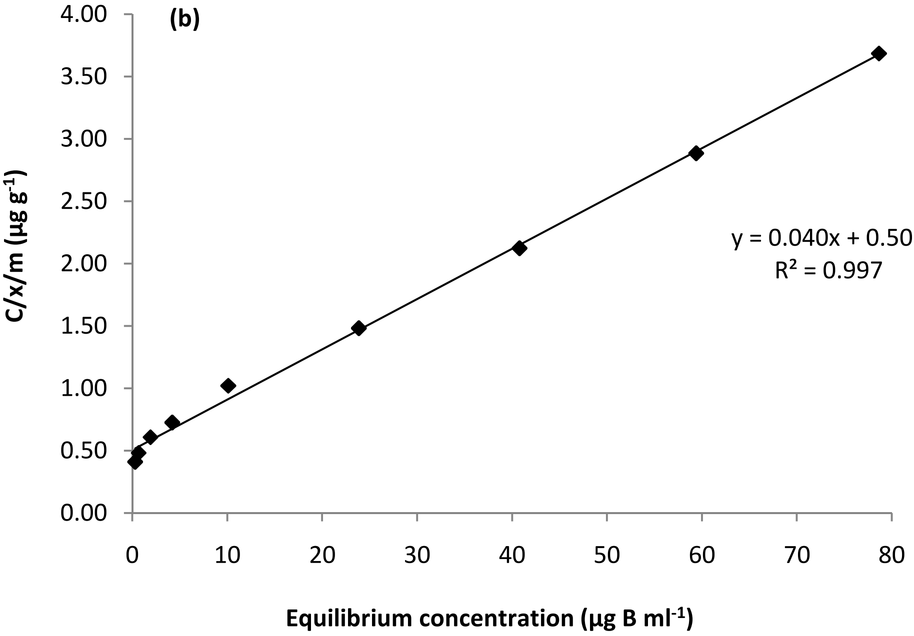
The data on boron adsorption were first calculated according to the Langmuir adsorption equation. The linear form of the equation used was;

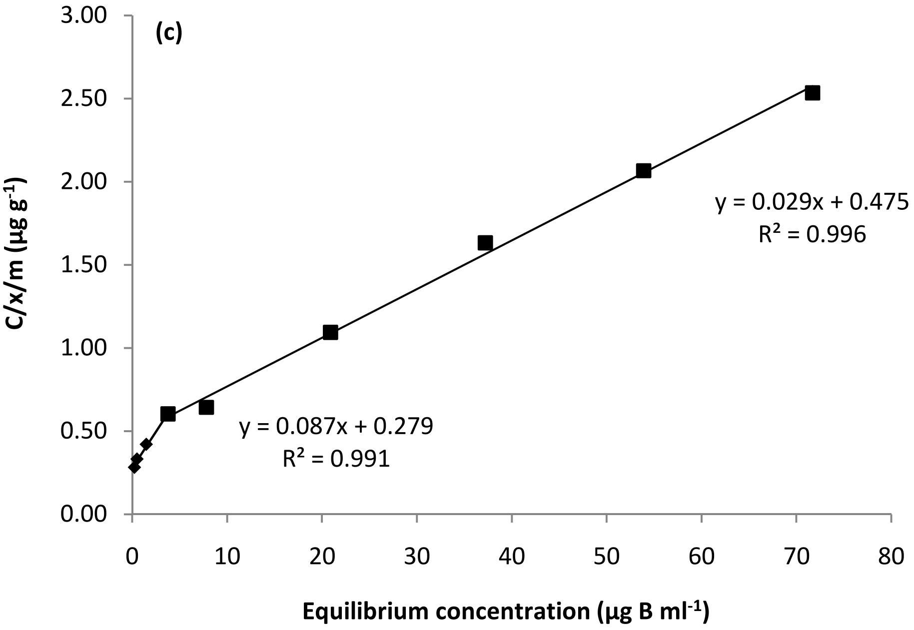
$$C/x/m=C/b+1/kb$$

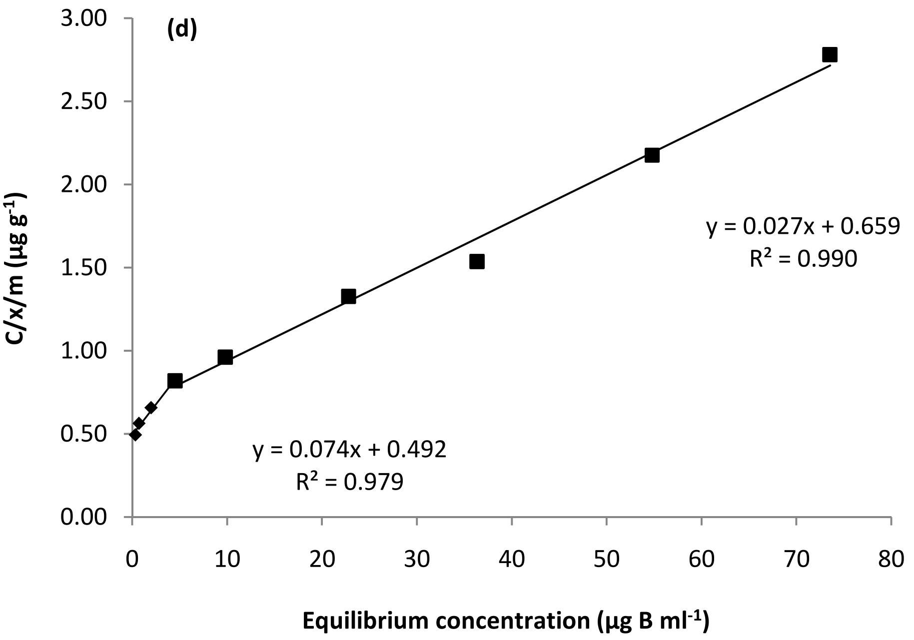
where, C is the equilibrium concentration (mg B ml^{-1}), x/m is the amount of boron adsorbed per unit weight of the soil (µg B g^{-1}soil), b is the adsorption maxima (µg Bg^{-1} soil) and k is a constant related to binding energy (ml g^{-1}). A plot of C/x/m versus C gave a straight line with slope 1/b and an intercept of 1/kb. The data fitted to the Langmuir equation and the Langmuir constants for boron adsorption by soils were calculated from the slope and the intercepts of the curves.

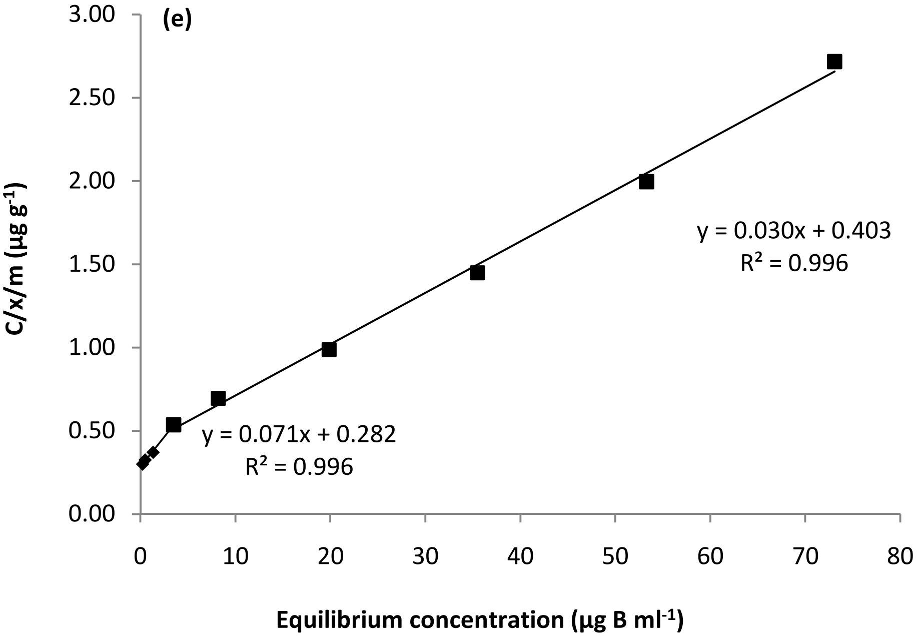
A straight line (linear curve) was observed in Khag, Bandipora and Sagipora soils. This showed that the adsorption data of these soils conform to the Langmuir adsorption over the entire range of equilibrium boron concentration. The soils of Tangmarg, Anantnag, Kulgam, Tral, Shalimar, Kangan and Shopian showed curvilinear isotherms (Figure 3).

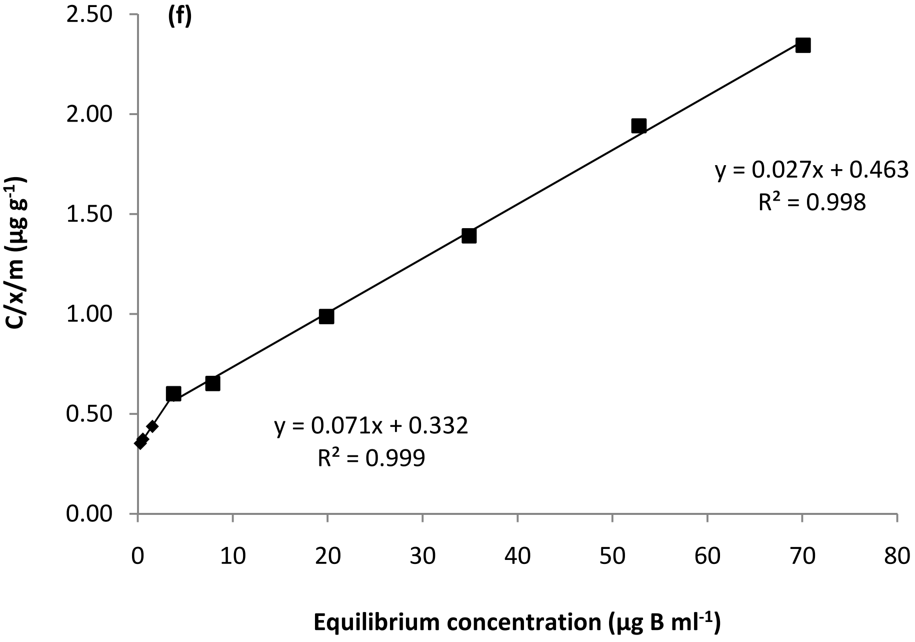

(a)
3.00
2.50
2.00
1.50
1.00
0.50
0.00
C/x/m (µg g-1)
y = 0.028x + 0.425
R² = 0.999
y = 0.075x + 0.274
R² = 0.991
0
10
20
30
40
50
60
70
80
Equilibrium concentration (µg B ml-1)

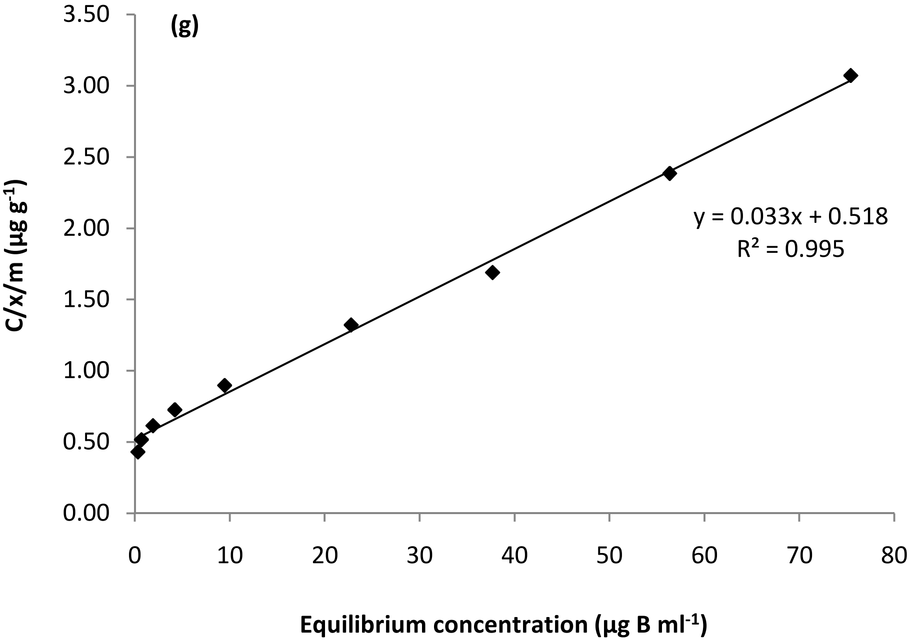

(b)
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
C/x/m (µg g-1)
y = 0.040x + 0.505
R² = 0.997
0
10
20
30
40
50
60
70
80
Equilibrium concentration (µg B ml-1)

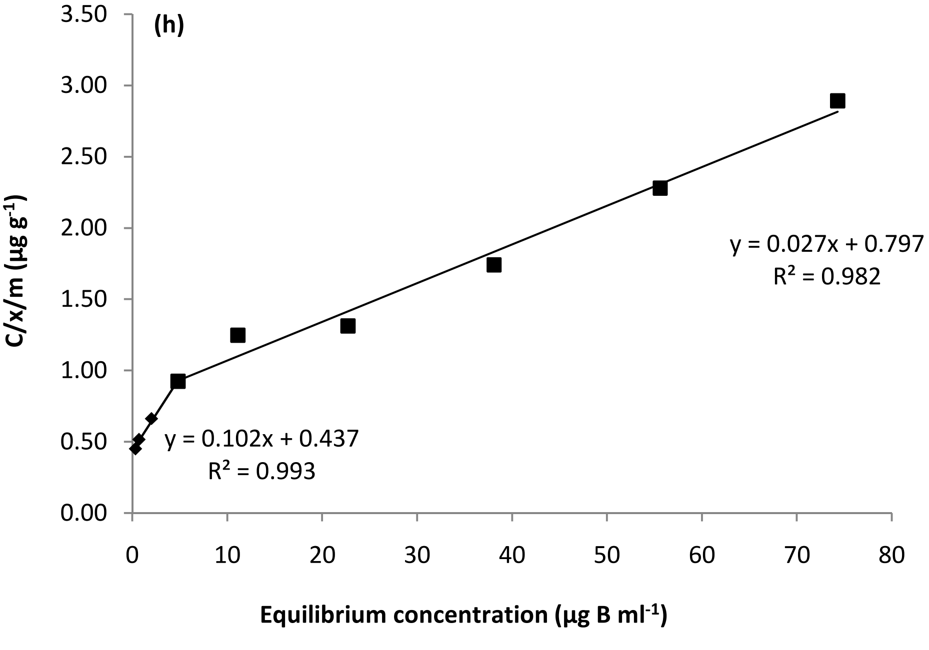

(c)
3.00
2.50
2.00
1.50
1.00
0.50
0.00
C/x/m (µg g-1)
0
10
20
30
40
50
60
70
80
Equilibrium concentration (µg B ml-1)
y = 0.029x + 0.475
R² = 0.996
y = 0.087x + 0.279
R² = 0.991

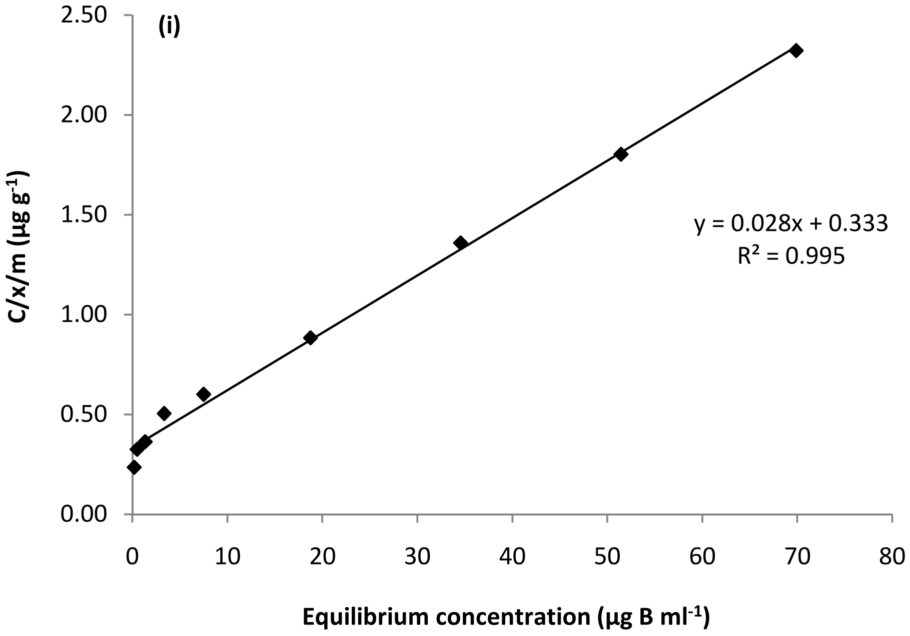

(d)
3.00
2.50
2.00
1.50
1.00
0.50
0.00
C/x/m (µg g-1)
0
10
20
30
40
50
60
70
80
Equilibrium concentration (µg B ml-1)
y = 0.027x + 0.659
R² = 0.990
y = 0.074x + 0.492
R² = 0.979


(e)
3.00
2.50
2.00
1.50
1.00
0.50
0.00
C/x/m (µg g^{-1})
0
10
20
30
40
50
60
70
80
Equilibrium concentration (µg B ml^{-1})
y = 0.030x + 0.403
R² = 0.996
y = 0.071x + 0.282
R² = 0.996


(f)
2.50
2.00
1.50
1.00
0.50
0.00
C/x/m (µg g^{-1})
0
10
20
30
40
50
60
70
80
Equilibrium concentration (µg B ml^{-1})
y = 0.027x + 0.463
R² = 0.998
y = 0.071x + 0.332
R² = 0.999


(g)
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
10
20
30
40
50
60
70
80
C/x/m (µg g-1)
Equilibrium concentration (µg B ml-1)
y = 0.033x + 0.518
R² = 0.995


(h)
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
10
20
30
40
50
60
70
80
C/x/m (µg g-1)
Equilibrium concentration (µg B ml-1)
y = 0.027x + 0.797
R² = 0.982
y = 0.102x + 0.437
R² = 0.993



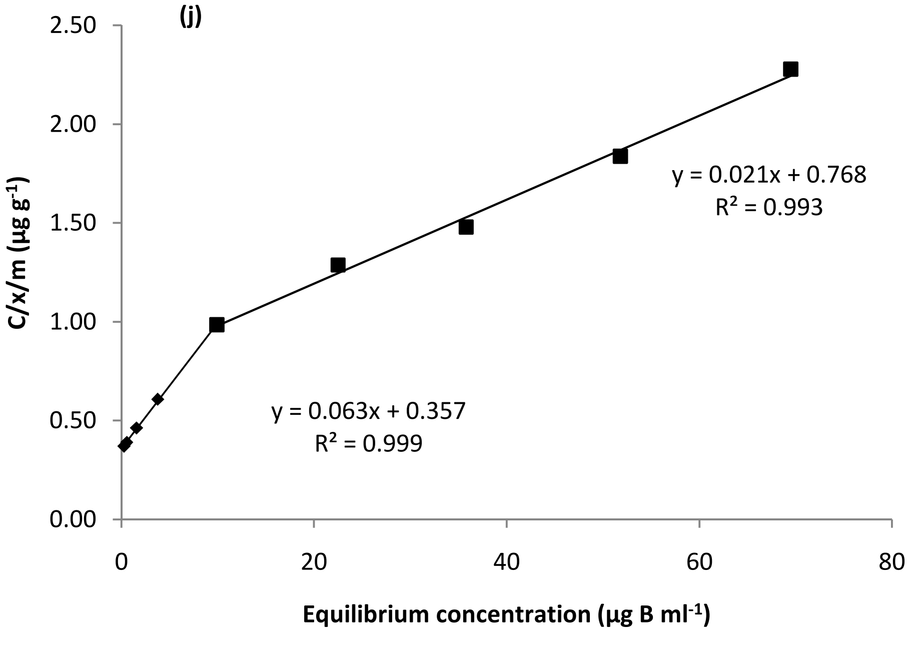


Fig 3: Langmuir adsorption Isotherms for boron adsorption by a)Tangmarg soil b) Khag soil c) Anantnag soil d) Kulgam soil e) Tral soil f) Shalimar soil g) Bandipora soil h)Kangan soil i) Sagipora soil and j) Shopian soil

The adsorption maxima (b) value was found to be maximum for Sagipora soils (34.84 µg Bg^{-1} soil) followed by Bandiporasoils (29.94µg Bg^{-1} soil) and Khag soil (24.81 µg Bg^{-1} soil) among these soils. The adsorption maxima for Tangmarg soil was 13.19 µg B g^{-1} soil, for Anantnag soil (11.44 µg B g^{-1} soil), Kulgam soil (13.50 µg B g^{-1} soil), Tral soil (13.91 µg B g^{-1} soil), Shalimar soil (14.07 µg B g^{-1} soil), Kangan soil (9.72 µg Bg^{-1} soil) and Shopian soil (15.75 µg Bg^{-1} soil), respectively. In these soils, the fit of data in Langmuir adsorption isotherm was curvilinear and was significant and excellent when the curves were resolved into two linear parts (Figure 3). The two portions of the curves were considered separately because the slopes and intercepts of the lower part of the isotherms were significantly different from those of the upper part and provide justification for considering separately. The values of adsorption maxima and bonding energy constant have been designated as b1 and k1 for lower part and b2 and k2 for upper part of the isotherm. The Langmuir constants from the isotherms for each soil are given in Table 4.8. The maximum value of b1 i.e. 34.84 µg B g^{-1} soil was observed in Sagipora soil and minimum value in 9.72 µg B g^{-1} soil in Kangan soil. The bonding energy constant (k1) was maximum 0.313 ml µg^{-1}in Anantnag soil and minimum of 0.064 ml µg^{-1}in Bandipora soil.

Table - 4.8 Langmuir's Coefficients of boron adsorption by different soils

Soils	**b1 (µg B g^{-1})**	**k1 (ml ug^{-1})**	**R^2**	**b2 (µg B g^{-1})**	**k2 (ml µg^{-1})**	**R^2**
S_1	13.193	0.276	0.991	34.722	0.068	0.999
S_2	24.814	0.080	0.997	-	-	-
S_3	11.442	0.313	0.991	34.130	0.062	0.997
S_4	13.495	0.150	0.980	34.842	0.042	0.991
S_5	13.908	0.255	0.996	32.468	0.076	0.997
S_6	14.065	0.214	0.999	36.900	0.058	0.998
S_7	29.940	0.064	0.996	-	-	-
S_8	9.718	0.235	0.993	36.900	0.034	0.983
S_9	34.843	0.086	0.995	-	-	-
S_{10}	15.748	0.177	0.999	47.170	0.028	0.994

The difference in slopes and intercepts of the two parts of adsorption isotherms gave highly different values of Langmuir constants. Regardless the type of soil, the adsorption maxima (b) were higher for part-2 (upper part) while bonding energy constant (k) were higher for part 1 (lower part) of the isotherms.

The nature of the Langmuir isotherms and magnitude of the constants calculated (Table 4.8) varied with the soil texture and organic carbon content of the soils. The values of Langmuir coefficients were markedly different for fine and coarse textured soils. The adsorption maxima (b1) were much higher for fine textured than those of coarse textured soils. The clay content and CEC of soils possessed significant and positive correlation with b1 (0.565**, and 0.506**, respectively) (Table 4.10). The relative bonding energy (k) of boron adsorption by soils also varied among the soils. The k1 was higher than the respective k2 for almost all the soils, thus showing firmer retention of boron at part 1 i.e. at lower concentration than at higher concentrations (part 2).

4.2.1.2 Freundlich adsorption Isotherms

The boron adsorption data has been fitted to the Freundlich equation. The linear form of the equation is given as under;

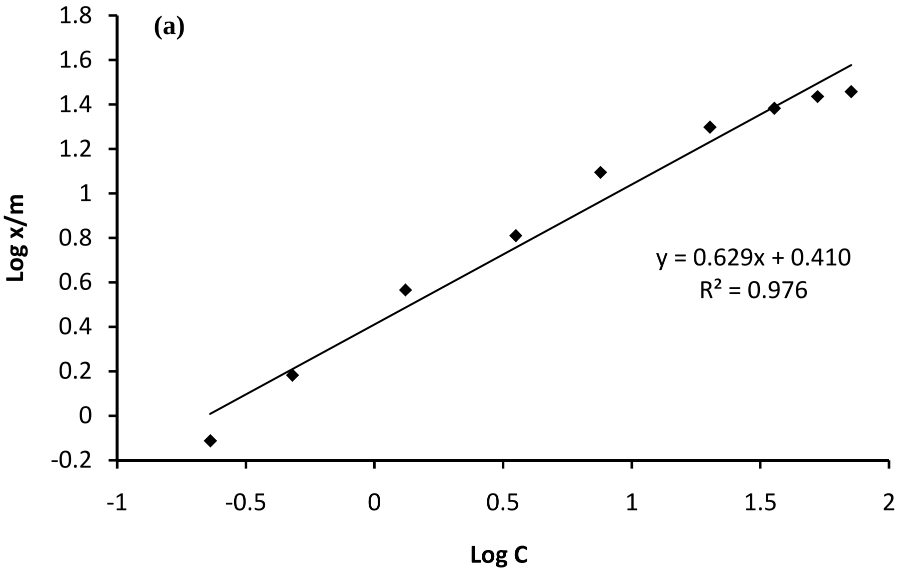
$$\text{Log } x/m = 1/n \log C + \log k$$

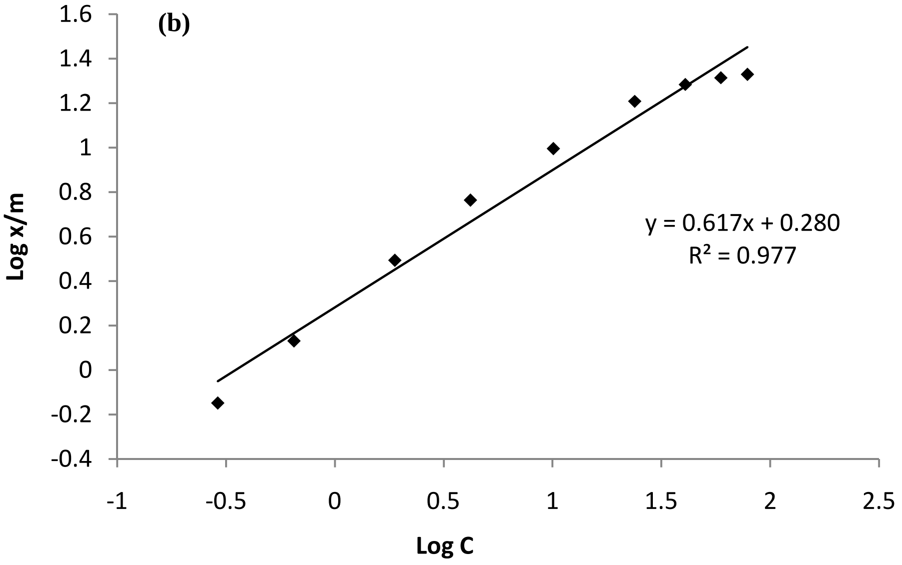
Where, C is the equilibrium boron concentration (μg B ml^{-1}), x/m is the amount of boron adsorbed for unit weight of the soil (μg g^{-1}), k and 1/n are the constants which depend upon the nature of the adsorbate and the adsorbent. The values of the constant k and 1/n can be determined by plotting log x/m versus log C. The plot should give a straight line if the data confirms to the Freundlich equation. k can be obtained from the intercept at unit concentration and 1/n is the slope of the plot k and 1/n provides the estimates of adsorbent capacity and intensity of adsorption. The values of 1/n also indicate the degree of non-linearity between solution concentration and adsorption.

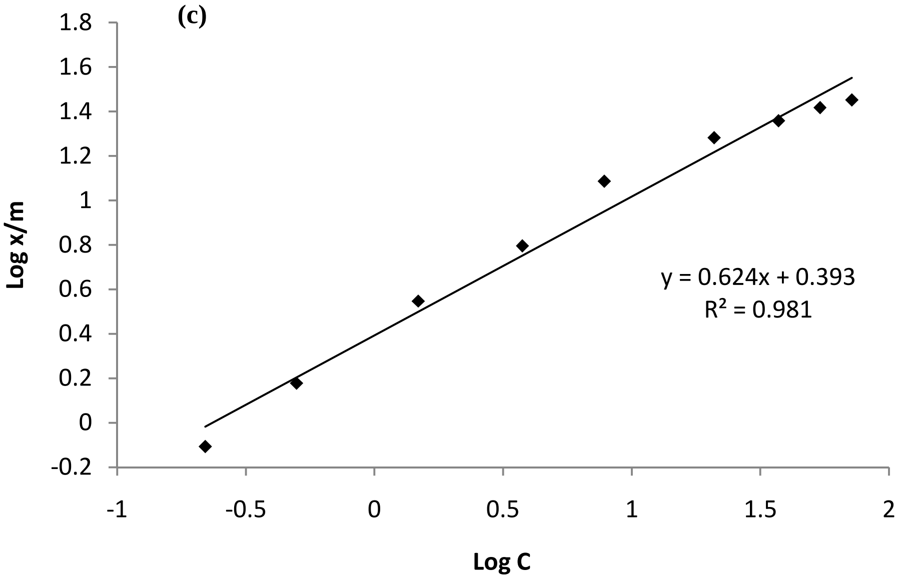
A plot of boron adsorbed against equilibrium boron concentration in a log-log scale gave linear relationship in all the soils. The concentration ranged from 1 to 100 µg Bml^{-1} (Fig 4).

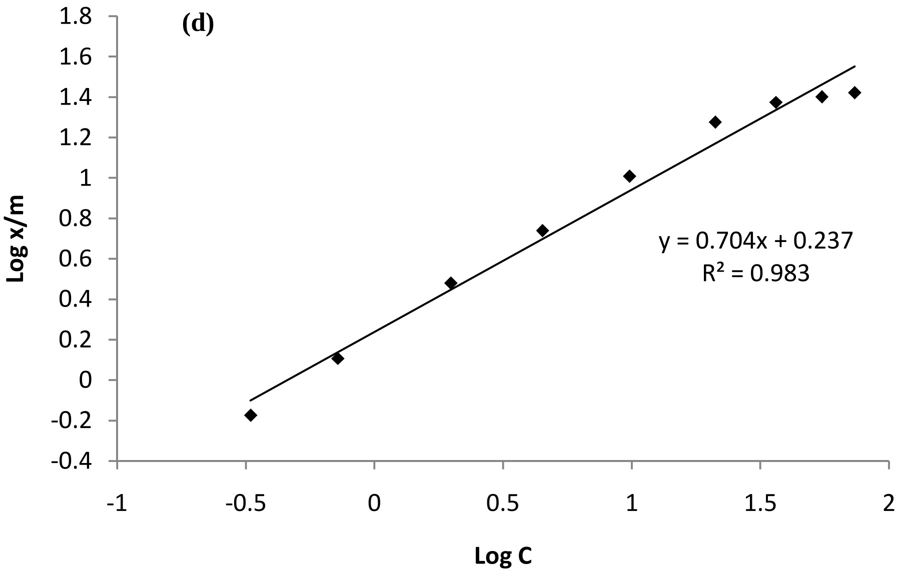
The results of the present investigation also indicated that Freundlich equation was valid for wider range of boron concentrations than by the Langmuir adsorption equation. Freundlich model assumes multilayer adsorptions and heterogeneity of the soils as compared to the monolayer adsorption and homogeneity of soils in Langmuir equation. A higher concentration of applied boron, multilayer adsorption and/or precipitation reaction appears to have occurred thereby this resulted in a better fit of the data on the latter than formal model.

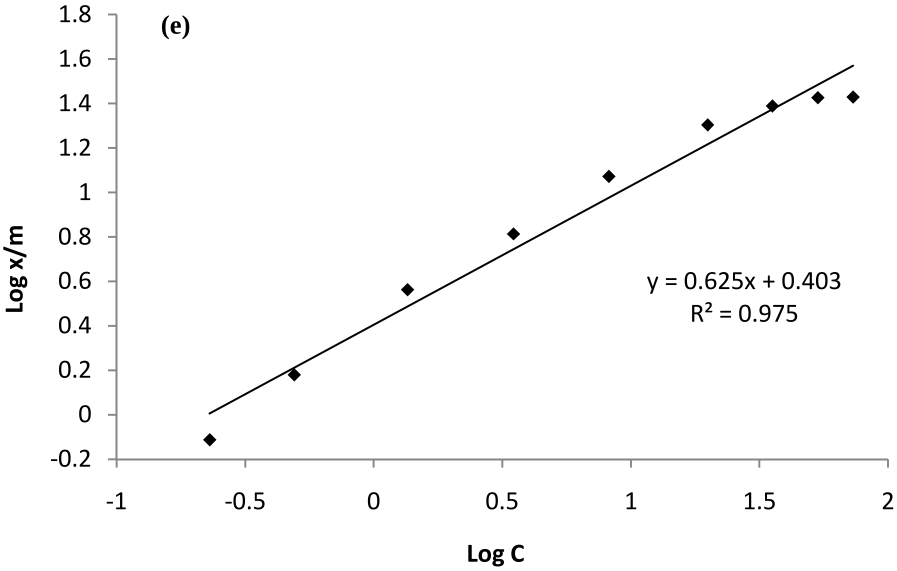
Freundlich k values ranged widely among the soils. The value was maximum of 2.72µg g^{-1} for Sagipora soil, followed by that of 2.57µg g^{-1} for Tangmarg soil, 2.53µg g^{-1} for Tral soil, 2.47µg g^{-1} for Annatnag soil, 2.31µg g^{-1} for Shalimar soil, 2.15 µg g^{-1} for Shopian soil, 1.91µg g^{-1} for Khag soil, 1.87µg g^{-1} for Bandipora soil, 1.75µg g^{-1} for Kangan soil, and 1.73 µg g^{-1} for Kulgam soil (Table 4.9).

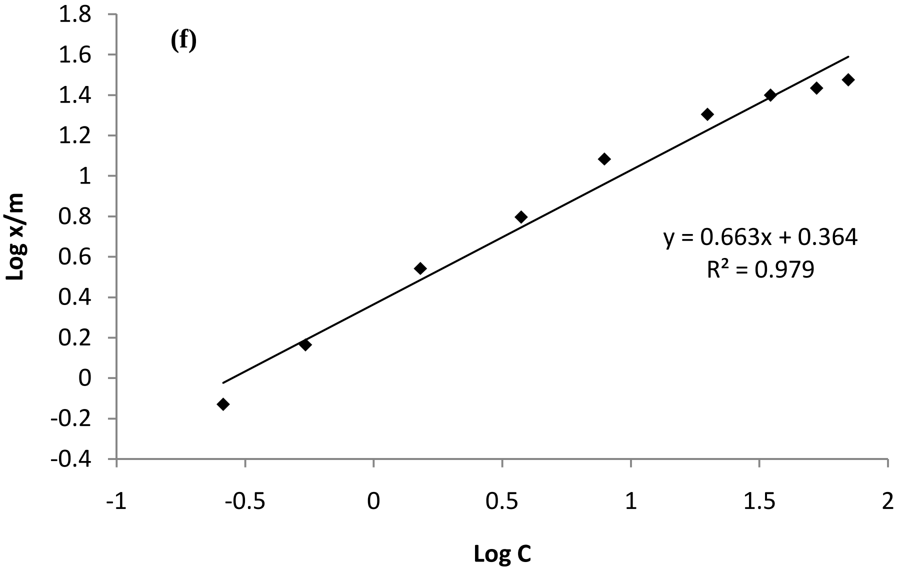

(a)
Log x/m
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-1
-0.5
0
0.5
1
1.5
2
Log C
y = 0.629x + 0.410
R² = 0.976

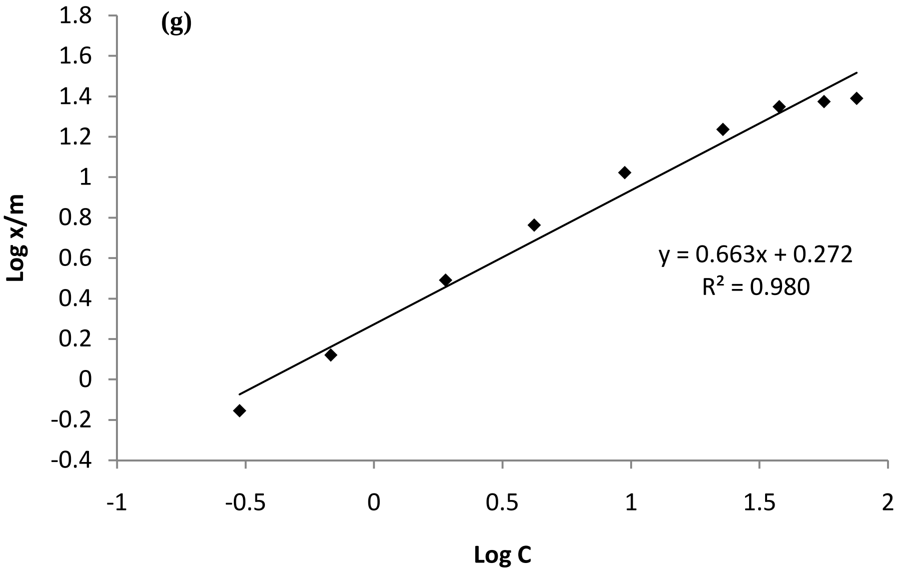

(b)
Log x/m
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-1
-0.5
0
0.5
1
1.5
2
2.5
Log C
y = 0.617x + 0.280
R² = 0.977

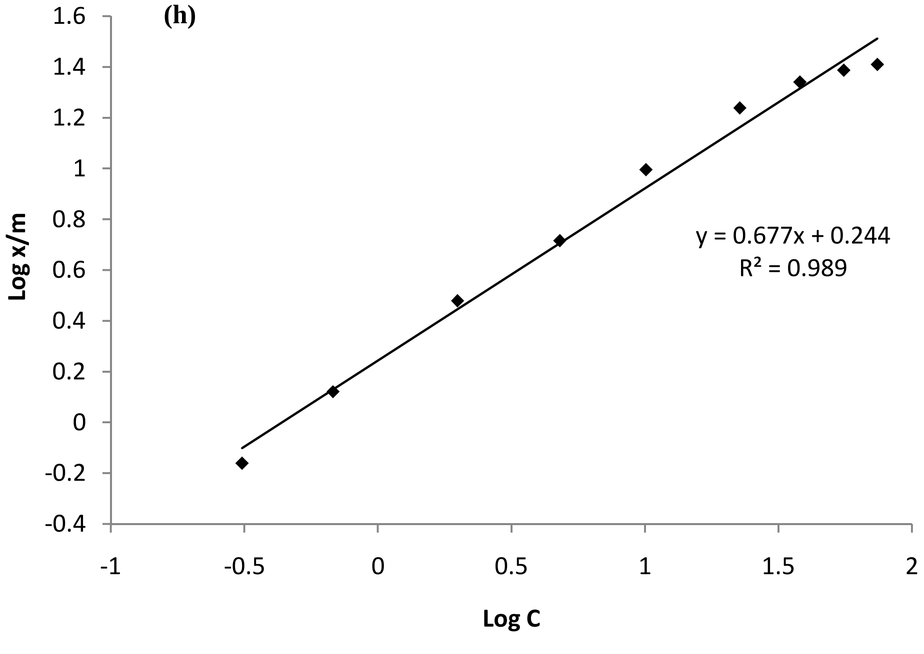

(c)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
Log x/m
y = 0.624x + 0.393
R² = 0.981
-1
-0.5
0
0.5
1
1.5
2
Log C

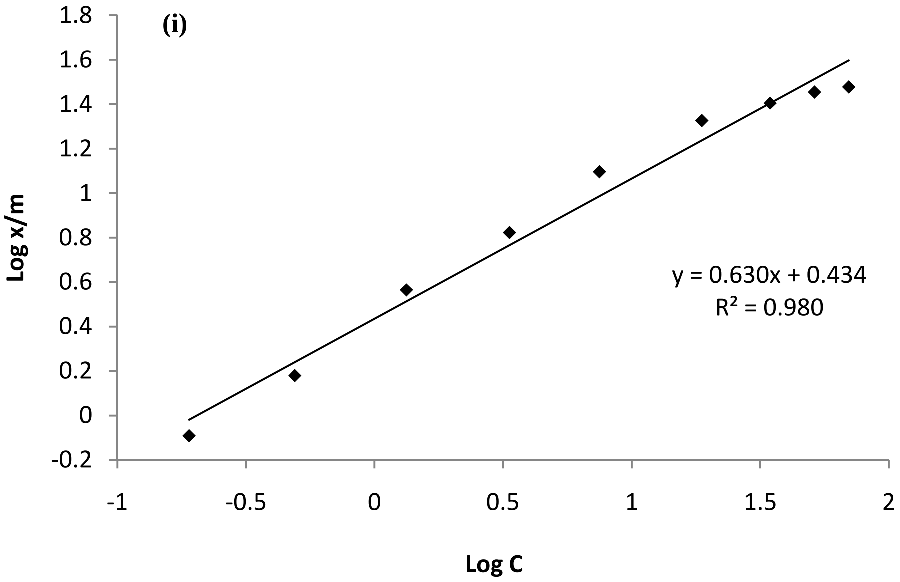

(d)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
Log x/m
y = 0.704x + 0.237
R² = 0.983
-1
-0.5
0
0.5
1
1.5
2
Log C


(e)
Log x/m
Log C
y = 0.625x + 0.403
R² = 0.975
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-1
-0.5
0
0.5
1
1.5
2


(f)
Log x/m
Log C
y = 0.663x + 0.364
R² = 0.979
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-1
-0.5
0
0.5
1
1.5
2


(g)
Log x/m
Log C
y = 0.663x + 0.272
R² = 0.980
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-1
-0.5
0
0.5
1
1.5
2


(h)
Log x/m
Log C
y = 0.677x + 0.244
R² = 0.989
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-1
-0.5
0
0.5
1
1.5
2



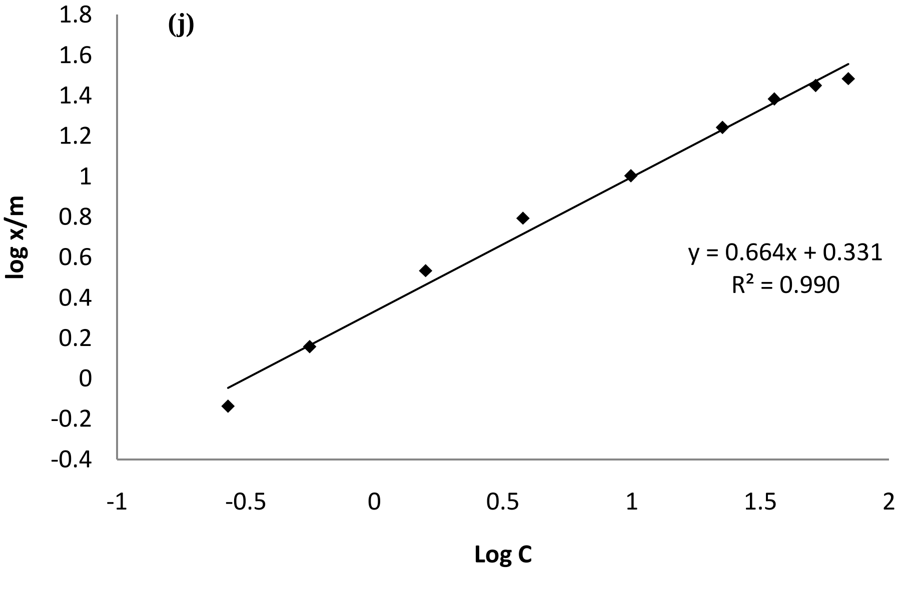


Fig 4: Freundlich adsorption Isotherms for boron adsorption by a)Tangmarg soil b) Khag soil c) Anantnag soil d) Kulgam soil e) Tral soil f) Shalimar soil g) Bandipora soil h) Kangan soil i) Sagipora soil and j) Shopian soil

Table - 4.9 Freundlich Coefficients of boron adsorption by different soils

Soils	1/n	k ($\mu g\ g^{-1}$)	R^2
S_1	0.6298	2.5722	0.976
S_2	0.6178	1.9085	0.977
S_3	0.6240	2.4729	0.982
S_4	0.7044	1.7278	0.983
S_5	0.6255	2.5345	0.975
S_6	0.6639	2.3142	0.979
S_7	0.6630	1.8746	0.981
S_8	0.6778	1.7543	0.990
S_9	0.6303	2.7221	0.981
S_{10}	0.6646	2.1468	0.991

The perusal of the data in Table 4.9 indicates that by and large, the difference in values of k was associated with the magnitude of variation in clay content of the soil. Highly significant relation of the k values with clay content (r=0.906**) substantiates these observations (Table 4.10).

The values of Freundlich constant 1/n are less than unity in all the soils indicating L-shape isotherms (Fig 4).The maximum value of 1/n was obtained in Kulgamsoil(0.704) and minimum in Khagsoil (0.618) (Table 4.9).

Table 4.10 Coefficient of Correlation of Langmuir and Freundlich constants of boron adsorption with soil characteristics

Soil properties	Langmuir constants				Freundlich constants	
	b1	b2	k1	k2	n	k
pH	0.241	-0.422	0.143	0.353	0.614*	0.446
EC	-0.121	-0.119	0.345	0.071	0.455	0.286
OC	-0.412	0.271	0.245	-0.122	-0.408	-0.065
CEC	0.506*	-0.714**	0.122	-0.910**	0.793**	0.691*
$CaCO_3$	0.011	0.396	0.048	0.045	0.171	0.323
Clay	0.565*	-0.142	0.254	0.694*	0.797**	0.906**
Sand	0.374	0.501*	-0.013	0.088	0.320	0.737**

4.2.2 Boron desorption by soils

It was of interest to determine whether the adsorbed boron of soils can be readily released. Desorption studies were undertaken by replacing the soil suspension after adsorption process by 10 ml of 0.01 M $CaCl_2$ solution. The amount of desorbed boron in different soils equilibrated for 24 hours are shown in Table 4.11.

The data in table 4.11 indicated that coarse textured soils tend to desorb higher amount of boron as compared to fine textured soils. The soils which have higher affinity for boron adsorption like Sagipora, Tangmarg, Tral and Kulgam tend to desorb less amount of boron per cent of adsorbed boron, respectively. This indicated that adsorption and desorption of boron were almost inversely related.

Table - 4.11 Amount of boron desorbed (µg g^{-1} soil) in 0.01 M $CaCl_2$ solution from different soils

Initial B added (µg B mL^{-1})	B desorbed (De) (µg B g^{-1})	% B desorbed*	De/S
S_1			
1	0.05	6.49	0.0649
2	0.15	9.87	0.0987
5	0.42	11.41	0.1141
10	0.93	14.40	0.1440
20	2.01	16.16	0.1616
40	3.55	17.86	0.1786
60	5.03	20.79	0.2079
80	6.33	23.19	0.2319
100	7.65	26.61	0.2661
S_2			
1	0.06	8.45	0.0845
2	0.12	8.89	0.0889
5	0.33	10.61	0.1061
10	0.67	11.55	0.1155
20	1.16	11.72	0.1172
40	2.43	15.07	0.1507
60	4.87	25.34	0.2534
80	6.01	29.17	0.2917
100	7.3	34.19	0.3419

S_3			
1	0.03	3.72	0.0372
2	0.18	11.98	0.1198
5	0.48	13.64	0.1364
10	0.89	14.26	0.1426
20	2.01	16.50	0.1650
40	3.98	20.83	0.2083
60	7.89	34.61	0.3461
80	8.32	31.88	0.3188
100	9.21	32.54	0.3254
S_4			
1	0.04	6.57	0.0657
2	0.14	10.94	0.1094
5	0.53	17.55	0.1755
10	1.1	20.00	0.2000
20	2.11	20.69	0.2069
40	4.2	22.22	0.2222
60	5.98	25.27	0.2527
80	6.09	24.17	0.2417
100	8.12	30.69	0.3069

S_5			
1	0.07	9.09	0.0909
2	0.19	12.58	0.1258
5	0.58	15.90	0.1590
10	0.99	15.21	0.1521
20	2.11	17.88	0.1788
40	3.55	17.64	0.1764
60	5.22	21.31	0.2131
80	6.25	23.41	0.2341
100	7.88	29.29	0.2929
S_6			
1	0.03	4.32	0.0432
2	0.17	11.67	0.1167
5	0.42	12.07	0.1207
10	0.79	12.64	0.1264
20	1.78	14.70	0.1470
40	4.56	22.65	0.2265
60	7.65	30.48	0.3048
80	9.55	35.11	0.3511
100	12.73	42.58	0.4258

S_7			
1	0.04	5.71	0.0571
2	0.13	9.85	0.0985
5	0.38	12.26	0.1226
10	0.68	11.72	0.1172
20	1.45	13.74	0.1374
40	2.58	14.97	0.1497
60	5.15	23.06	0.2306
80	7.1	30.02	0.3002
100	9.15	37.24	0.3724
S_8			
1	0.08	11.59	0.1159
2	0.18	13.64	0.1364
5	0.42	13.95	0.1395
10	0.93	17.88	0.1788
20	1.89	19.09	0.1909
40	4.45	25.72	0.2572
60	7.88	35.98	0.3598
80	10.58	43.36	0.4336
100	13.67	53.19	0.5319

S_9			
1	0.05	6.05	0.0605
2	0.16	10.60	0.1060
5	0.48	13.08	0.1308
10	0.87	13.08	0.1308
20	2.04	16.32	0.1632
40	3.66	17.23	0.1723
60	5.12	20.13	0.2013
80	6.02	21.09	0.2109
100	7.66	25.45	0.2545
S_{10}			
1	0.05	6.85	0.0685
2	0.11	7.64	0.0764
5	0.32	9.36	0.0936
10	0.79	12.70	0.1270
20	1.82	18.06	0.1806
40	4.23	24.19	0.2419
60	7.11	29.38	0.2938
80	10.65	37.77	0.3777
100	13.01	42.66	0.4266

*% of B adsorbed (Table 4.7)

The initial adsorption of boron in soils is followed by slow changes that ultimately govern the rate of boron release from soils. Moreover, the difference between magnitude of adsorption and desorption of boron depends on the time of contact of boron solution and intensity of boron bonding in soils. The data in the table 4.11 also revealed that the rate of desorption was slow at low saturation of solid phase matrix and at high saturation, the desorption of boron was fast and these results suggested that soils having higher adsorption, releases boron slowly into the solution and vice-versa.

Desorption of boron was found to be maximum in Kangan, Shopian, and Shalimar soil and this showed that these soils were prone to release the applied boron. Whereas the soils of Sagipora, Tangmarg and Tral show less desorption. Very interesting results were obtained in case of Kangan soil where large amount of boron was desorbed although the soil is heavy in texture.

The data of boron desorption when analysed statistically showed that desorption of boron by these soils is positively and significantly correlated with sand content (r = 0.662*) and negatively with clay content (r = -0.479) and CEC (r = -0.587*).

The data of boron desorption was applied to Langmuir type equation. Very few workers have tried this equation for boron desorption, although it is commonly used to describe phosphate desorption (Wani and Bhat, 2010). In present study, keeping in view the good applicability of this equation describing phosphorous desorption, an attempt has been made to apply Langmuir type equation for boron desorption. Desorbed boron (De) when plotted against boron desorbed/boron adsorbed (De/S) for different soils, a linear relation was obtained in all the soils. The straight line relationship showed that the desorption of boron in these soils as determined by 0.01 M $CaCl_2$ solution could be described by Langmuir type equation as given below;

$$De/S = 1/kdDm + De/Dm$$

Where,

S= Boron adsorbed (μg g^{-1})

De=Boron desorbed (μg g^{-1})

Dm= desorption maxima (mg g^{-1})

kd =Constant related to mobility of boron (ml g^{-1})

The Langmuir desorption parameters such as desorption maxima (Dm) and constant related to mobility of solid phase (kd) were worked out from the linear plots of De versus De/S according to the Langmuir desorption relationship and presented in Table 4.12.

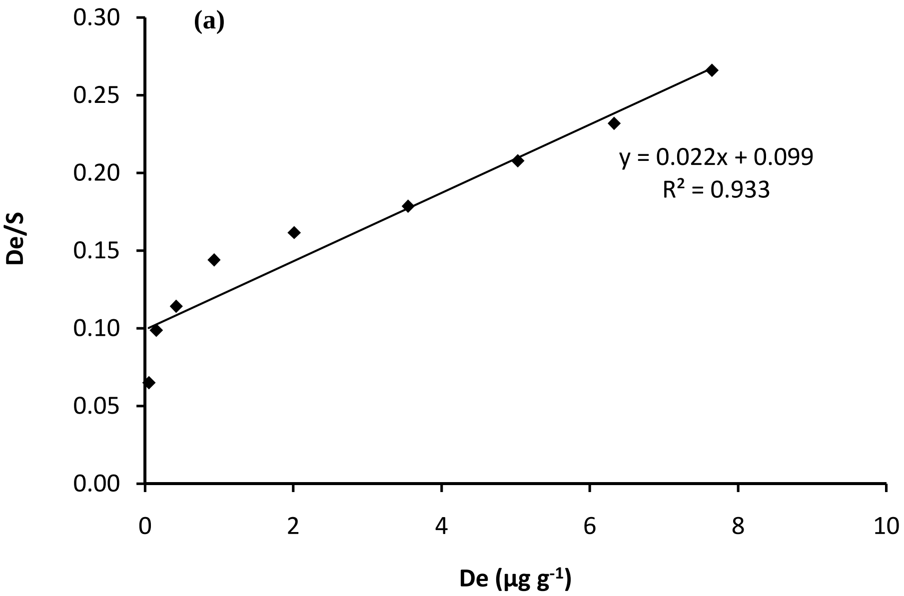
The plot was found to be linearly correlated for each of the soils (Fig 5). The desorption constants computed from these plots clearly indicates the differential behaviour of each soil sample in supplying boron to the plants. Desorption maxima (Dm) indicate the maximum desorbable capacity of the soils. More the Dm values, less is the potential of the soil to release boron for meeting the requirements of the crop. Similarly, kd values (a constant related to the boron mobility) are also indicative of boron supply to the crops. Smaller the kd value, less is the desorption of boron from soils.

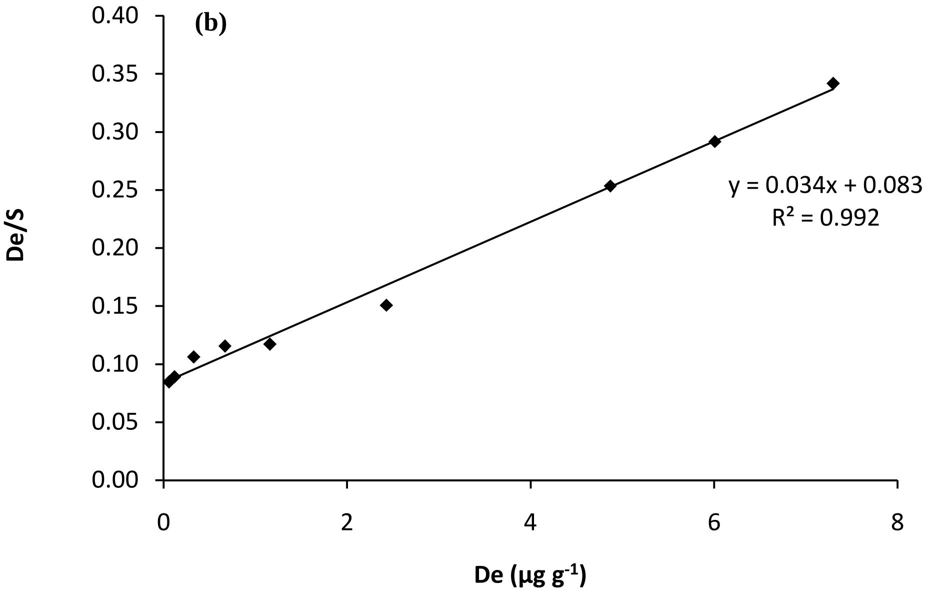
The desorption constants worked out are presented in Table 4.12, revealed that fine textured soils had higher desorption maxima as compared to coarse textured soils. The values of Dm varied from 28.90 to 50.76 mg g^{-1} and kd values ranged from 0.163 to 0.412 ml g^{-1} in the soils studied. The maximum value of 50.76 mg g^{-1} for Dm was observed in Sagipora soil followed by 50.51 mg g^{-1}in Tral soil, 46.51 mg g^{-1} in Kulgam soil, 45.45mg g^{-1}in Tangmargsoil, 37.45 mg g^{-1} in Shalimar and Shopian soil, 36.76mg g^{-1}in Anantnagsoil, 34.36mg g^{-1}in Kangansoil, 33.00 mg g^{-1} in Bandiporasoil, and 28.90 mg g^{-1}in Khagsoil, respectively. The values of kd, a constant related to boron mobility was found to be maximum in Khag soil (0.412 ml g^{-1}) and minimum in Tral soil (0.163 ml g^{-1}).

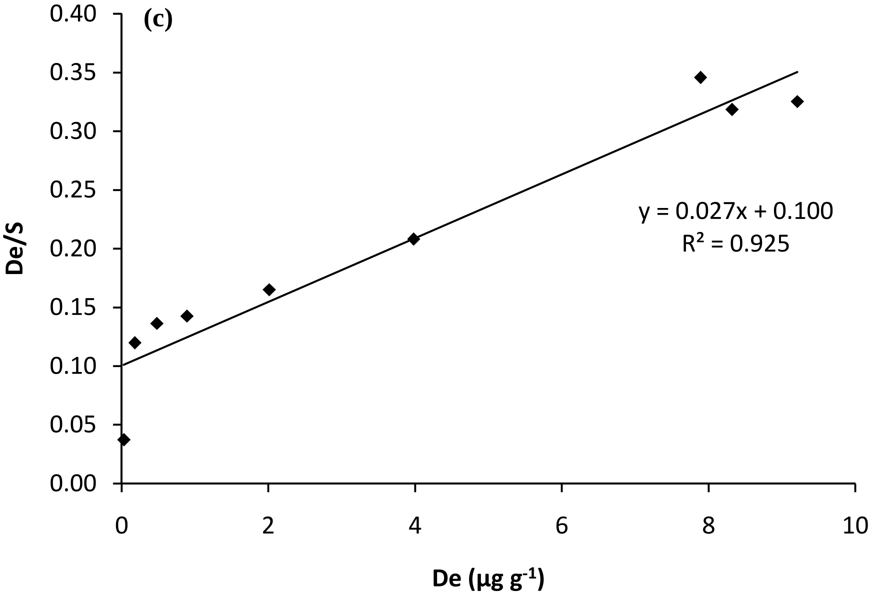
The mobility constant has almost inverse relationship with bonding energy of boron adsorption. This showed that the mobility of adsorbed boron in heavy textured soils was at the lower rates.

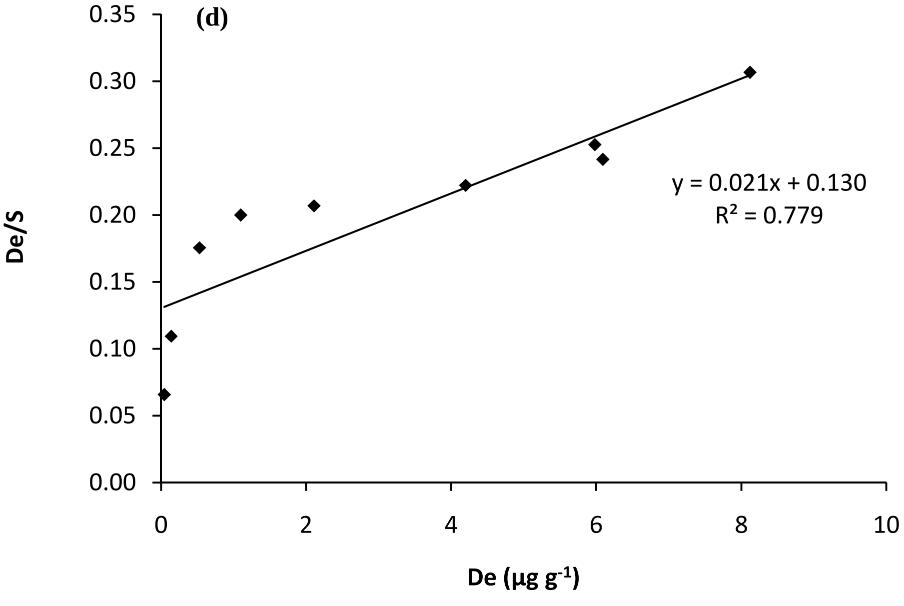
Table - 4.12 Langmuir coefficients of borondesorption for different soils

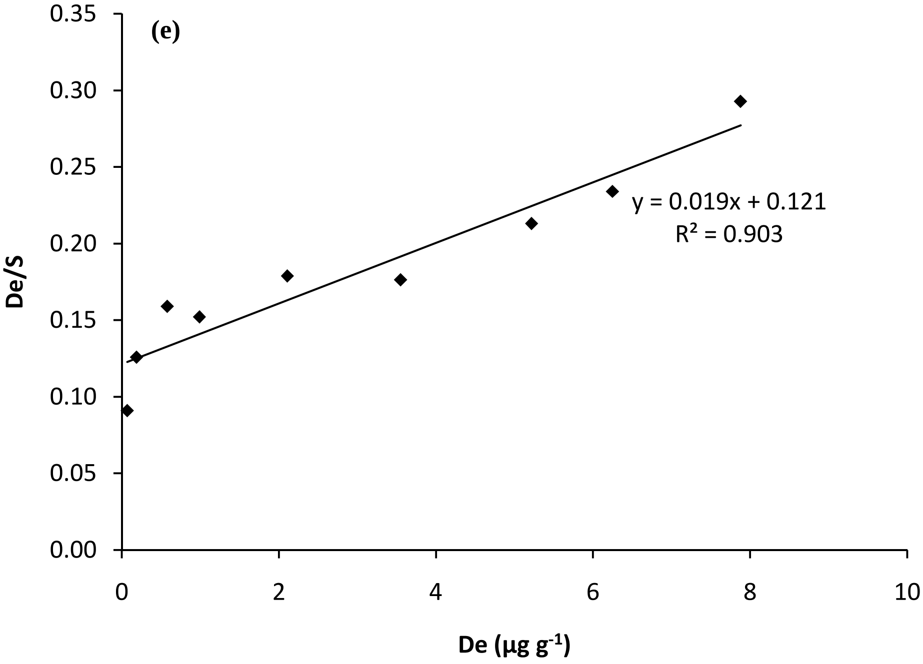
Soils	Dm ($mg\ g^{-1}$)	Kd ($ml\ g^{-1}$)	R^2
S1	45.45	0.222	0.934
S2	28.90	0.412	0.993
S3	36.76	0.271	0.925
S4	46.51	0.165	0.780
S5	50.51	0.163	0.903
S6	37.45	0.281	0.973
S7	33.00	0.350	0.974
S8	34.36	0.222	0.995
S9	50.76	0.194	0.898
S10	37.45	0.276	0.970

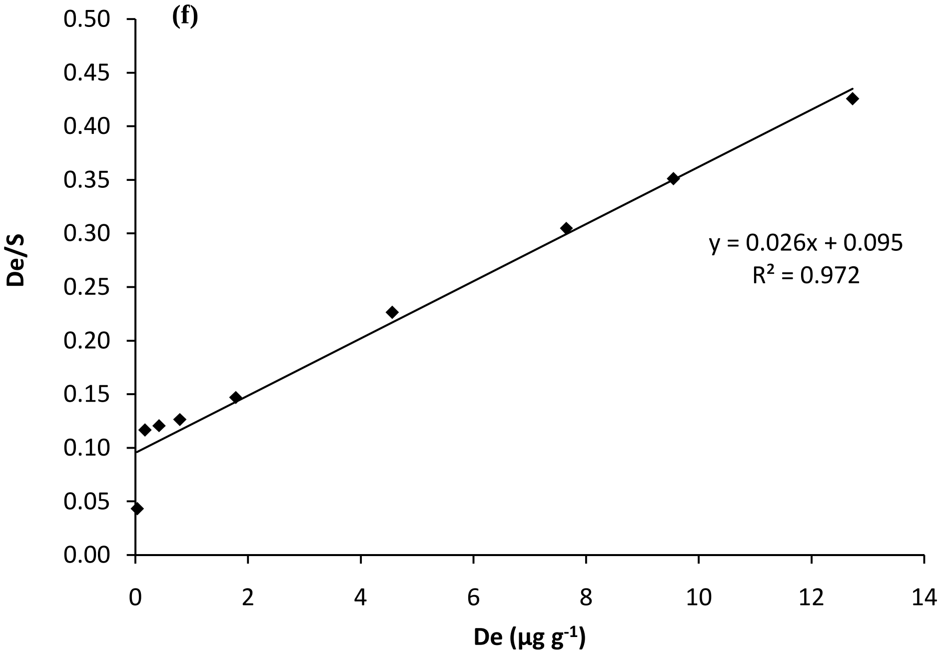

(a)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
De/S
0
2
4
6
8
10
De (µg g-1)
y = 0.022x + 0.099
R² = 0.933

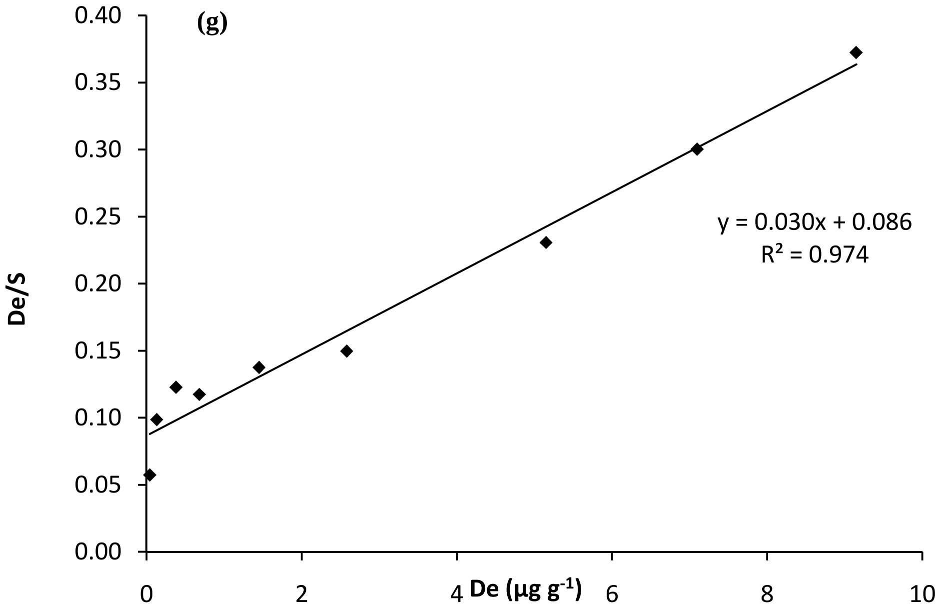

(b)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
De/S
0
2
4
6
8
De (µg g-1)
y = 0.034x + 0.083
R² = 0.992

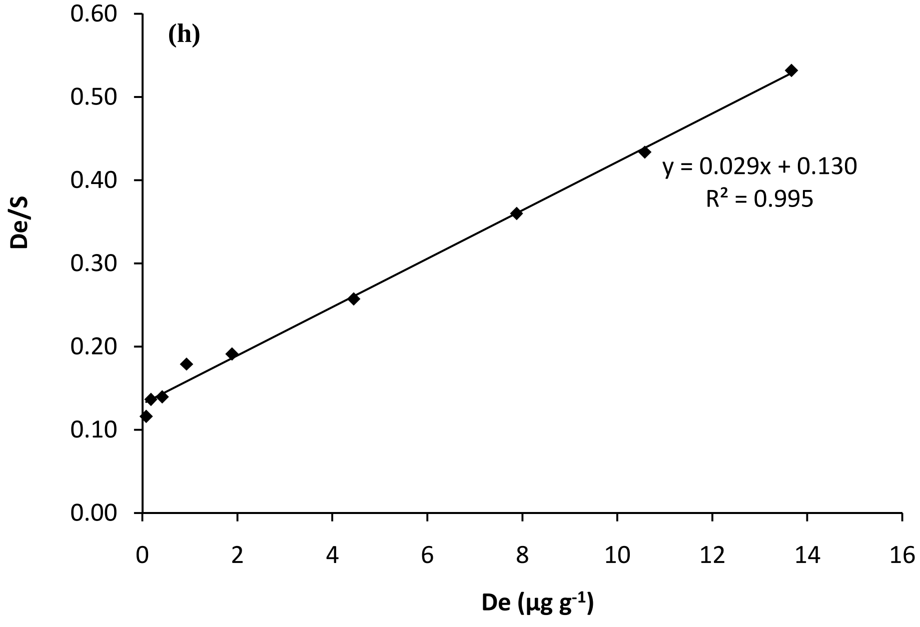

(c)
De/S
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
2
4
6
8
10
De (µg g-1)
y = 0.027x + 0.100
R² = 0.925


(d)
De/S
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
2
4
6
8
10
De (µg g-1)
y = 0.021x + 0.130
R² = 0.779


(e)
De/S
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
2
4
6
8
10
De (µg g-1)
y = 0.019x + 0.121
R² = 0.903


(f)
De/S
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
2
4
6
8
10
12
14
De (µg g-1)
y = 0.026x + 0.095
R² = 0.972


(g)
De/S
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
2
4
6
8
10
De (μg g-1)
y = 0.030x + 0.086
R² = 0.974


(h)
De/S
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
2
4
6
8
10
12
14
16
De (μg g-1)
y = 0.029x + 0.130
R² = 0.995

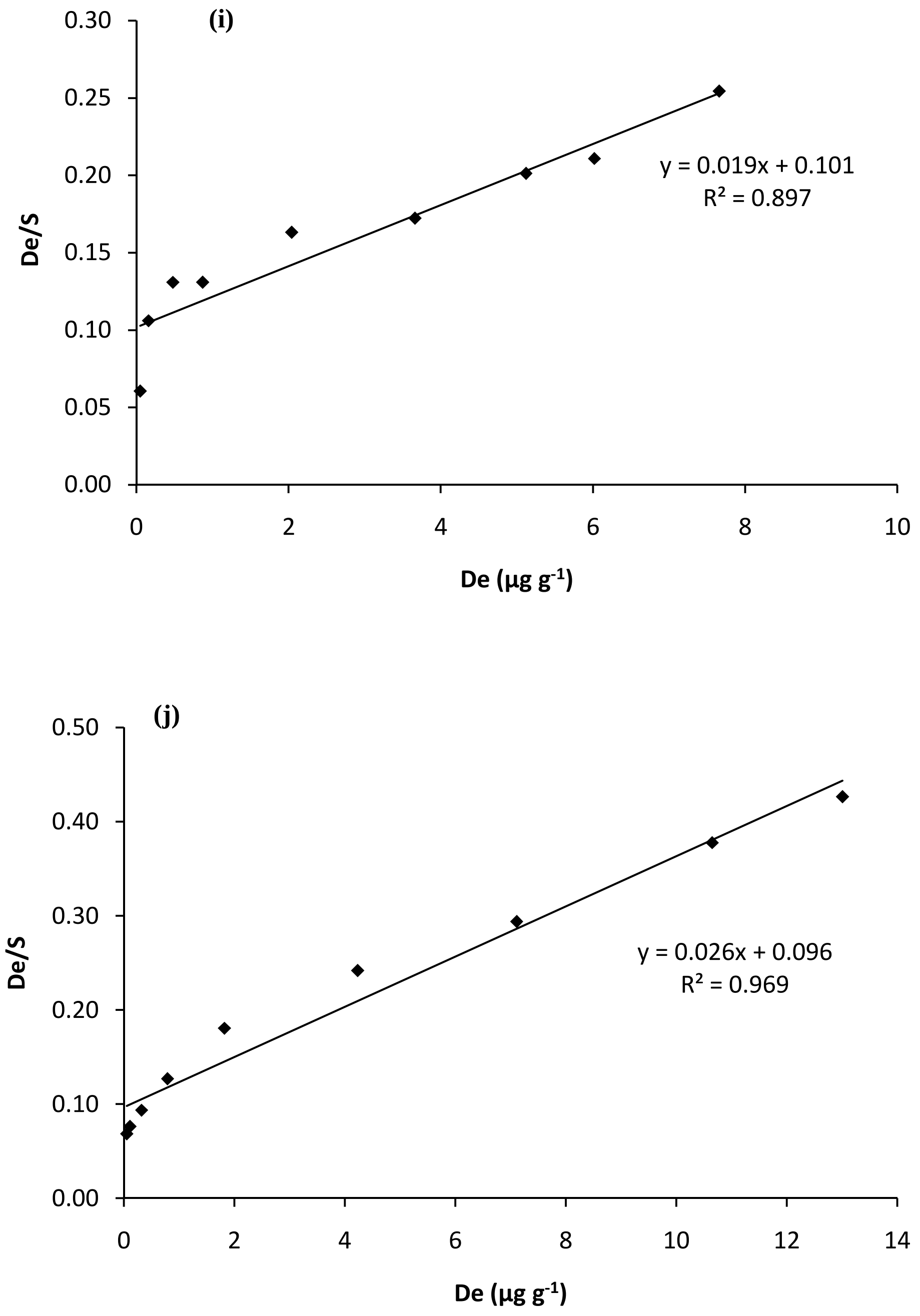


Fig 5: Langmuir desorption isotherms for boron desorption by a)Tangmarg soil b) Khag soil c) Anantnag soil d) Kulgam soil e) Tral soil f) Shalimar soil g) Bandipora soil h) Kangan soil i) Sagipora soil and j) Shopian soil

4.3 Kinetics of Boron adsorption-desorption

4.3.1 Kinetics of boron adsorption by soils

Batch studies were used to investigate the kinetics of boron adsorption process. Calcium chloride (0.01 M) solution containing 40 µg ml^{-1} boron (as boric acid) was added to each 10 g soil in 50 ml polyethylene centrifuge tubes. In all the soils, the boron adsorption was characterized by an initial fast reaction followed by a slow process. Initial adsorption by soils from Anantnag, Sagipora and Tral sites was fast, followed by Khag, Bandipora, Tangmarg, Shalimar, Kulgam, Kangan and by Shopian soil was the slowest (Table 4.13). Adsorption of boron was almost complete after 24 hours in all the soils, though complete equilibrium was not attained until 48 hours had elapsed.

The concentration of boron in the equilibrium solution ranged from 27.5 to 36.1 µg ml^{-1} at the completion of the adsorption reaction. The equilibrium concentration of boron for Tangmarg, Khag, Anantnag, Kulgam, Tral, Shalimar, Bandipora, Khag, Sagipora and Shopian soils at 24 hours was 31.6, 30.8, 29.8, 32.7, 30.2, 31.5, 32.1, 33.0, 30.0 and 33.1µg ml^{-1}, respectively. Finer the texture, the lower was the concentration of boron in the equilibrium solution. Texture and CEC of the soils influenced the boron in the equilibrium solution. The boron equilibrium concentration was negatively and significantly correlated with clay content (r= -0.757**) and positively and significantly correlated with sand (r= 0.776**), which strengths the above statements. Maximum boron was absorbed by Anantnag soil, followed by Sagipora, Tral, Khag, Shalimar, Tangmarg, Bandipora, Kulgam and Kangan soils, respectively, while minimum boron was adsorbed by Shopian soil.

Six different Kinetic models viz. Zero order, First order, Second order, Elovich, Power function and Parabolic diffusion were tested by least square regression analysis for describing boron adsorption in soils representing major soils of Kashmir. The model which had the highest coefficient of determination (R^2) and the lowest standard error of estimates (S.E) values was considered to be best fit.

The first orders kinetic equation could not describe the adsorption of boron by soils, as Coefficient of determination (R^2) values were very low (0.733 to 0.857) and S.E values were large (5.1 to 8.2). Power function model also did not described boron adsorption quite sufficiently in all the soils studied, as is evident by large S.E values of power function model (5.0 to 8.0) although the coefficient of determination (R^2) values were high (0.959 to 0.975). The second order kinetic model also could not describe the adsorption of boron by soils because of considerably large S.E (6.9 to 10.6) values and lowest coefficient of determination (R^2) values (0.639 to 0.759) for second order model.

The Parabolic diffusion was best of the other kinetic equations studied to describe the rate of boron adsorption as evidenced by the overall highest values of coefficient of determination (R^2) and lowest standard error of estimates (SE) over the entire time range (Table 4.14: Figure 6). In the present investigation the R^2 value was maximum of 0.997 in Kulgam soil followed by 0.995 in Kangan soil, 0.994 in Shopian soil, 0.988 in Tangmarg soil, 0.976 in Anatnag soil, 0.973 in Khag soil, 0.969 in Tral soil, 0.968 in Sagipora soil, 0.967 in Shalimar soil and 0.949 in Bandipora soil.

Elovich kinetic model was as good as parabolic diffusion equation in describing the boron adsorption kinetics in all the soils (Table 4.15: Fig 7). The values of coefficient of determination (R^2) were quite high and standard error of estimates (SE) values were lowest. The Elovich kinetic equation was followed by zero order equation which was nearly as good as Elovich model in describing boron adsorption kinetics in all the soils (Table 4.15). The values of coefficient of determination (R^2) were high and standard error of estimates (SE) values were low.

Table - 4.13 Amount of boron adsorbed (μg g^{-1}) by the soils under investigation with respect to time

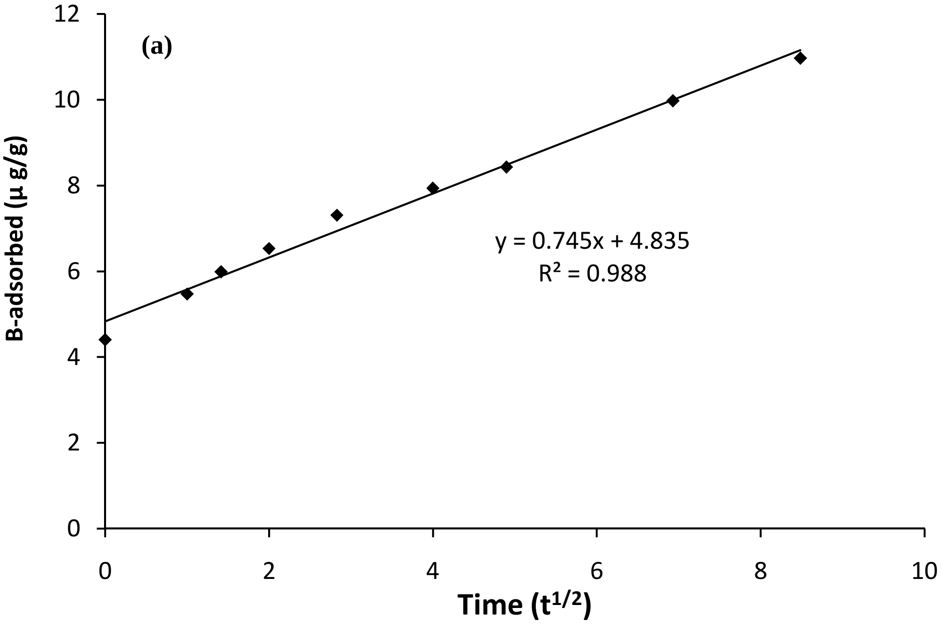
Soils	Time (h)								
	0	**1**	**2**	**4**	**8**	**16**	**24**	**48**	**72**
S1	35.6	34.5	34.0	33.5	32.7	32.1	31.6	30.0	29.0
S2	34.6	33.8	33.2	32.4	31.5	31.0	30.8	29.4	28.1
S3	33.6	32.8	32.3	31.8	30.7	30.0	29.8	28.4	27.5
S4	35.7	35.0	34.9	34.2	33.8	33.1	32.7	31.1	30.0
S5	34.4	33.4	33.0	32.2	31.1	30.8	30.2	29.1	28.0
S6	35.5	34.7	34.6	33.4	32.0	31.7	31.5	29.7	28.7
S7	35.6	34.9	34.6	34.0	33.2	32.8	32.1	30.8	29.9
S8	36.0	35.1	35.0	34.4	34.0	33.3	33.0	31.8	30.7
S9	34.2	33.1	32.9	32.0	31.0	30.5	30.0	28.9	28.0
S10	36.1	35.7	35.1	34.8	34.1	33.8	33.1	31.8	31.0

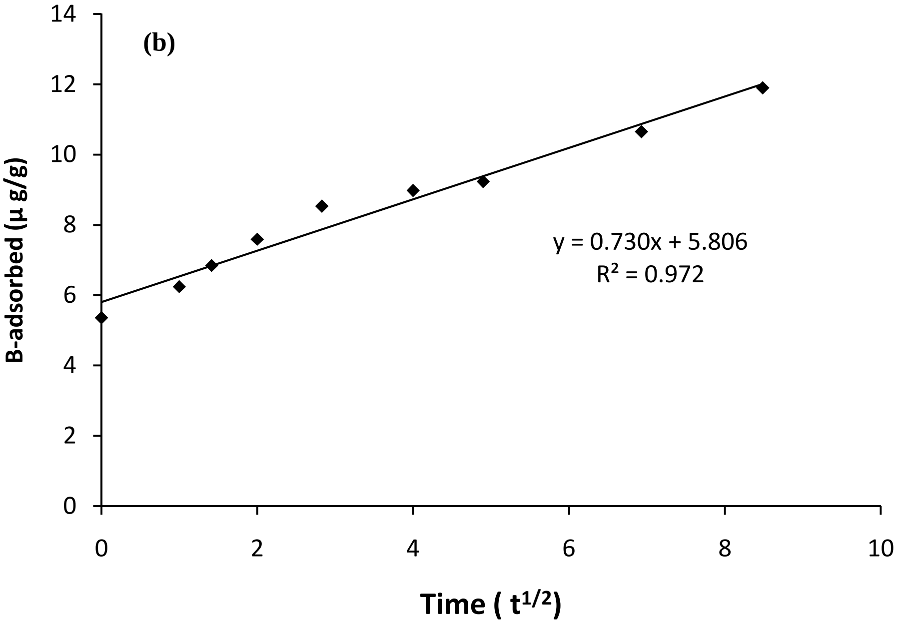
Table - 4.14 Parameters of Parabolic diffusion Kinetic equation for B-adsorption

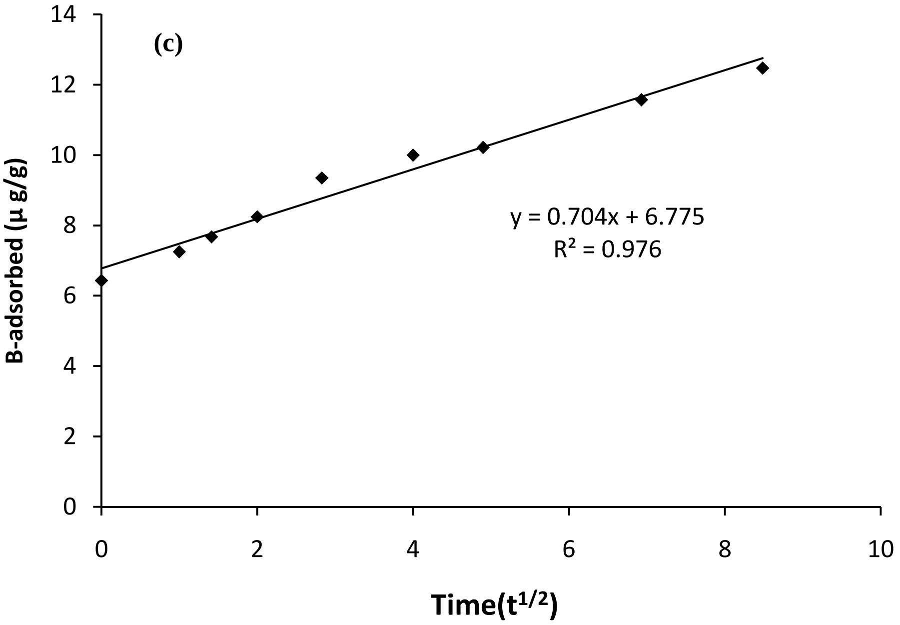
Soils	β	R^2	SE
S1	4.8359	0.988	0.2496
S2	5.8062	0.973	0.3715
S3	6.7754	0.976	0.3321
S4	4.2887	0.997	0.1116
S5	6.1046	0.969	0.3895
S6	4.7638	0.967	0.4519
S7	5.2347	0.949	0.7402
S8	4.2163	0.995	0.1325
S9	6.3248	0.968	0.3922
S10	3.9587	0.994	0.1419

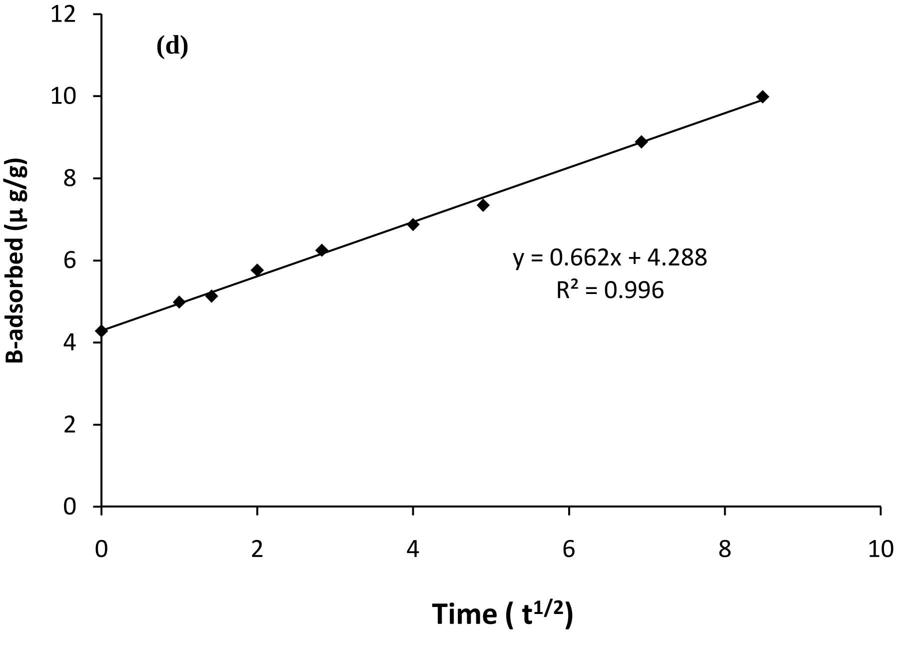
Table 4.15 Parameters of Elovich and Zero order Kinetic equation for B-adsorption

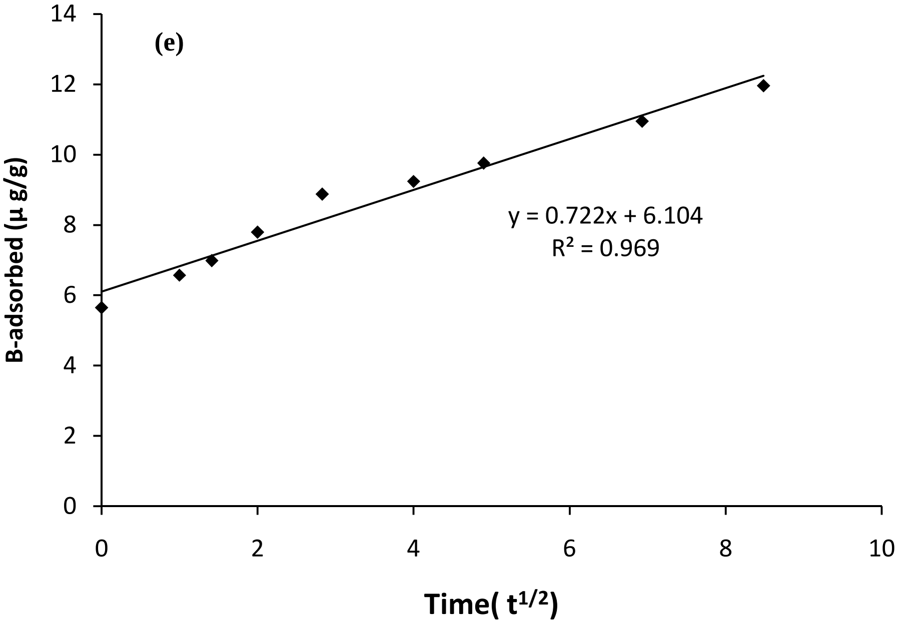
Soils	**Elovich**			**Zero order**		
	β	**R^2**	**SE**	**β**	**R^2**	**SE**
S1	4.831	0.956	0.478	5.906	0.871	0.816
S2	5.773	0.962	0.441	6.863	0.848	0.876
S3	6.731	0.974	0.346	7.802	0.841	0.861
S4	4.328	0.928	0.539	5.198	0.932	0.575
S5	6.051	0.974	0.362	7.166	0.827	0.925
S6	4.713	0.965	0.465	5.931	0.844	0.985
S7	4.555	0.958	0.422	5.509	0.892	0.672
S8	4.239	0.937	0.453	5.048	0.907	0.551
S9	6.272	0.972	1.305	7.377	0.818	0.935
S10	3.970	0.948	0.421	4.815	0.913	0.543

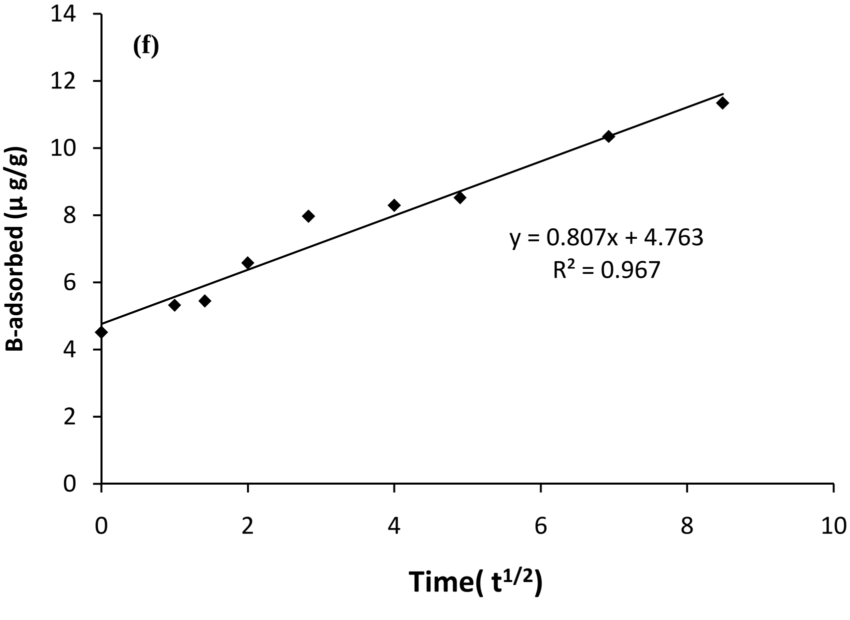

(a)
B-adsorbed (µ g/g)
0
2
4
6
8
10
12
Time (t^1/2)
0
2
4
6
8
10
y = 0.745x + 4.835
R² = 0.988

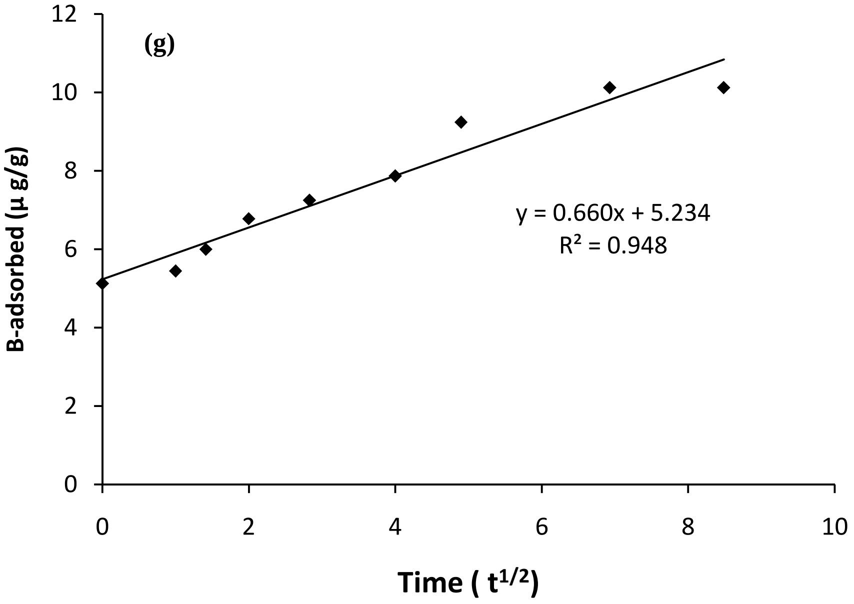

(b)
B-adsorbed (µ g/g)
0
2
4
6
8
10
12
14
Time (t^1/2)
0
2
4
6
8
10
y = 0.730x + 5.806
R² = 0.972

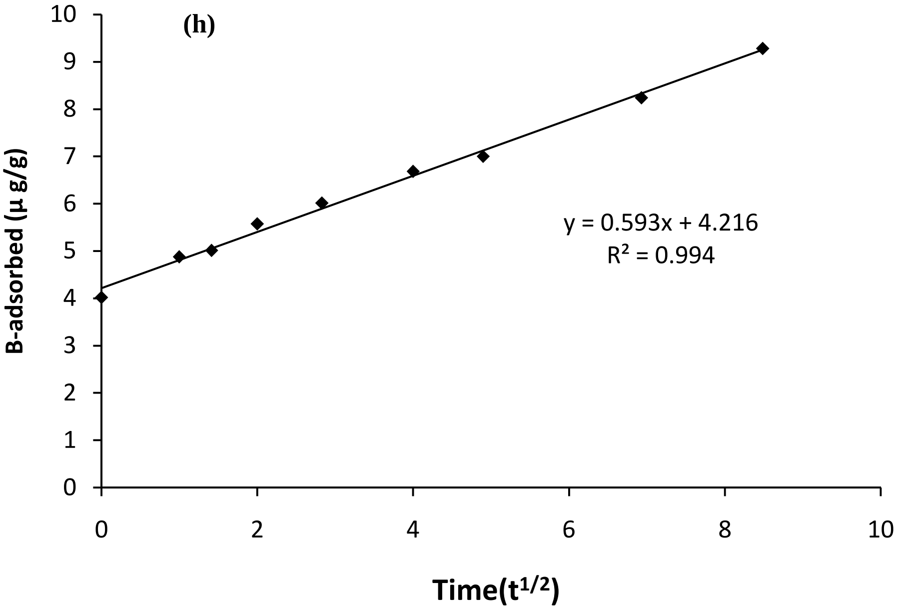

(c)
B-adsorbed (µ g/g)
Time(t^1/2)
y = 0.704x + 6.775
R² = 0.976
0
2
4
6
8
10
12
14
0
2
4
6
8
10

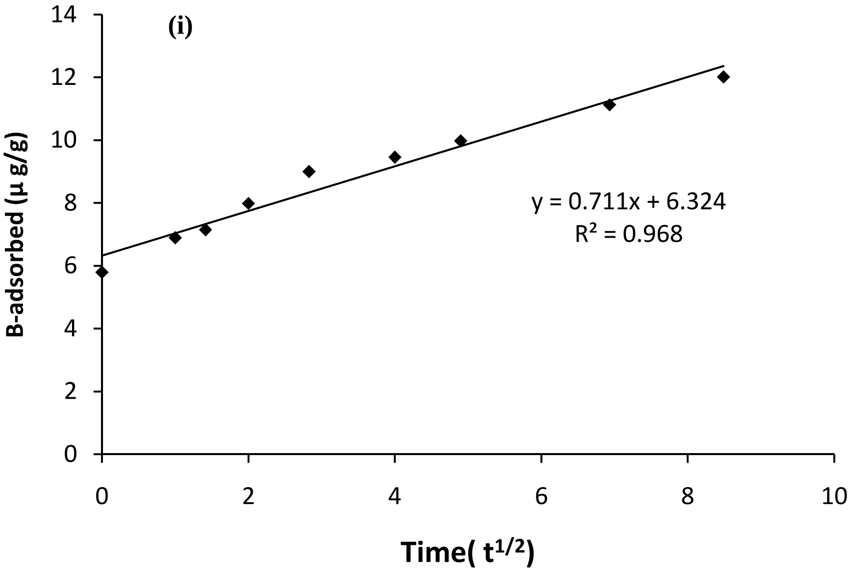

(d)
B-adsorbed (µ g/g)
Time (t^1/2)
y = 0.662x + 4.288
R² = 0.996
0
2
4
6
8
10
12
0
2
4
6
8
10


(e)
B-adsorbed (µ g/g)
Time($t^{1/2}$)
y = 0.722x + 6.104
R^2 = 0.969
0
2
4
6
8
10
12
14
0
2
4
6
8
10


(f)
B-adsorbed (µ g/g)
Time($t^{1/2}$)
y = 0.807x + 4.763
R^2 = 0.967
0
2
4
6
8
10
12
14
0
2
4
6
8
10


(g)
12
10
8
6
4
2
0
0
2
4
6
8
10
B-adsorbed (µ g/g)
Time (t^1/2)
y = 0.660x + 5.234
R² = 0.948


(h)
10
9
8
7
6
5
4
3
2
1
0
0
2
4
6
8
10
B-adsorbed (µ g/g)
Time(t^1/2)
y = 0.593x + 4.216
R² = 0.994



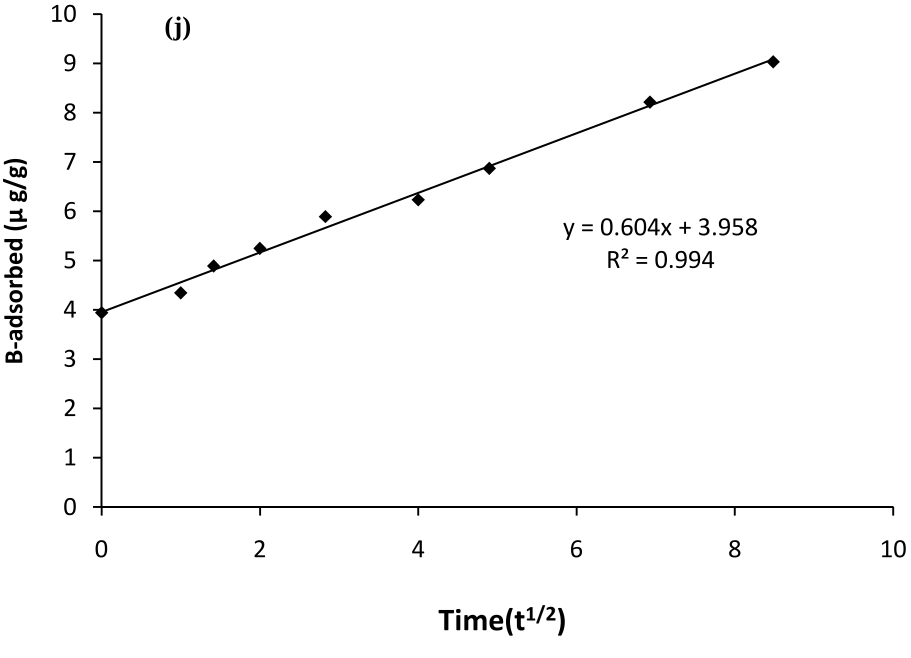
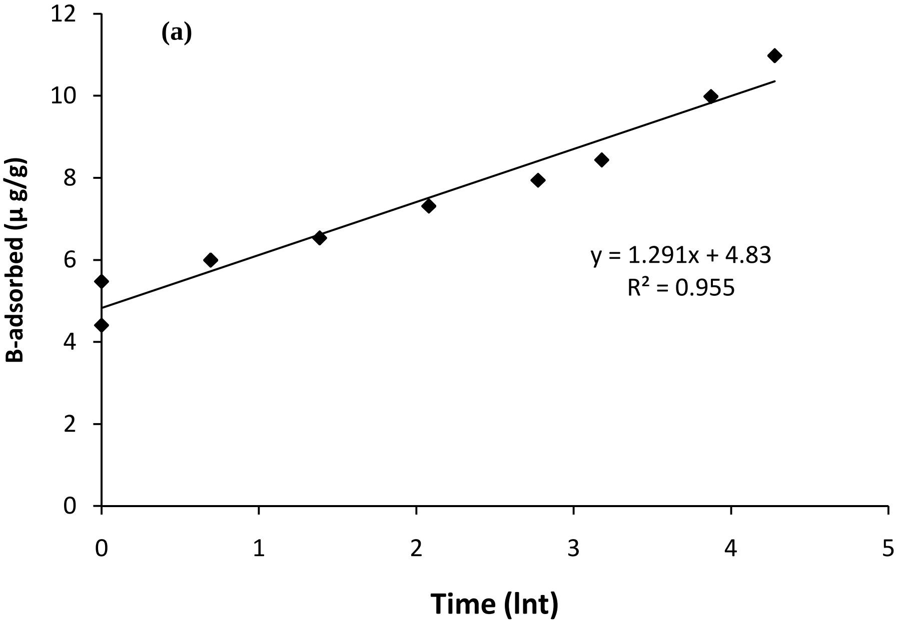
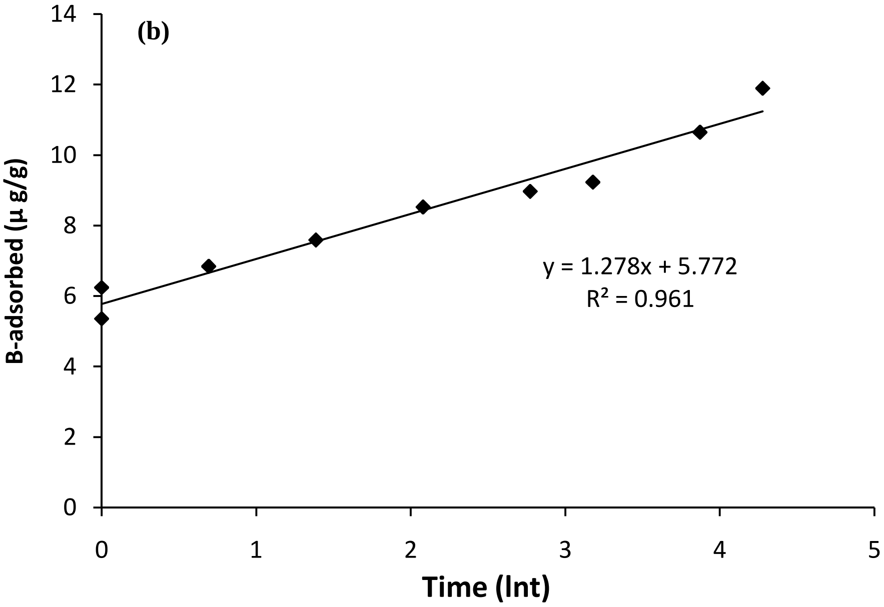
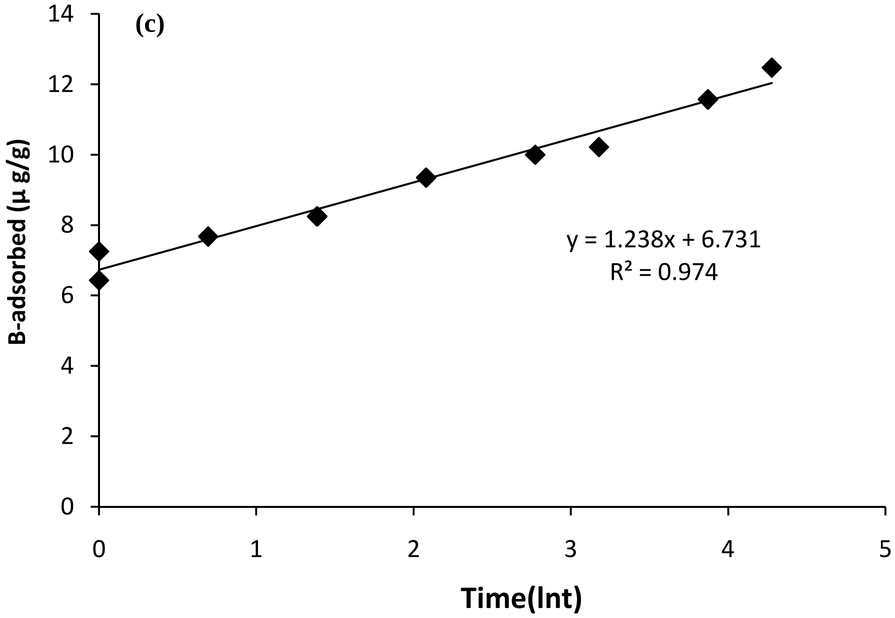
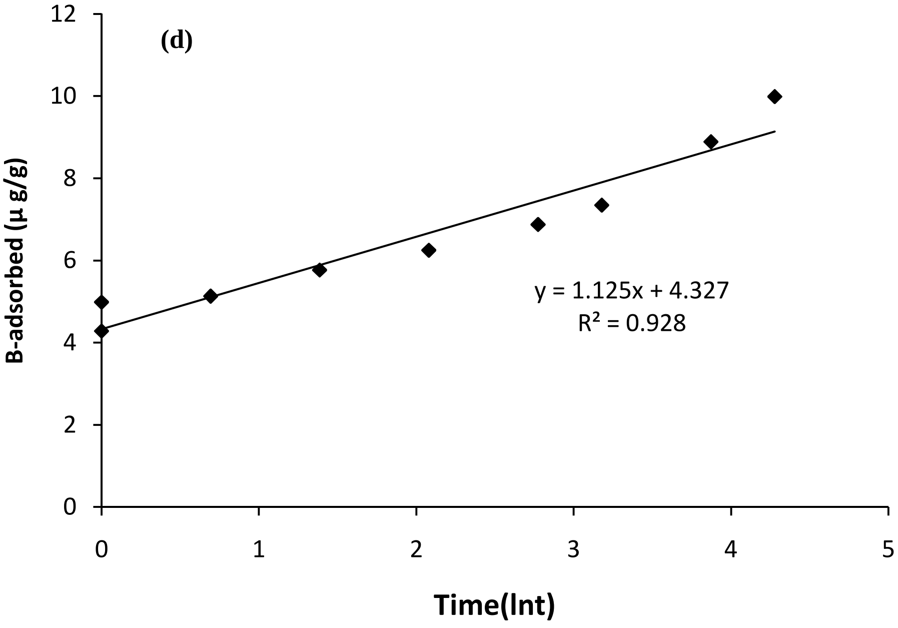


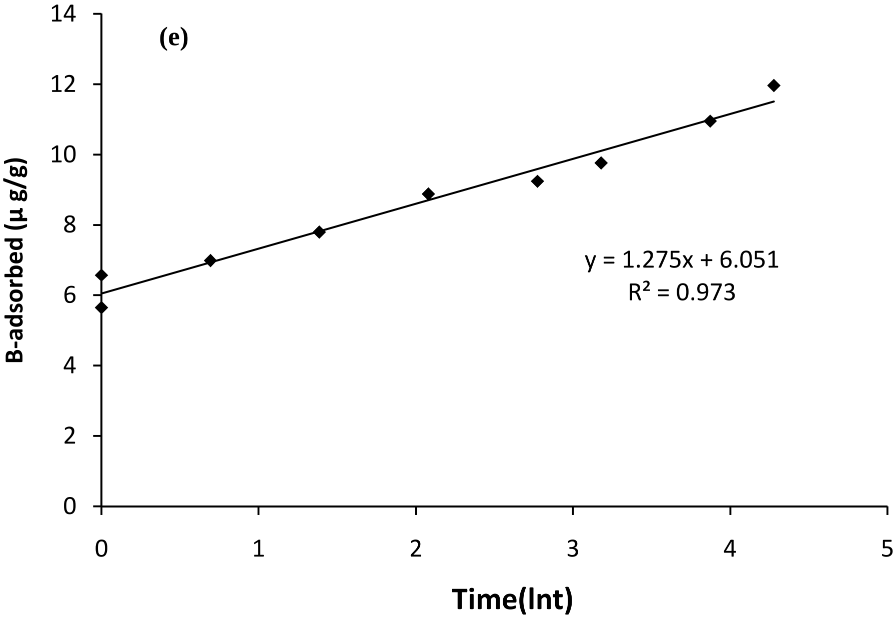
Fig 6. Analysis of Kinetic data into Parabolic diffusion equation for Boron adsorption by a)Tangmarg soil b) Khag soil c) Anantnag soil d) Kulgam soil e) Tral soil f) Shalimar soil g) Bandipora soil h) Kangan soil i) Sagipora soil and j) Shopian soil

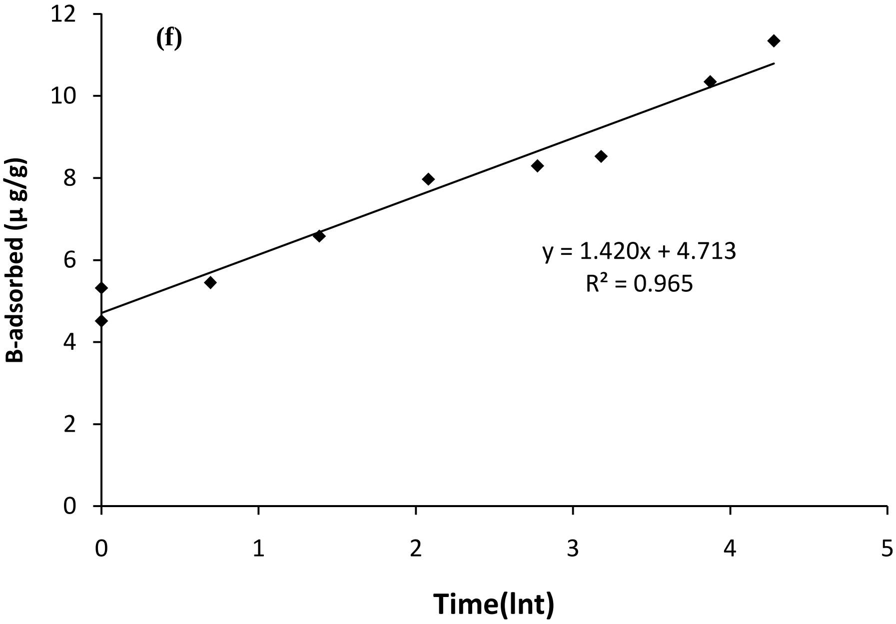

(a)
B-adsorbed (µ g/g)
Time (lnt)
y = 1.291x + 4.83
R² = 0.955
0
2
4
6
8
10
12
0
1
2
3
4
5

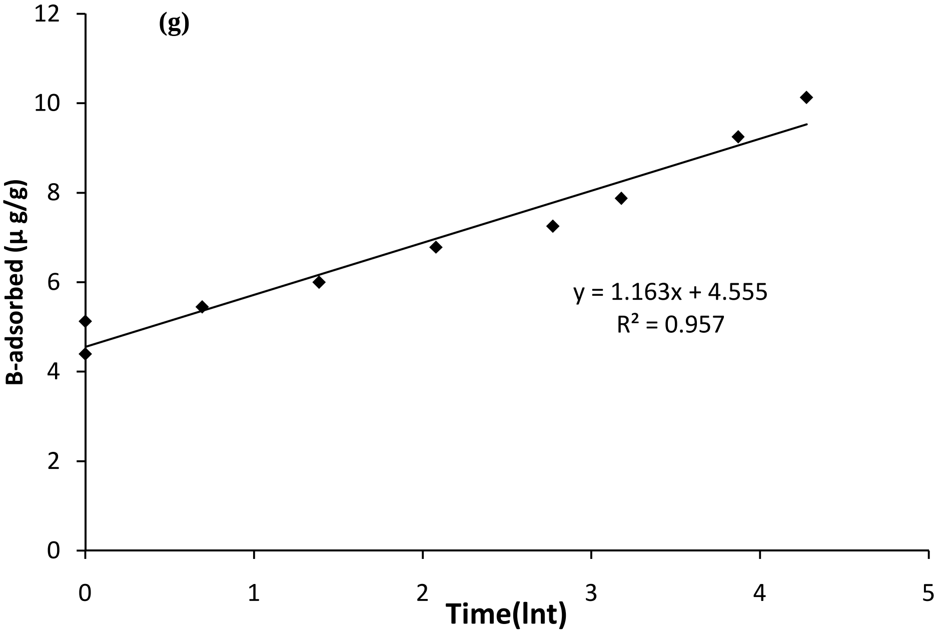

(b)
B-adsorbed (µ g/g)
Time (lnt)
y = 1.278x + 5.772
R² = 0.961
0
2
4
6
8
10
12
14
0
1
2
3
4
5

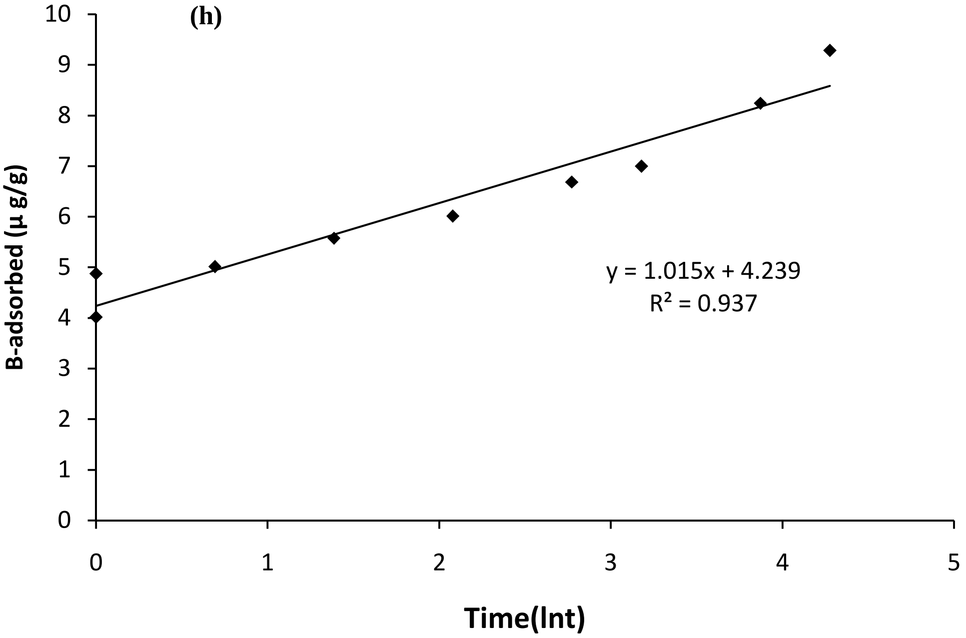

(c)
B-adsorbed (µ g/g)
Time(lnt)
y = 1.238x + 6.731
R² = 0.974
0
2
4
6
8
10
12
14
0
1
2
3
4
5

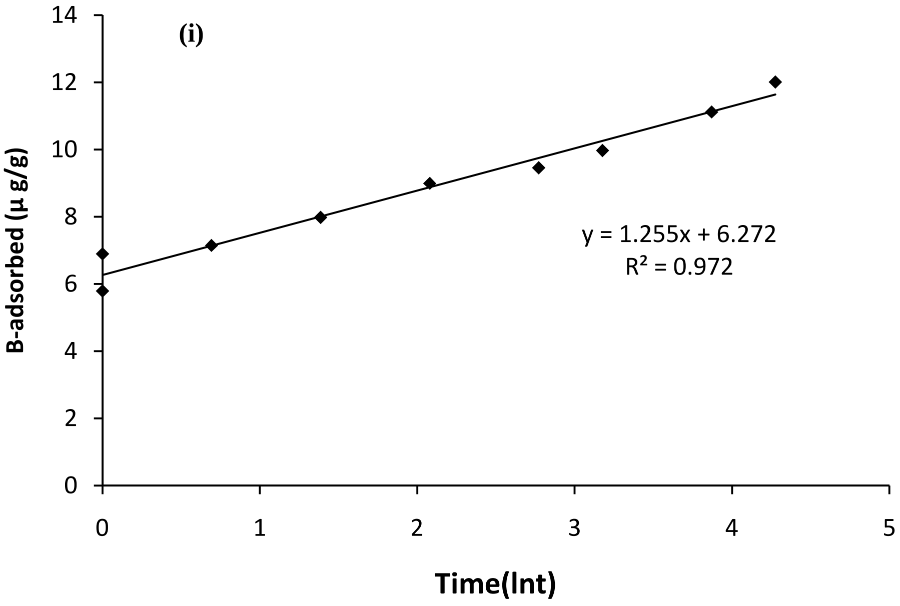

(d)
B-adsorbed (µ g/g)
Time(lnt)
y = 1.125x + 4.327
R² = 0.928
0
2
4
6
8
10
12
0
1
2
3
4
5


(e)
y = 1.275x + 6.051
$R^2 = 0.973$
B-adsorbed (µ g/g)
Time(lnt)
0
2
4
6
8
10
12
14
0
1
2
3
4
5


(f)
y = 1.420x + 4.713
$R^2 = 0.965$
B-adsorbed (µ g/g)
Time(lnt)
0
2
4
6
8
10
12
0
1
2
3
4
5


(g)
B-adsorbed (µ g/g)
Time(lnt)
y = 1.163x + 4.555
R² = 0.957
0
2
4
6
8
10
12
0
1
2
3
4
5


(h)
B-adsorbed (µ g/g)
Time(lnt)
y = 1.015x + 4.239
R² = 0.937
0
1
2
3
4
5
6
7
8
9
10
0
1
2
3
4
5



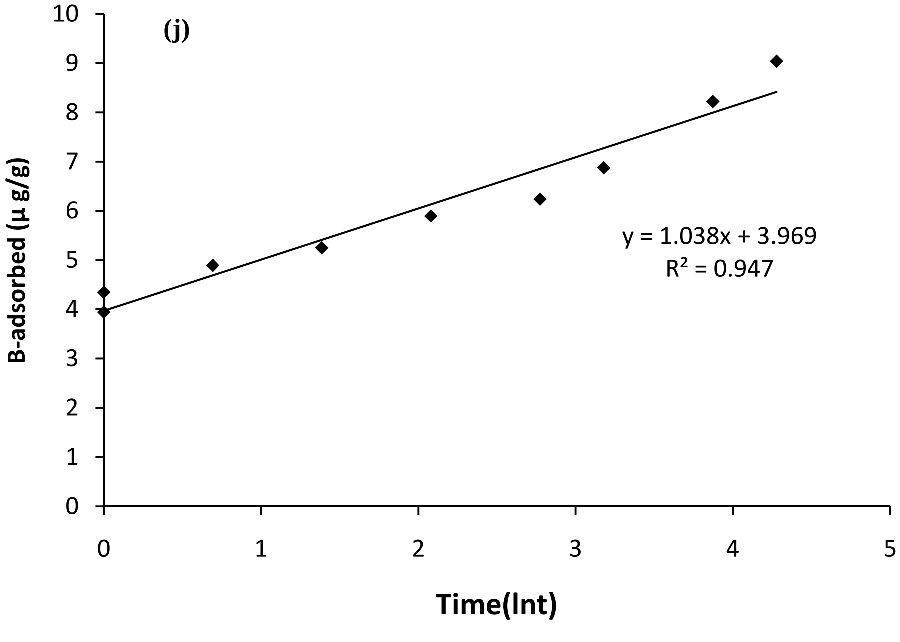


Fig 7.Analysis of Kinetic data into Elovich equation for Boron adsorption by a)Tangmarg soil b) Khag soil c) Anantnag soil d) Kulgam soil e) Tral soil f) Shalimar soil g) Bandipora soil h) Kangan soil i) Sagipora soil and j) Shopian soil

4.3.2 Kinetics of boron desorption by soils

All the soils used for boron adsorption kinetics were also subjected to desorption study after 48 hours of adsorption study. The soils were pre-treated with 40 µg B g^{-1} soil. The concentration of boron desorbed (C) in 0.05 M manitol solution as a function of time (t) for ten soils are shown in Table 4.16.

The amount of desorbable boron was strikingly higher in the coarse textured soils as compared to the fine textured soils. It increased with decrease in CEC and vice versa. Desorbed boron when expressed as percentage of adsorbed was higher in soils with low CEC as compared to soils with high CEC. The difference in the desorbable boron appears to have largely resulted from less number of boron retentive sites as well as their ability to retain boron with great tenacity in coarse textured soils. Furthermore, the desorption of boron took relatively lesser time i.e. 48 hours in soils with low CEC and coarse texture and 72 hours in soils with high CEC and fine texture and still it was not complete.

The desorption reaction was initially fast and thereafter desorption of boron became slow. The desorption reactions seemed to have completed in 48 hours in Tangmarg, Kulgam, Shalimar, Kangan and Sagipora soils. In Khag, Anantnag, Tral, Bandipora and Shopian soils, the reaction was not complete even up to 72 hours and therefore, the values of total desorbable boron could not be ascertained. For kinetic treatment of the data, the concentration of solution boron at the plateau of the curves was considered as the total desorbable boron (Bo) with the assumption that the desorption reaction at that stage was complete in these soils. The values of Bo thus obtained were 10.25, 10.22, 11.28, 12.95, 11.54, 11.59, 11.62, 13.58, 9.55 and 14.58 µg g^{-1} for Tangmarg, Khag, Anantnag, Kulgam, Tral, Shalimar, Bandipora, Kangan, Sagipora, and Shopian soils, respectively (Table 4.16).

Table - 4.16 Amount of boron desorbed (μg g^{-1}) from the soils in 0.05 M mannitol solution with respect to time.

Soils	Time (h)								
	0	**1**	**2**	**4**	**8**	**16**	**24**	**48**	**72**
S1	7.65	7.94	8.35	8.56	8.85	9.25	9.79	10.25	10.25
S2	7.11	7.44	7.78	8.56	8.89	9.22	9.46	9.87	10.22
S3	6.82	7.28	7.78	8.55	8.69	9.42	9.84	10.23	11.28
S4	9.33	9.92	10.56	10.98	11.94	12.29	12.63	12.95	12.95
S5	6.89	7.73	8.89	9.04	9.72	10.67	11.15	11.41	11.54
S6	7.33	7.84	9.47	9.63	10.45	11.09	11.29	11.59	11.59
S7	8.88	9.35	9.45	9.78	9.98	10.22	10.49	11.16	11.62
S8	8.76	9.35	10.13	10.55	11.02	11.78	12.18	13.58	13.58
S9	6.35	6.80	7.52	7.76	8.34	9.03	9.14	9.55	9.55
S10	9.82	10.27	10.89	11.65	11.88	12.88	13.45	13.86	14.58

Table - 4.17 Relative amounts of total desorbed boron and that associated with each retention site

Soils	Total desorbed boron (μg g^{-1})	Desorbed boron				Relative amount of desorbed boron [A/B]
		Site - 1		Site - 2		
		(μg g^{-1}) [A]	% of Total	(μg g^{-1}) [B]	% of Total	
S1	10.25	8.01	78.16	2.24	21.84	3.58
S2	10.22	8.41	82.34	1.81	17.66	4.66
S3	11.28	8.43	74.75	2.85	25.25	2.96
S4	12.95	10.34	79.84	2.61	20.16	3.96
S5	11.54	8.87	76.91	2.67	23.09	3.33
S6	11.59	9.03	77.90	2.56	22.10	3.53
S7	11.62	9.38	80.71	2.24	19.29	4.18
S8	13.58	9.97	73.42	3.61	26.58	2.76
S9	9.55	7.26	76.00	2.29	24.00	3.17
S10	14.58	11.39	78.14	3.19	21.86	3.57

The data was then tested for kinetic treatment using the integrated rate equation (Frost and Pearson, 1961) given as under;

$$\text{Log (Bo-C)} = \text{log Bo-(K/2.303)}$$

Where Bo is the total desorbable boron and K refers to the rate constant, the values of log (Bo-C) for different soils are presents in Table 4.19 and the plots of log (Bo-C) versus time (t) are presented in figure 8. The curves of all the soils indicate two distinct linear portions suggesting the involvement of two types of pseudo-first order reactions in boron desorption. The slopes of the two linear portion of the curves represent different sites of boron retention by the soils, the sites 1 and 2 corresponding to the upper and lower line i.e. to the steep and less steep slopes of the curves, belonged to fast and slow boron desorption reaction sites, respectively.

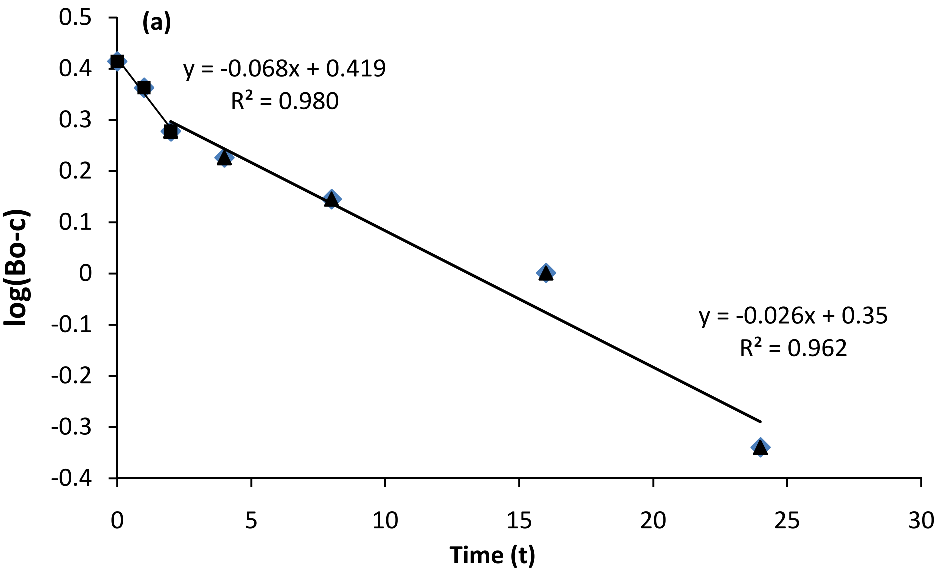
In the present study, the values of desorbable boron for the site 2 were calculated taking antilog of the intercepts of these sites in different soils. The values of desorbable boron from site-1 were worked out as the difference between the total desorbable boron and the desorbable ascribed to site 2. It is evident that about 73 and 82 percent of the total desorbable boron could be attributed to site-1, which represents the most rapidly desorbable fraction and the rest meagre amount of about 17 and 27 per cent from site-2 which comprises less readily desorbable fraction (Table 4.17).

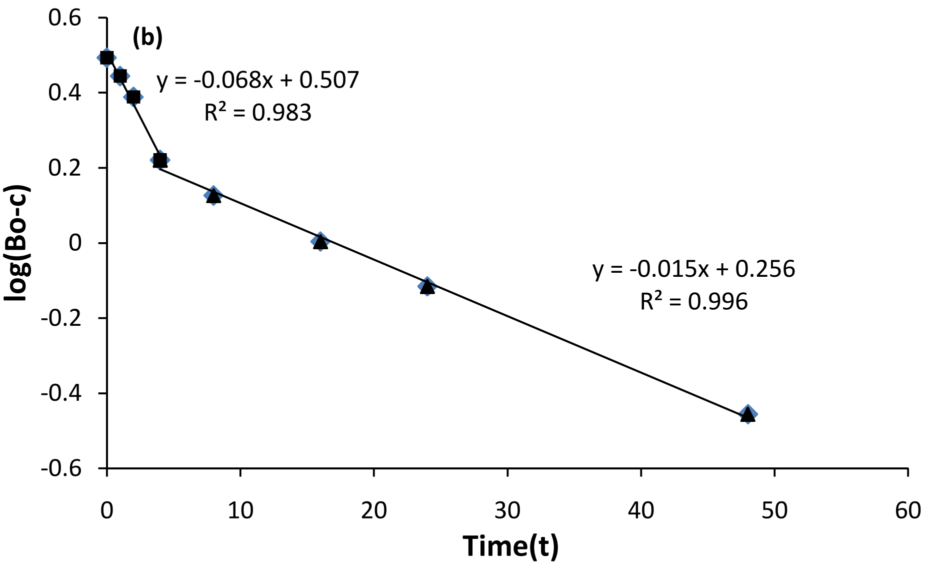
These results thus indicate the existence of two types of boron desorption sites in these soils. The R^2 and SE values for pseudo-order kinetics of boron desorption described by two curves indicating two respective sites are presented in Table 4.18. The relative constancy of the percentages of desorbable boron at site 1 and 2 indicated the desorption of boron has originated from two sites of retention on the same substance, possibly the hydroxyl Al and Fe compounds. Boron may also be adsorbed on the edges and inter layer regions of clay minerals by anion exchange and/or hydroxyl substitution.

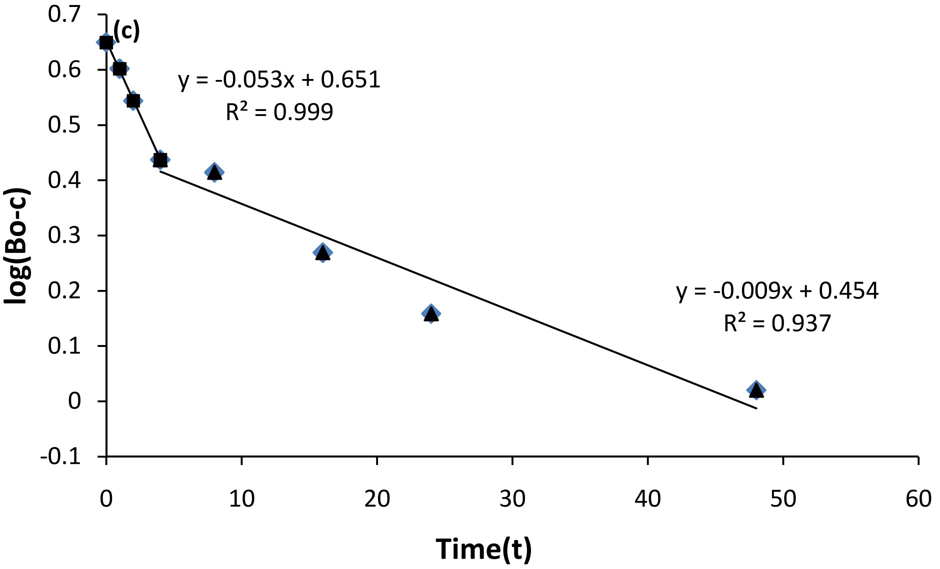
The data of boron desorption was also fitted to various kinetic models like zero order, first order, second order, power function, Elovich and parabolic diffusion and were tested by least square regression analysis for describing boron desorption from the soils. The models which had highest coefficient of determination (R^2) and the lowest standard error of estimates (SE) values was considered to be the best fit.

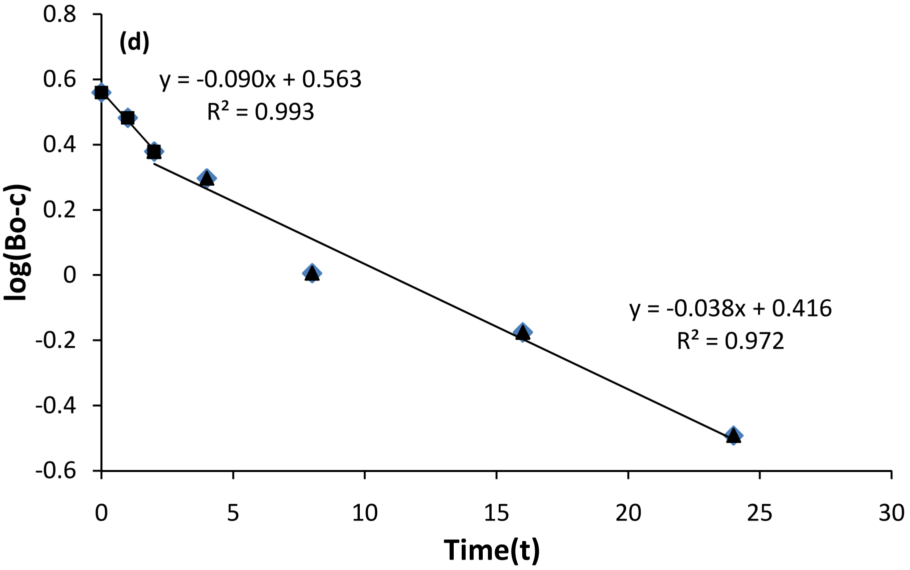
The perusal of the data presented in Table 4.20 showed that Elovich kinetic equation was best among different models as evident by the overall highest values of coefficient of determination (R^2) and lowest standard error of estimates (SE) values over the entire range of time. The maximum R^2 value of 0.986 was obtained in Shopian soils, followed by 0.982 in Khag soils, 0.976 in Tangmarg soils, 0.974 in Kangan soils, 0.971 in Anantnag soils, 0.964 in Sagipora soils, 0.954 in Kulgam soils, 0.946 in Tral soils, 0.936 in Bandipora soils, and 0.908 in Shalimar soils.

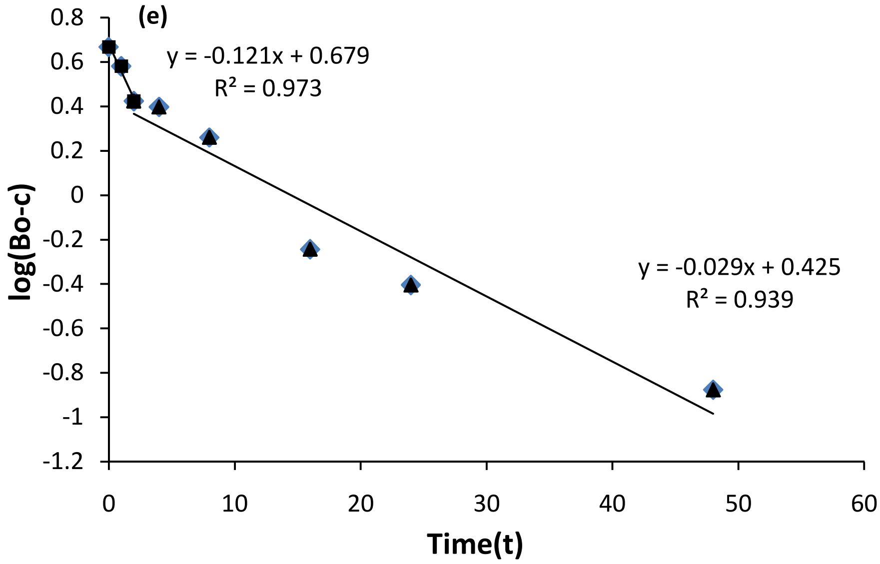
The Power function model was found to be equally good in describing boron desorption kinetics in all the soils. The R^2values were quite high and SE values were low. The R^2 values ranged between 0.874 and 0.983 while SE values varied from 0.0174 to 0.0644. The data further revealed that zero order, first order, second order and parabolic diffusion models could not describe the boron desorption rate satisfactorily as the R^2 values were low. Though in some soils R^2 values were high indicating the suitability of parabolic diffusion model in Tangmarg soils (0.948), Khag soils (0.910), Anantnag soils (0.959), Bandipora soils (0.987), Kangan soils (0.960) and Shopian soils (0.948). The values of SE were also found to be somewhat low for some soils in case of parabolic diffusion model.

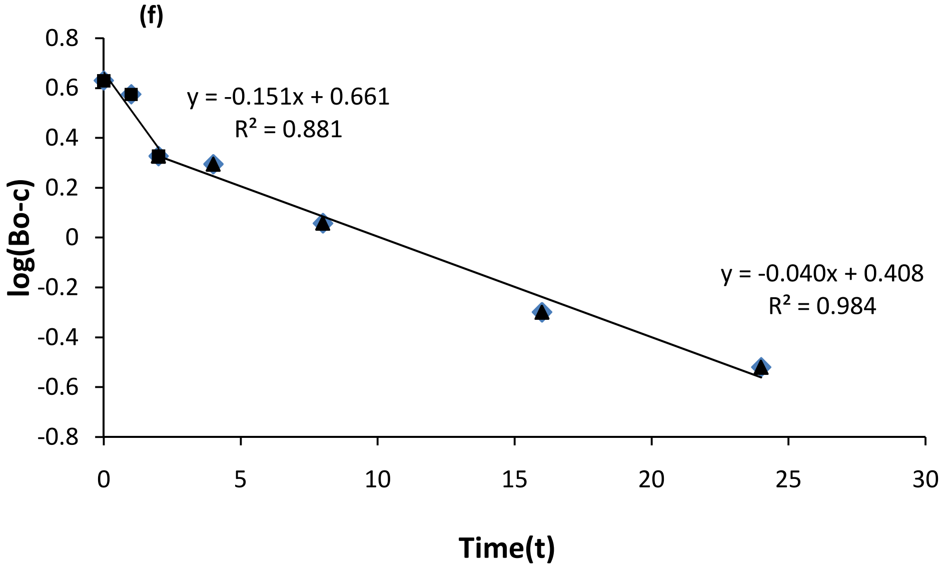

(a)
y = -0.068x + 0.419
R² = 0.980
y = -0.026x + 0.35
R² = 0.962
log(Bo-c)
Time (t)
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
0
5
10
15
20
25
30

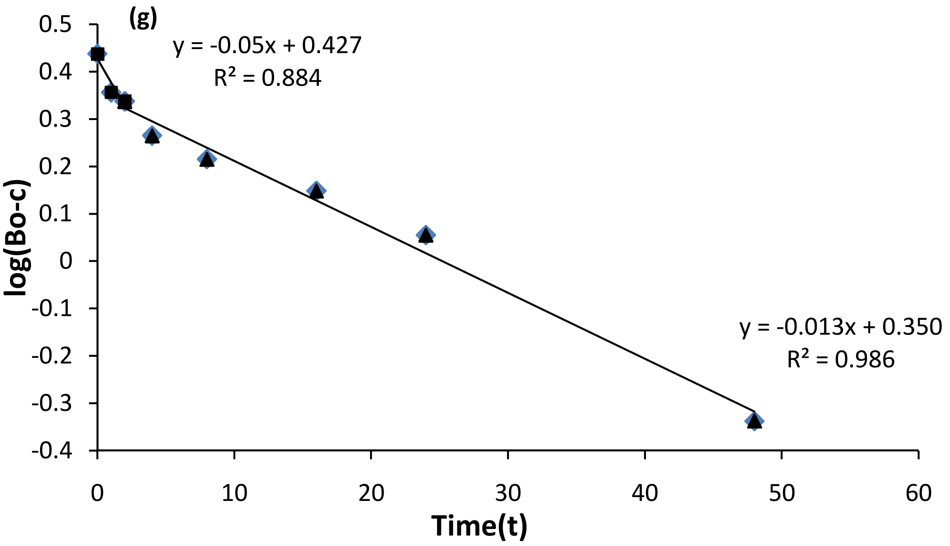

(b)
y = -0.068x + 0.507
R² = 0.983
y = -0.015x + 0.256
R² = 0.996
log(Bo-c)
Time(t)
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
0
10
20
30
40
50
60

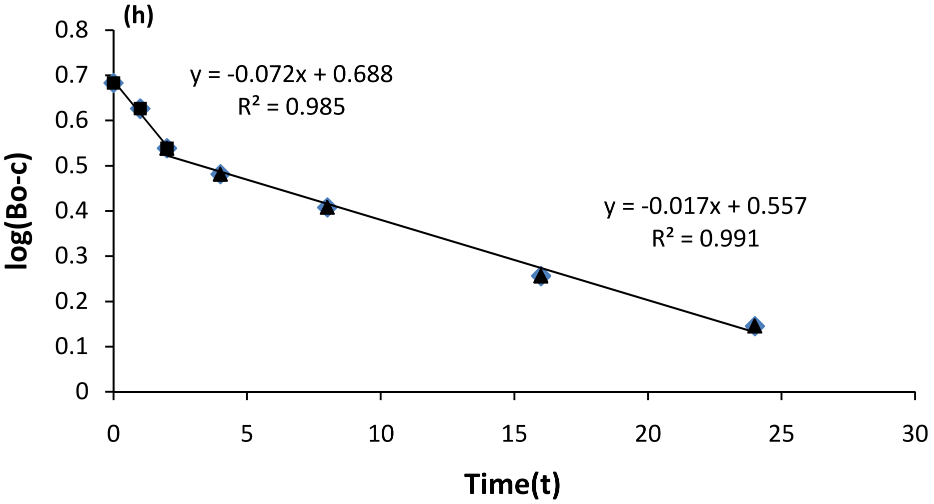

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
(c)
y = -0.053x + 0.651
R² = 0.999
y = -0.009x + 0.454
R² = 0.937
log(Bo-c)
0
10
20
30
40
50
60
Time(t)

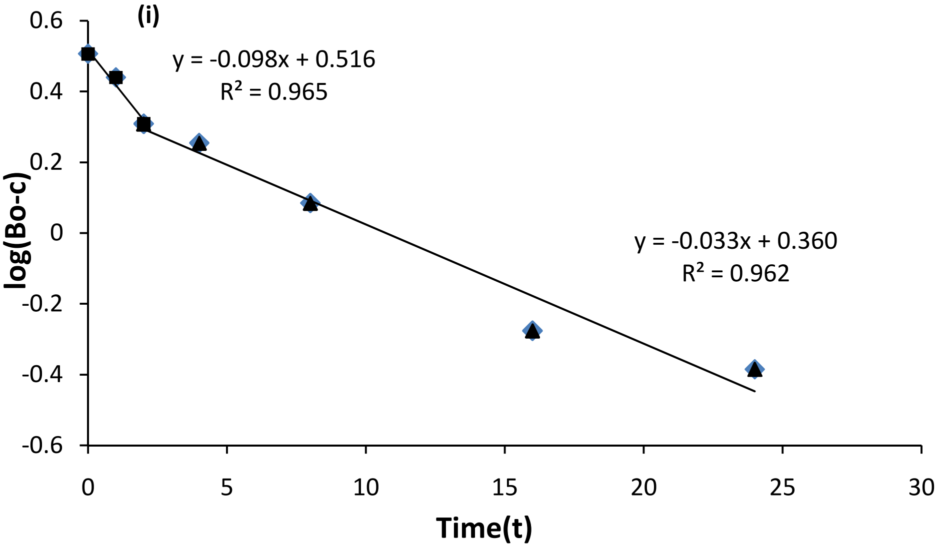

0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
(d)
y = -0.090x + 0.563
R² = 0.993
y = -0.038x + 0.416
R² = 0.972
log(Bo-c)
0
5
10
15
20
25
30
Time(t)


(e)
y = -0.121x + 0.679
R² = 0.973
y = -0.029x + 0.425
R² = 0.939
log(Bo-c)
Time(t)
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
0
10
20
30
40
50
60


(f)
y = -0.151x + 0.661
R² = 0.881
y = -0.040x + 0.408
R² = 0.984
log(Bo-c)
Time(t)
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
0
5
10
15
20
25
30


(g)
y = -0.05x + 0.427
R² = 0.884
y = -0.013x + 0.350
R² = 0.986
log(Bo-c)
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
0
10
20
30
40
50
60
Time(t)


(h)
y = -0.072x + 0.688
R² = 0.985
y = -0.017x + 0.557
R² = 0.991
log(Bo-c)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
30
Time(t)



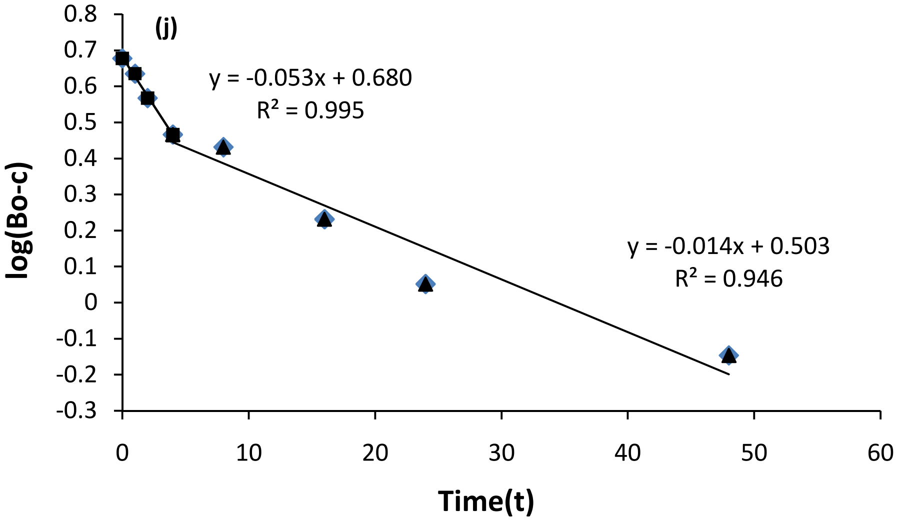


Fig. 8 Plots of log (Bo-C) versus time (t) for a)Tangmarg soil b) Khag soil c) Anantnag soil d) Kulgam soil e) Tral soil f) Shalimar soil g) Bandipora soil h)Kangan soil i) Sagipora soil and j) Shopian soil

Table - 4.18 Coefficient of determination and standard error of estimates for boron desorption kinetics in different soils of Kashmir

Soils	Site - 1		Site - 2	
	R^2	SE	R^2	SE
S1	0.981	0.0136	0.963	0.0429
S2	0.983	0.0190	0.996	0.0163
S3	0.999	0.0031	0.937	0.0440
S4	0.993	0.0104	0.972	0.1687
S5	0.973	0.0287	0.939	0.4158
S6	0.881	0.0787	0.985	0.0413
S7	0.885	0.0256	0.986	0.0283
S8	0.985	0.0125	0.992	0.0131
S9	0.966	0.0264	0.963	0.0541
S10	0.996	0.0074	0.947	0.0648

Table - 4.19 Values of log (Bo-C) against time for different soils of Kashmir

Soils	Time (h)								
	0	**1**	**2**	**4**	**8**	**16**	**24**	**48**	**72**
S1	0.414	0.363	0.278	0.226	0.146	0.001	-0.339	-	-
S2	0.493	0.444	0.388	0.221	0.126	0.003	-0.116	-0.456	-
S3	0.650	0.602	0.544	0.437	0.414	0.269	0.159	0.020	-
S4	0.559	0.481	0.378	0.296	0.005	-0.176	-0.492	-	-
S5	0.668	0.581	0.424	0.398	0.261	-0.060	-0.404	-0.876	-
S6	0.630	0.574	0.327	0.294	0.057	-0.299	-0.520	-	-
S7	0.438	0.356	0.338	0.265	0.215	0.149	0.055	-0.337	-
S8	0.683	0.626	0.539	0.481	0.408	0.256	0.146	-	-
S9	0.506	0.439	0.308	0.254	0.084	-0.277	-0.385	-	-
S10	0.677	0.635	0.567	0.466	0.431	0.231	0.052	-0.146	-

Table - 4.20 Parameters of boron desorption kinetics

Soils	Zero order		First order		Second order		Parabolic diffusion		Elovich		Power function	
	R^2	SE	R^2	SE	R^2	SE	R^2	SE	R^2	SE	R^2	SE
S1	0.779	0.4821	0.752	0.0569	0.723	0.0068	0.948	0.2347	0.976	0.1595	0.977	0.0174
S2	0.721	0.6172	0.678	0.0775	0.635	0.0098	0.910	0.3494	0.982	0.1557	0.971	0.0233
S3	0.818	0.6648	0.761	0.0864	0.699	0.0113	0.959	0.3171	0.971	0.2649	0.972	0.0297
S4	0.607	0.9072	0.577	0.0842	0.546	0.0079	0.842	0.5759	0.954	0.3092	0.939	0.0321
S5	0.627	1.0895	0.574	0.1268	0.518	0.0151	0.856	0.6773	0.946	0.4154	0.915	0.0566
S6	0.533	1.1646	0.489	0.1297	0.446	0.0146	0.775	0.8081	0.908	0.5165	0.874	0.0644
S7	0.899	10.4215	0.873	0.0328	0.844	0.0036	0.987	3.0561	0.936	0.2378	0.945	0.0217
S8	0.803	0.8147	0.757	0.0813	0.705	0.0082	0.960	0.3684	0.974	0.2985	0.973	0.0269
S9	0.640	0.7614	0.600	0.1010	0.558	0.0136	0.866	0.4648	0.964	0.2417	0.945	0.0375
S10	0.781	0.8278	0.739	0.0751	0.695	0.0069	0.948	0.4042	0.986	0.2075	0.983	0.0190

4.4 Response of Berseem to Boron and its critical limits in soils and plants

4.4.1 Response of berseem

A greenhouse experience was conducted to study the response of berseem to boron application at 0, 1.0 and 2.0 mg B kg^{-1} soil. The bulk soil samples from different areas of Kashmir were selected varying in physico-chemical properties and available boron content (Table 4.1). The plants were harvested for after two cuttings, first at 60 days of growth and second, 30 days after first cutting. The observation recorded on growth characteristics, dry matter content and uptake of boron by berseem as influenced by boron application at 60 and 90 days of growth are presented in Table 4.21 and 4.26.

Boron deficiency symptoms

The boron deficiency symptoms on berseem plants grown on control treatments were observed at 45 days after seeding. The deficiency symptoms ranged from mild to severe (Plate 1). Mild deficiency symptoms were characterised as younger leaf margins acquiring a purplish red tinge that spread and engulf the whole leaf in case of severe deficiency (Plate 2). The severe deficiency symptoms of boron were noted in plants grown in control treatments of Kangan and Shopian soils. Whereas mild to moderate visual deficiency symptoms were observed in control pots of Khag and Bandipora soils.

First cutting (60 days growth)

The data on dry matter yield of berseem at first cutting after 60 days of growth is given in table 4.21. There was significant increase in dry matter of berseem at 1.0 mg B kg^{-1} and 2.0 mg B kg^{-1} soil over control. Application of 2.0 mg B kg^{-1} soils resulted in non-significant increase in dry matter yield of berseem as compared to 1.0 mg B kg^{-1} soil.

The dry matter yield of berseem in control pots varied in different soils and it ranged from 1.073 to 2.500 g pot^{-1} with a mean value of 1.480 g pot^{-1}. With the application of 1.0 mg B kg^{-1} soil, the DMY on different soils varied from 1.410 to 2.763 g pot^{-1} with a mean value of 2.057 g pot^{-1}. These values with the application of 2.0 mg B kg^{-1} soil ranged between 1.483 to 2.843 g pot^{-1} with a mean value yield of 2.137 g pot^{-1} (Table 4.21). On an average the dry matter yield of berseem in control treatments was 1.480 g pot^{-1} and it increased to 2.057 g pot^{-1} with the application of 1.0 B Kg^{-1} soil, showing 27.78 per cent increase over control. Further application of 2.0 mg B kg^{-1} soil increased the dry matter in the soils but the increase was non-significant. The overall mean was 2.137 g pot^{-1} which showed 44.43 and 3.9 per cent increase over control and 1.0 mg B kg^{-1} soil.

The soils differed in their response to applied boron. The maximum response to boron was observed in Anantnag soil, which gave the relative yield of 97.30 per cent. The lower responses were observed in Shalimar, Bandipora, Kangan and Sagipora soils, which gave 60 per cent or more of relative dry matter yield. The data showed that 62.98 to 97.30 per cent (dry matter with boron application=100), with a mean value of 76.90 per cent was observed without boron application.

The data pertaining to the effect of boron application on boron concentration in berseem at 60 days of growth are presented in table 4.22. The boron concentration in plants grown in control pots ranged from 12.26 to 35.400 µg g^{-1} with a mean value of 19.477 µg g^{-1}. The concentration of boron in plants increased with application of 1.0 and 2.0 mg B kg^{-1} soil. It ranged from 16.767 to 34.533 µg g^{-1} with a mean value of 21.707 µg g^{-1} with the application of 1.0 mg B kg^{-1} soil, where as it varied from 22.900 to 38.833 µg g^{-1} with a mean value of 27.950 µg g^{-1} with the application of 2.0 mg B kg^{-1} soil (Table 4.22). The mean boron concentration in the control pots was 19.477µg g^{-1} and it increased to 21.707 and then to 27.950 µg g^{-1} with 1.0 and 2.0 mg B kg^{-1} soil applied,respectively. There was a successive increase in boron concentration with the rates of boron application. The soils used for present study also gave significant differences in their boron concentration behaviour in plants grown in them. The highest mean boron concentration in plants (36.255 µg g^{-1}) was observed in Shopian soil and lowest (17.311 µg g^{-1}) in Tral soil.

The uptake of boron by berseem with the application of boron is presented in Table 4.23. Boron uptake in control pots varied from 17.620 to75.085 µg pot^{-1} with a mean value of 33.609 µg pot^{-1}.The boron uptake ranged from 28.670 to 93.663 µg pot^{-1} with a mean value of 45.980 µg pot^{-1} at 1.0 mg B kg^{-1} soil application. It increased from 37.588 to109.674 µg pot^{-1} with a mean value of 61.026 µg pot^{-1} when 2.0 mg B kg^{-1} was applied (Table 4.23). The boron uptake in plants increased significantly and successively with the application of increasing rates of boron. The mean increase in boron uptake with 1.0 and 2.0 mg B kg^{-1} over control was 36.81 and 81.58 per cent, respectively. Boron uptake by plants was markedly lower in the soils with low levels of boron as compared to moderate and adequate levels of available boron. The boron uptake highly increased with the application of 2.0 mg B kg^{-1}. In the absence of boron application, the highest boron uptake was found in Shopian soil (75.085 µg pot^{-1}), followed by Kulgam soil (66.60 µg pot^{-1}), and lowest in Tral soil (17.620 µg pot^{-1}). The relative boron uptake was highest in Kulgam soil (68.48 %), followed by Shopian soil (68.46 %) and lowest in Shalimar soil (36.99 %).

Table -4.21 Effect of Boron applications on dry matter yield of Berseem at first cutting

Soils	**Dry matter yield (g pot^{-1})** **Boron levels (mg kg^{-1} soil)**				
	0.0	**1.0**	**2.0**	**Mean**	**Bray's % yield**
S1	1.663	1.867	1.953	1.828	85.15
S2	2.257	2.540	2.670	2.489	84.52
S3	1.443	1.730	1.483	1.552	97.30
S4	2.500	2.730	2.783	2.671	89.82
S5	1.417	1.727	1.790	1.644	79.14
S6	1.250	1.883	1.970	1.701	63.45
S7	1.367	1.927	2.170	1.821	62.98
S8	1.367	1.993	2.127	1.829	64.26
S9	1.073	1.410	1.583	1.356	67.79
S10	2.123	2.763	2.843	2.577	74.68
Mean	1.480	2.057	2.137	-	76.90
	CD at 5 %			Soil= 0.19 B level= 0.17 Soil x B level= NS	

Table - 4.22 Effect of Boron application on boron concentration in berseem plant at first cutting

Soils	**Boron concentration (µg g^{-1})**				
	Boron levels (mg kg^{-1} soil)			**Mean**	**% B concentration**
	0.0	**1.0**	**2.0**		
S1	15.933	17.067	25.333	19.444	62.89
S2	15.733	16.833	22.900	18.489	68.70
S3	16.467	20.100	25.367	20.644	64.91
S4	26.600	29.700	34.967	30.422	76.07
S5	12.267	16.767	22.900	17.311	53.57
S6	14.833	16.833	25.433	19.033	58.32
S7	17.867	20.800	28.133	22.267	63.51
S8	19.467	22.167	27.600	23.078	70.53
S9	20.200	22.267	28.033	23.500	72.06
S10	35.400	34.533	38.833	36.255	91.16
Mean	19.477	21.707	27.950	-	68.17
	CD at 5 %			Soil= 0.81 B level= 1.49 Soil x B level= 2.57	

Table - 4.23 Effect of Boron application on boron uptake in berseem plant at first cutting

Soils	**Boron uptake(µg pot^{-1})**				
	Boron levels (mg kg^{-1} soil)			**Mean**	**Bray's % B uptake**
	0.0	**1.0**	**2.0**		
S1	26.765	32.233	49.449	36.149	54.13
S2	35.535	42.761	60.845	46.380	58.40
S3	23.809	34.772	37.588	32.057	63.34
S4	66.601	81.029	97.252	81.627	68.48
S5	17.620	28.670	41.179	29.156	42.79
S6	18.537	31.098	50.116	33.251	36.99
S7	23.997	40.071	61.068	41.712	39.29
S8	26.445	44.195	58.755	43.132	45.01
S9	21.696	31.308	44.338	32.447	48.93
S10	75.085	93.663	109.674	92.807	68.46
Mean	33.609	45.980	61.026	-	52.58
	CD at 5 %			Soil= 4.91 B level= 8.95 Soil x B level = NS	

Second cutting

The data on dry matter yield of berseem at second cutting taken at 30 days after first cutting is presented in Table 4.24. The dry matter yield of berseem in control pots varied in different soils and it ranged between 2.367 to 5.007 g pot^{-1} with a mean value of 3.483 g pot $^{-1}$. The dry matter in different soils with the application of 1.0 mg B kg^{-1} varied from 2.917 to 5.417 g pot^{-1} with a mean value of 3.977 g pot $^{-1}$. It ranged from 3.267 to 5.687 g pot^{-1} with a mean value of 4.293 g pot^{-1} with the application of 2.0 mg B kg^{-1} soil (Table 4.24).

The mean dry matter in control was 3.483 g pot^{-1} and it increased to 3.977 g pot^{-1} with the application of 1.0 mg B kg^{-1} soil. Further application of boron at 2.0 mg B kg^{-1} soil resulted in further increase in dry matter yield of berseem. There was 14.18 per cent and 23.27 per cent increase in dry matter yield of berseem with 1.0 and 2.0 mg B kg^{-1} soil application over control, respectively. The relative dry matter in different soils ranged between 70.41 to 94.07 per cent. Some soils responded more to boron application than others. The maximum response of 94.07 per cent was observed in Anantnag soil, followed by 88.04 per cent in Khag soil.

The perusal of data in Table 4.25 indicated that boron concentration in berseem plants in control treatments varied from 12.067 to 36.00 µg g^{-1} with a mean value of 19.404 µg g^{-1}. It increased with the application of 1.0 and 2.0 mg B kg^{-1} soil, respectively. The boron concentration varied between 15.500 to 31.233 µg g^{-1} with a mean value of 21.620 µg g^{-1} at 1.0 mg B kg^{-1} soil application where as it ranged from 20.767 to 37.300 µg g^{-1}with a mean value of 27.440 µg g^{-1}at 2.0 mg B kg^{-1} soil application. The mean boron concentration in the control pots was 19.404 µg g^{-1} and it increased to 21.620 and 27.440 µg g^{-1} with the application of 1.0 and 2.0 mg B kg^{-1} soil, respectively. There was a significant increase in boron concentration in berseem plants with the successive increase in boron addition in soils. Similarly boron concentration in different soils varied widely. Irrespective of boron levels, the mean boron concentration in soils varied from as low as 16.878 µg g^{-1} in plants grown in Tral soil to as high as 34.844 µg g^{-1} in plants grown in Sagipora soil.

The data on boron uptake by second cutting of berseem are given in Table 4.26. Boron uptake in control treatments varied from 28.561 to 151.923 µg pot^{-1} with a mean value of 68.829 µg pot^{-1}. The boron uptake in plants increased significantly with the application of 1.0 and 2.0 mg boron kg $soil^{-1}$ application. The boron uptake varied between 46.658 to 155.955 µg pot^{-1} with 1.0 mg boron kg^{-1} soil application. However, it ranged between 67.871 to 195.703 µg pot^{-1} when boron was applied at the rate of 2.0 mg B kg^{-1} soil (Table 4.26). The mean boron uptake in control pots was 68.829 mg pot^{-1} and it increased to 87.155 and 118.776 µg pot^{-1} with the application of 1.0 and 2.0 mg B kg^{-1} soil, respectively. The mean per cent increase in boron uptake with 1.0 and 2.0 mg B kg^{-1} soil application was 26.62 to 72.57 per cent, over control, respectively. The boron uptake in different soils varied significantly to as low as 50.694 µg pot^{-1} in Tral soil to as high as 167.860 µg pot^{-1} in Shopian soil. The relative boron uptake varied from as low as 42.08 per cent in Tral soil to as high as 77.63 per cent in Shopian soil.

Table - 4.24 Effect of Boron application on dry matter yield of Berseem at second cutting

Soils	**Dry matter yield (g pot^{-1})**				
	Boron levels (mg kg^{-1} soil)			**Mean**	**Relative dry matter (%)**
	0.0	**1.0**	**2.0**		
S1	2.573	3.023	3.340	2.979	77.05
S2	5.007	5.417	5.687	5.370	88.04
S3	4.497	4.893	4.780	4.723	94.07
S4	2.720	3.463	3.863	3.349	70.41
S5	2.367	3.127	3.267	2.920	72.45
S6	2.643	2.917	3.367	2.976	78.51
S7	3.507	4.003	4.253	3.921	82.45
S8	3.697	3.997	4.613	4.102	80.13
S9	3.597	3.933	4.517	4.016	79.63
S10	4.220	4.993	5.247	4.820	80.43
Mean	3.48	3.97	4.29	-	80.31
	CD at 5 %			Soil= 0.16 B level= 0.28 Soil x B level= NS	

Table - 4.25 Effect of Boron application on boron concentration at second cutting

Soils	**Boron concentration ($\mu g\ g^{-1}$)**				
	Boron levels (mg kg^{-1} soil)			**Mean**	**Relative boron Concentration (%)**
	0.0	**1.0**	**2.0**		
S1	13.667	15.500	23.467	17.544	58.24
S2	14.200	16.767	21.200	17.389	66.98
S3	16.500	20.200	25.400	20.700	64.96
S4	27.600	30.467	35.200	31.089	78.41
S5	12.067	17.800	20.767	16.878	58.11
S6	14.967	16.000	25.233	18.733	59.31
S7	18.267	21.333	28.100	22.567	65.01
S8	19.900	21.700	25.600	22.400	77.73
S9	20.867	25.200	32.133	26.067	64.94
S10	36.000	31.233	37.300	34.844	96.51
Mean	19.40	21.62	27.44	-	69.02

CD at 5 %	Soil= 0.17 B level= 0.31 Soil x B level= NS

Table - 4.26 Effect of Boron application on boron uptake at second cutting

Soils	**Boron uptake (µg pot^{-1})**				
	Boron levels (mg kg^{-1} soil)			**Mean**	**Relative boron uptake (%)**
	0.0	**1.0**	**2.0**		
S1	35.162	46.839	78.476	53.492	44.81
S2	71.118	90.812	120.575	94.168	58.98
S3	74.195	98.849	121.366	98.137	61.13
S4	75.098	105.530	136.051	105.560	55.20
S5	28.561	55.651	67.871	50.694	42.08
S6	39.560	46.658	84.958	57.059	46.56
S7	64.053	85.403	119.518	89.658	53.59
S8	73.569	86.725	118.101	92.798	62.29
S9	75.055	99.126	145.136	106.439	51.71
S10	151.923	155.955	195.703	167.860	77.63
Mean	68.82	87.15	118.77	-	55.39
	CD at 5 %			Soil= 3.42 B level = 6.25 Soil xB level = 10.83	

4.4.2 Relationship of different extractants with crop yield and B- uptake

Evaluation of soil tests as a measure of boron availability was carried out by the crop response in terms of relative dry matter yield relative boron uptake. Correlation coefficients were also worked out between the boron extracted by different extractants and absolute yield and absolute boron uptake and values are presented in Table 4.27.

First cutting

The coefficient of correlation between plant parameters and boron extracted by different methods indicated that water soluble extracted boron had the highest correlation with Bray's per cent yield of berseem (r=0. 884**), followed by hot water extracted boron (r=0.854**). Also boron extracted by 0.01 M$CaCl_2$ gave significant coefficient of correlation with Bray's per cent boron uptake (r=0.755**) at first cutting (Table 4.27)

All the methods except AB-DTPA gave significant coefficient of correlation with boron concentration. The highest coefficient of correlation was observed with 0.01M $CaCl_2$ extractant (r=0.595**), followed by hot water extractant, water soluble, 0.05 N HCl , 0.01 M $CaCl_2$ + 0.01 M mannitol (r= 0.560**, 0.547**, 0.521** and 0.472*) respectively. However there was non-significant and positive correlation with AB-DTPA extractant (r=0.272). Similarly the boron extracted with different extractants gave significant correlation with Bray's per cent boron uptake, the highest coefficient of correlation was observed by hot water soluble extraction (r= 0.835**) followed by 0.01M $CaCl_2$ soluble extraction (r= 0.755**), water soluble extraction (r^2=0.710**), 0.05 N HCl (r=0.659**) and 0.01 M $CaCl_2$+ 0.01 M mannitol extraction (r= 0.612**). However, there was non-significant correlation with AB-DTPA extractable boron.

Table - 4.27 Coefficient of correlation between different extractants and plant parameters

Extractants	First cutting			Second cutting		
	B concentration	Bray's % yield	Bray's % B uptake	B concentration	Bray's % yield	Bray's % B uptake
Water	0.547**	0.884**	0.710**	0.640**	0.913**	0.695**
Hot water	0.560**	0.854**	0.835**	0.684**	0.886**	0.884**
0.01 M $CaCl_2$	0.595**	0.850**	0.755**	0.702**	0.883**	0.724**
0.05 N HCl	0.521**	0.762**	0.659**	0.595**	0.785**	0.668**
0.01 M $CaCl_2$- 0.01M mannitol	0.472*	0.616**	0.612**	0.548**	0.748**	0.642**
AB-DTPA	0.272	0.305	0.287	0.352	0.321	0.366

* Significant at 5 % level of significance

** Significant at 1 % level of significance

Second Cutting

The data in Table 4.27, showed that among different parameters water soluble extraction gave the highest coefficient of correlation with Bray's per cent yield (r= 0.913**) followed by hot water soluble, 0.01 M $CaCl_2$, 0.05 N HCl, 0.01 M $CaCl_2$+0.01 M mannitol extractants (r= 0.886**, 0.883**, 0.785**, 0.748**, respectively). All the extractants gave significant coefficient of correlation with Bray's per cent yield except AB-DTPA extractant. There was significant and highest coefficient of correlation between Bray's per cent uptake with hot water soluble (r= 0.884**) followed by 0.01 M $CaCl_2$ extractable, water soluble, 0.05 N HCl, 0.01 M $CaCl_2$+ 0.01 M mannitol (r= 0.724**, 0.695**, 0.668** and 0.642**, respectively) and lowest with AB-DTPA (r = 0.366). The results also showed that the extractants which are highly correlated with Bray's per cent yield and Bray's per cent boron uptake were water soluble and 0.01 M $CaCl_2$. Keeping in view all the methods except AB-DTPA, all other extractants showed positive and significant coefficient of correlation with different parameters of plants. 0.01 M $CaCl_2$ (r= 0.702**) extractant showed the highest coefficient of correlation with boron concentration followed by hot water soluble (r= 0.684**), water soluble (r=0.640**), 0.05 N HCl (r= 0.595**), 0.01 M $CaCl_2$+ 0.01 M mannitol (r= 0.548**) respectively. Lowest value for correlation of coefficient was seen with AB-DTPA with r^2 value of 0.352.

4.4.3 Critical levels of boron in soils and plants.

The critical level of boron in soils and plants was determined by plotting Bray's per cent dry matter yield against soil boron and plant boron concentration, respectively, adopting graphical method of Cate and Nelson (1965). The critical levels below which soils are expected to give response to added boron varied appreciably for different extractants because of different extracting power of each extractant.

Critical deficiency level in soils

The critical deficiency level of boron in soils was determined at both the cutting stages of berseem.

First cutting

The critical limit for available boron extracted by 0.01 M $CaCl_2$+ 0.01 M mannitol was found to be 0.74 mg kg^{-1} soil, showing the highest value, followed by 0.01 M $CaCl_2$ i.e. 0.70 mg kg^{-1} soil. This extractant also showed highly significant correlation with Bray's per cent yield (r= 0.762**), Bray's per cent boron uptake (r= 0.612**) and non-significant correlation with boron concentration (r= 0.472*) at first cutting. Boron extracted by hot water was highly and significantly correlated with Bray's per cent yield (r=0.854**) and Bray's per cent boron uptake (r= 0.835**) and the critical value for this extractant was found to be 0.48 $mgkg^{-1}$ soil (Table 4.28: Fig 9). Hot water parameter also showed better correlation with plant parameters.

Second Cutting

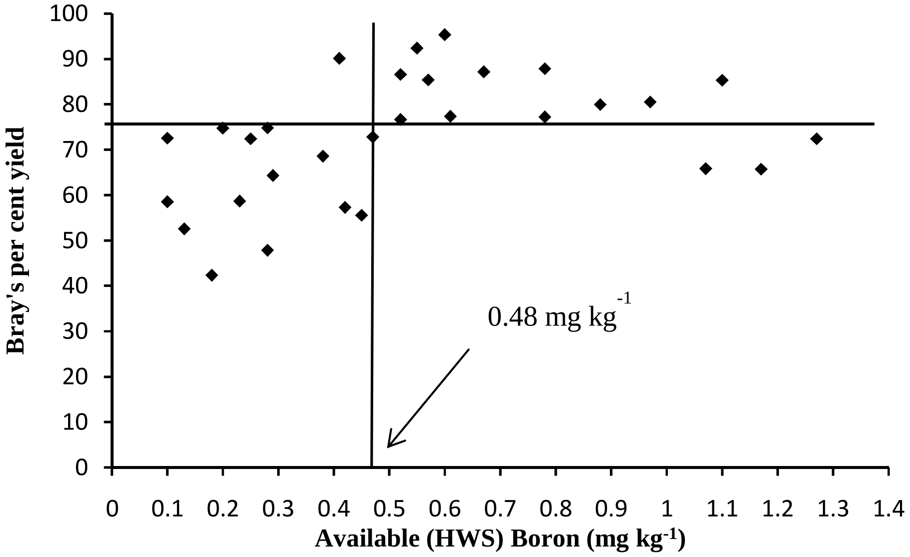
The critical limit of available boron extracted by 0.01 M $CaCl_2$+ 0.01 M was found to be 0.94 mg kg^{-1} soil (Table 4.28). This extractant also showed highly significant correlation with Bray's per cent yield (r=0.748**), Bray's per cent boron uptake (r= 0.642**) and plant boron concentration (r=0.548**). Boron extracted by hot water was significantly correlated with Bray's per cent yield (r= 0.886**) and Bray's per cent boron uptake (r= 0.884**) and the critical values of this extractant was found to be 0.49 mg kg^{-1} soil. Hot water extractant also showed better correlation with plant parameters (Table 4.27; Fig 9). The critical values of water soluble and 0.05 N HCl was found to be 0.34 and 0.63 mg kg^{-1}, respectively. These extractants also showed significant correlation with Bray's per cent yield and Bray's per cent boron uptake (r= 0.748** and r^2= 0.642**, respectively). Boron extracted with AB-DTPA extractant was not correlated significantly with any of the plant parameters.

Critical deficiency level in plants

The critical value for boron in berseem plant at first and second cutting was 23.0 and 19.0 µg g^{-1} on dry weight basis, respectively (Table 4.28: Fig 10).

Table - 4.28 Critical levels of boron in soils and plants at different cutting of berseem

S. No	Parameters	Critical levels	
		First cutting	Second cutting
1.	**Water**	0.34	0.34
2.	**Hot water**	0.48	0.49
3.	**0.01 M $CaCl_2$**	0.70	0.71
4.	**0.05 N HCl**	0.62	0.63
5.	**0.01 M $CaCl_2$- 0.01M mannitol**	0.74	0.74
	Plant		
	Total boron concentration in berseem plant	23.0	19.0



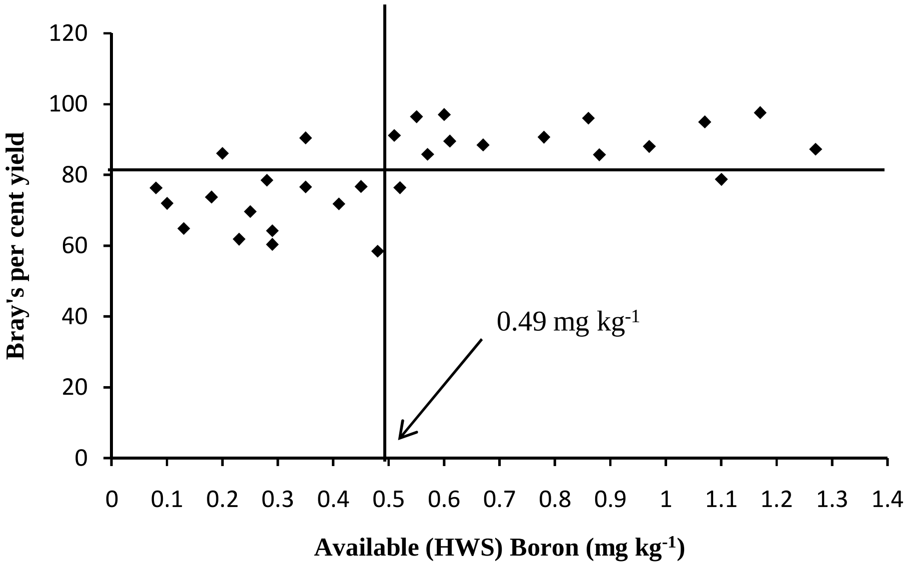
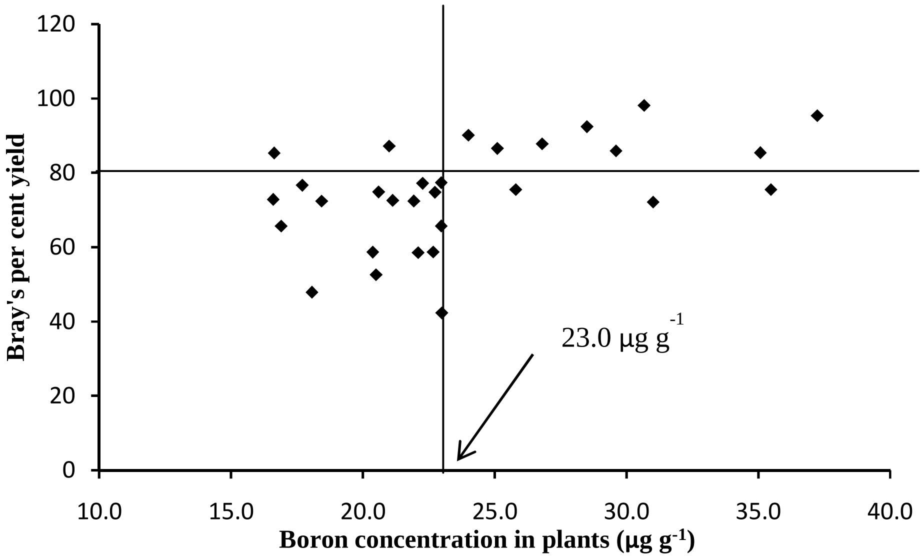


Figure 9 Critical limits of hot water soluble boron in soil for berseem at 60 and 90 days of growth



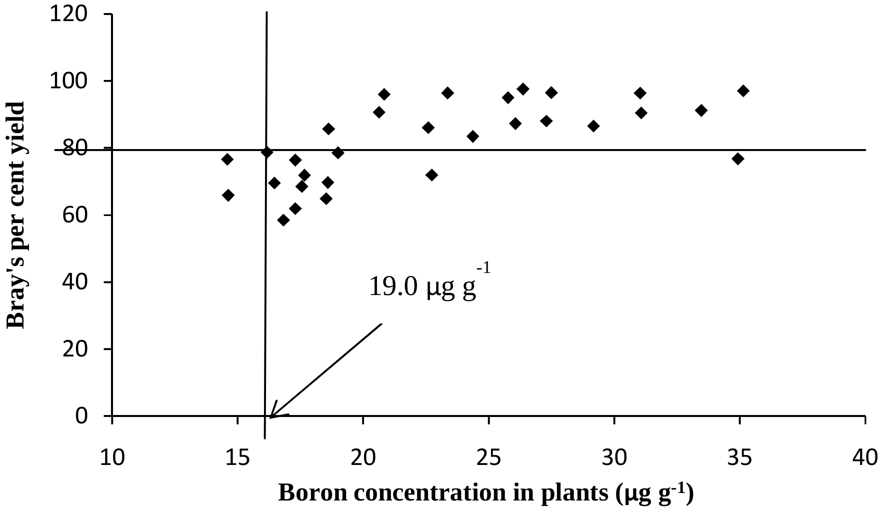


Figure 10 Critical limits of boron for berseem at 60 and 90 days of growth

Chapter – 5

DISCUSSION

The results of different experiments carried out in the present investigation are discussed in the chapter under the following heads:

- 5.1 Distribution of different forms of boron in soils.
- 5.2 Boron adsorption-desorption by soils
- 5.3 Kinetics of boron adsorption-desorption
- 5.4 Response of berseem to boron and its critical limits in soils and plants

5.1 Distribution of different forms of Boron in soils

The different forms of boron presented in Table 4.2 are discussed as under;

5.1.1 Water soluble boron

The concentration of water soluble boron in the soil samples ranged from 0.07 to 0.95 mg kg^{-1} with a mean value of 0.35 mg kg^{-1} and there was no specific distribution pattern. Water soluble boron content of Egyptian soils ranged from 0.1 to 26 µg ml^{-1} with a mean of 0.6 µg ml^{-1} (Elseewi and Elmalky, 1979). Nathani *et al.* (1970) reported that water soluble boron in soils of Rajasthan varied from 0.42 to 8.2 ppm with an average of 1.72 ppm. The content of water soluble boron varied from 0.43 to 1.29 ppm with an average of 0.73 ppm in non-saline soils and 0.43 and 2.58 ppm with an average of 1.21 ppm in low saline soils of Delhi (Gajbhiye*et al.*, 1980). Water soluble boron in saline alkaline soils of Punjab varied from 3.0 to 11.8 ppm as compared to 0.18 and 2.44 ppm in normal soils (Kanwar and Singh, 1961 and Mair,1965).

Clay and silt were positively and significantly correlated with water soluble boron (r = 0.572** and 0.374**). Singh and Kanwar (1963) also observed significant and positive relationship between water soluble boron and soil texture. Water soluble boron and silt and clay content was correlated significantly (r= 0.840**) in both non-saline and low saline soils of Delhi (Gajbhiye*et al.*, 1980), indicating that water soluble boron increases with increasing content of silt and clay. Many other workers have reported that fine textured soils contain more available boron than coarse textured soils (Moghe and Mathur, 1966; Paliwal and Anjaneyulu, 1967; Singh and Randhawa, 1977, Sharma, 1984). Water soluble boron also showed significant relation with pH (r=0.872**). Hingston (1964) and Sims and Bhingam (1967) foundboron retention as a function of pH, and was maximum between pH 7.5 to 8.5 and, therefore may explain the reason for the lower value of correlation coefficients obtained in the present study. Kanwar and Singh (1961) and Sharma (1984) also reported that available boron content of saline-alkaline soils increased with the increase in pH. A significant positive correlation (r=0.468 **) was observed between pH and water soluble boron (Nathani *et al.*, 1970).

Significant positive correlation of water soluble boron with EC (r= 0.609**) of soils suggested that boron concentration increases during the process of salt accumulation. Similar results have also been reported by Mair (1965) and Paliwal and Anjaneyulu (1967). Gajphiyee*etal.* (1980) reported that water soluble boron content and EC of low saline soils were correlated significantly (r= 0.860**). Water soluble boron showed negatively significant relationship with organic carbon content (r= -0.451*) of the soils. It may be due to low organic matter status of some soils and might not have contributed to a considerable extent in releasing water soluble boron. Similar results were shown by Afrifa*et al.* (2010) in some coffee growing areas of Ghana. Diana and Beni (2006) also observed negative correlation of different forms of boron with organic carbon content of soils. Calcium carbonate content showed positive and non-significant relationship with water soluble boron, these observations are inline with those reported by Singh and Singh (1972) ; Sharma (1984); Gandhi and Mehta (1985 a& b).

5.1.2 Hot water soluble boron

Results showed that hot water soluble varied from 0.10 to 1.27 mg kg^{-1} soil, with a mean value of 0.46 mg kg^{-1} soil. The average concentration of hot water soluble boron ranged from 0.10 to 2.0 mg kg^{-1} on worldwide basis (Aubert and Pinta,1977). The range of available boron in soils of different soils of India varied from traces to 12.2 mg kg^{-1} (Das, 2000). Katyal (1982) reported that mean available boron content of Aridisols, Vertisols and Alfisols of Punjab to be 1.70, 0.59 and 1.06 mg kg^{-1} soil, respectively. The hot water soluble boron content of alluvium derived soils from Ferozpur and Faridkot districts of Punjab ranged from 0.2 to 3.85 mg kg^{-1} soil (Singh and Nayyar, 1999).Nazif*et al.* (2006) studied the status of micronutrients in soils of district Bhimber (Azad Jammu & Kashmir) and found that hot water soluble boron ranged from 0.02-0.84mg kg^{-1}.

The clay content was positively and significantly correlated (r=0.477*) with hot water soluble boron content of soil. These results are in line with the findings of Singh (1970). Singh and Sinha (1976) also reported that hot water soluble boron content tends to increase with increasing clay content of the soils and is negatively and significantly correlated with organic carbon content (r=-0.362*). Singh and Randhawa (1977) also found a significant but negative relationship between available boron and organic matter of the soils. Calcium carbonate content of soil showed non-significant negative correlation (r=-0.095) with hot water soluble boron. This may be due to the affinity of $CaCO_3$ towards boron adsorption. These results are in line with those of Singh (1970). Soni *et al.* (1961) also showed that calcareous soils of Bihar contained considerably less boron than non-calcareous soils. The silt content showed positive and significant correlation with hot water soluble boron (r=0.419*) whereas relationship with sand content was negatively significant (r=-0.783**).Cation exchange capacity, pH and EC also showed positive and significant correlation (r=0.492*, r=0.773** and r=0.589**, respectively). Positive significant correlation was also noted between hot water soluble and CEC by Borkakati (1988). Similar results were observed by Sharma and Katyal (2006), who found that the content of hot water soluble boron increased linearly with an increase in EC and pH when fifty-seven benchmark soils of India were investigated.

5.1.3 $CaCl_2$ extractable boron

Perusal of data showed that 0.01 M $CaCl_2$ extractable boron in different soils range between 0.27 to 1.44 mg kg^{-1} with an average value of 0.63 mg kg^{-1}soil. Saha *etal.* (1998)reported that swell-shrink soils of Madhya Pradesh contained 0.13 to 1.51 mg kg^{-1} of$CaCl_2$ extractable boron. Calcium chloride extractable boron was positively and significantly correlated with pH (r=0.742**) and EC (r=0.593**) of the soil. The clay content was positively and significantly correlated (r=0.576**) with calcium chloride soluble boron while as silt content was positively and non-significantly correlated (r=0.163) with calcium chloride soluble boron. Clay content contributed positively to boron extracted by $CaCl_2$ (Datta *et al.,* 1998). The results are also in accordance with the findings of Saha *et al.* (1998). Alleoni *et al.*(1999) studied the correlations between hot calcium chloride-extracted boron and chemical and physical attributes of some Brazilian soils and found that $CaCl_2$ extractable boron was significantly correlated with clay content (r = 0.690*), specific surface area (r = 0.680*), and CEC (r = 0.630*).

Significant negative correlation (r=-0.432*) was observed between $CaCl_2$ extractable boron and organic carbon content of soils. Calcium Carbonate showed positive but non-significant relationship (r=0.110) with $CaCl_2$extractable boron. Su *et al.* (1994) also showed that amount of $CaCl_2$ extractable boron decreased with addition of calcium carbonate. Similar results were obtained by Datta *et al.* (1998). Positive and significant correlation (r=510**) between cation exchange capacity and $CaCl_2$ extractable boron was observed. Significant and negative relationship was observed between $CaCl_2$ extractable boron and sand content of soils (r=-0.608**).

5.1.4 Acid extractable boron

The content of boron extracted in 0.05 N HCl varied from 0.36 to 1.24 mg kg^{-1} soil with an average value of 0.64 mg kg^{-1} soil. Acid extractable boron content ranged from 1.4 to 22.8 mg kg^{-1} soil with an average of 10.2 mg kg^{-1} in soils of Egypt (Elseewi and Elmalky, 1979). Sharma *et al.* (1989) observed that 0.05 N HCl extractable boron in the profiles of salt affected soils of Punjab ranged from 0.1 to 25.3 ppm with an average of 3.3 ppm. Acid extractable boron ranged between 0.1 to 2.1 with an average of 0.6 mg kg^{-1} in the soils of North East hills of India (Diwedi *et al.*, 1993). Acid extractable boron was higher than water soluble, hot water soluble and $CaCl_2$ extractable boron in most of the soils. This could be attributed to the dissolution of some insoluble salts of boron under acid conditions.

There was a significant positive curvilinear correlation between 0.05 N HCl extractable boron and clay (r=0.564**), pH (r=0.637**) and EC (r=0.520**) of the soils. The acid extractable boron was positively and significantly related with calcium carbonate content of the soils (r=0.460*) as was also reported by Elseewi and Elmalky (1979). Organic carbon content of the soils was negatively and non-significantly correlated (r=-0.148) with acid extractable boron. Significant and positive correlation of acid soluble boron with pH, EC and negative and non-significant correlation with organic carbon suggested that in these soils, high in pH and EC, the dilute acid could not extract appreciable amount of boron that is associated with organic matter. These results clearly revealed that the available boron (water soluble, hot water soluble, $CaCl_2$ and acid extractable) were mainly associated with silt and clay fractions followed by pH and EC. There was positive and non-significant correlation (r=0.359) between cation exchange capacity and acid soluble boron. A negative but significant correlation (r=-0.677**) was observed between acid soluble boron and sand content of the soils under study. The content of boron extractable in 0.05 N HCl has been reported to be a better index of boron availability by Ponnamperuma*et al.* (1981). The water soluble, hot water soluble, $CaCl_2$ and 0.05 N HCl extractable forms of boron were found to be highly and significantly correlated with each other (Table 4.5). This suggests that all the forms of boron can be considered to be almost equally efficient indices of boron availability in the soils under study.

5.1.5 Leachable boron

Leachable boron consists of “adsorbed + soluble B” (Rhoades*et al.*, 1970 b). It ranged from 0.57 to 1.74mg kg^{-1} soil with a mean value of 0.93 mg kg^{-1} soil. This shows that most of the boron is prone to leach from the soils. The manitol-$CaCl_2$ extractable boron ranged from 0.3 to 2.5 mg kg^{-1} soil with a mean value of 1.22 mg kg^{-1} soil in soils of Meghalaya(Dwivedi *et al.*, 1993).

Leachable boron was significantly and positively correlated with silt, clay, pH and EC following curvilinear relationship with these parameters. Leachable boron content was strikingly higher in fine textured soils as compared to coarse textured alluvial and lateritic soils of Assam (Borkakati, 1988). Non-significant and positive correlation between mannitol+$CaCl_2$ extractable boron and pH was also reported by Dwivedi*et al.* (1993).

5.1.6 AB-DTPA extractable boron

The recently developed AB-DTPA extractant has proven to be effective for boron on alkaline soils (Gupta, 1993). The extractant consists of 1.0 M NH_4HCO_3 and 0.005 M DTPA maintained at the pH of 7.6 (Soltanpour and Workman, 1979). The concentration of AB-DTPA extractable –boron ranged from 0.77 to 1.94 mg kg^{-1} soil with a mean value of 1.13 mg kg^{-1}soil. Similar results were reported by Dwivedi*et al.* (1993) for Meghalaya soils. pH and EC were significantly correlated with AB-DTPA extractant with coefficient values of r=0.874** and r=0.684**, respectively. Dwivedi*et al.*(1993) also reported positive but non-significant correlation between pH and AB-DTPA extractable boron.Gestringand Soltanpour (1984) also concluded that clay and pH governs the AB-DTPA extractable boron content of the soils. It is interesting to note that this form of boron was significantly correlated with other forms of boron. Thus it can also be used as an index of boron availability in these soils. This method of extraction of boron is easy and the extractants are cheaper and easily available (Soltanpour and Workman, 1979).

5.1.7 Total boron

Although total boron does not affect the plant growth and its contribution is low as compared to other forms of boron, but it helps in knowing its potential reserve in soil. Total boron content ranged from 40.72 to 50.55 mg kg^{-1} soil with an average value of 45.46 mg kg^{-1} soil. The magnitude of total boron appears to be quiet comparable to those reported earlier. Dass (2000) stated that total boron in Indian soils varied from 7 to 630 ppm. Total boron content showed significant correlation with pH (r=0.686**), EC (r=0.421*), CEC (r=0.766**), silt (r=0.498*) and clay content (r=0.563**) of the soil. Total boron was associated with finer fractions of soil. Negative but significant correlation was seen fortotal boron with sand (r=-0.928**) and non-significant with organic carbon (r=-0.219).

5.2 Boron adsorption-desorption by soils

5.2.1 Adsorption of boron by soils

The results of boron adsorption by the soils under study clearly showed that all the soils have affinity for boron adsorption. The amount of boron adsorbed for all the soils was plotted against the equilibrium boron concentration to obtain the adsorption isotherm, indicating the effect of boron concentration on boron adsorption. The adsorption isotherm indicated that though the adsorption of boron increased with increasing concentration in the equilibrium solution, yet the percentage of adsorbed boron decreased. This may be because of an increase in the ratio of adsorbate to adsorbent. Bloesch *et al*. (1987) also reported that adsorption of boron increased with the increasing concentration of boron in solution. The amount of boron adsorbed is different for different soils. The shape of adsorption curve has been classified on the basis of the classification given by Giles *et al*. (1960). The adsorption isotherms were L-shaped and indicated that more sites in the substrate were occupied thus the solute molecules faced great difficulty to find any vacant site available. This leads to a suggestion that either the adsorbed molecule was not vertically oriented or that there is no strong competition from the solvent. L-shaped adsorption isotherms for boron adsorption have also been obtained by Krishnaswamy *et al.* (1997) in the soils of Tamil Nadu and by Arora and Chahal (2010) in the soils of Punjab.

The data on boron adsorption by different soils showed that the adsorption capacity of different soils for boron was different and the behaviour of adsorption of boron by different soils was not uniform in the whole concentration range. Adsorption of boron was found to be maximum in Sagipora soils and this may be attributed to the high clay content and CEC of the soils. Khag soils have the least adsorption capacity of boron which is likely due to coarse texture and low CEC. From these results, it could be concluded that adsorption of boron was mainly governed by clay content and CEC of the soils. Keren and Talpaz (1984) reported that the increase in boron adsorption on the smaller clay particles was related to the increase in CEC of the clay with fineness. The data of boron adsorption when analysed statistically showed that adsorption of boron by these soils were positively and significantly correlated with clay content (r=0.906**), CEC (r=0.726**) and negatively and non-significantly with organic carbon (r=-0.222) of the soils. The clay content and CEC of the soils was also significantly correlated with adsorbed boron (Elrashidi and O’ Connor, 1982). They also showed positive relation between organic matter and boron adsorbed, but could not find any precise correlation.

5.2.1.1 Langmuir adsorption Isotherms

The data of boron adsorption was first calculated according to the Langmuir adsorption equation. The linear form of the equation used was;

C/x/m=C/b+1/kb

A plot of C/x/m versus C gave a straight line with slope 1/b and an intercept of 1/kb. The Langmuir constants for boron adsorption by soils were calculated from the slope and the intercepts of the curves. A straight line (linear curve) was observed in Khag, Bandipora and Sagipora soils. This showed that the adsorption data of these soils confirm to the Langmuir adsorption over the entire range of equilibrium boron concentration.

The adsorption maxima (b) value ranged from 9.72to 34.84 µg B g^{-1} soil. Maximum value was found in Sagipora soils and least in Kangan soils. The bonding energy constant (k1) was maximum (0.313 ml g^{-1}) in Anantnag soils and minimum of 0.064 ml g^{-1} in Bandipora soils. Boron adsorption data of Assam soils also confirmed the Langmuir equation (Dekamedhi *et al.*, 1998) with adsorption maxima and bonding energy of 12.04 to 14.49 g kg^{-1} and 0.046 to 0.098 L mg^{-1}, respectively. In case of Khag, Bandipora and Sagipora soils, a straight line relationship for boron adsorption was observed up to limited boron concentration. This showed that the Langmuir equation was found to be applicable only up to the concentration rate of 40 µg B ml^{-1} in the equilibrium solution. Rest of the soils showed curvilinear isotherms. Curvilinear relationship has also been reported by Sakal *et al.* (1994) and Arora and Chahal (2010). The two portions of the curve were considered separately because the slopes and intercepts of the lower part of the isotherms were significantly different from those of the upper part and provide justification for considering separately. The values of adsorption maxima and bonding energy constant have been designated as b1 and k1 for lower part and b2 and k2 for upper part of the isotherm. The data for Langmuir constants confirms to the results of Singh (1964) and Arora and Chahal (2010). The data for part 1 of the curve fitted very well indicating that the Langmuir isotherm explains best the adsorption phenomena at low concentrations of adsorbent which of course was different for different soils.

The marked variation in slopes and intercepts of the two parts of isotherms suggest two types of reaction of boron with soil. The lower part of the isotherm resulting largely from monolayer adsorption of boron and upper part from multilayer adsorption and/or precipitation reactions as well as heterogeneity of the sites at higher concentration of boron against the monolayer reaction and homogeneity of the soil assumed in Langmuir equation. Syers*et al.* (1973) also observed two types of adsorption reaction of phosphorous in soils because of two population of sites, which have widely differentaffinity for phosphorous and each of which was defined by the Langmuir relationship. Similar Langmuir adsorption isotherms for boron were obtained by Borkakati (1998) and Arora and Chahal (2010) in soils of Assam and Punjab, respectively. Raikly and Takkar (1981) reported the lower part as mono and upper part as multilayer adsorption for zinc and copper. Hingston (1964) concluded that deviations from the Langmuir model at higher concentration resulted due to different reactions occurring at higher than at low boron concentration. However, he did not give the nature of reactions.

The difference in slopes and intercepts of the two parts of adsorption isotherms gave significantly different values of Langmuir constants. Regardless of the soil, the adsorption maxima (b) was higher for upper part while bonding energy constant (k) were higher for lower part of the isotherm. This suggests strong retention of boron applied in lower amounts. The strength of retention decreased with increasing concentrations of boron in the equilibrium solution as a result of precipitation reactions. The similar results were obtained by Elrashidi and O'Conner (1982) and Arora and Chahal (2010). The nature of Langmuir isotherms and the magnitude of the constants varied with soil texture and organic carbon contents of soils. Singh (1964) also found that soils with high clay content have high "b" values on the other hand Singh (1998) reported the higher boron capacity of Bhopal soils than Indore soils which might be due to high clay content. This is also due to high clay, CEC of soils, which possessed significant correlation with b1 (r=0.565* and 0.506*, respectively). Boron adsorption maxima were significantly correlated with organic carbon in soils of Assam (Dekamedhi*et al.,* 1998). Very poor relation of b2 with these soil properties indicated the multilayer adsorption and/or precipitation reaction of boron at site 2 of the adsorption isotherm.

The relative bonding energy (k) of boron adsorption by soils also varied among soils. k1was higher than k2 for almost all soils, thus showing firmer retention of boron at site-1 i.e. at lower concentration than at higher concentration (site-2). The very low values of k2 are possibly because of multilayer adsorption and/or precipitation of boron at higher boron concentrations while high value of k1 has resulted from the adsorption of boron ions at low concentrations in the equilibrium solution. These results are in line with those obtained by Borkakati (1998) and Arora and Chahal (2010).

In fine textured soils, having high amount of clay and organic carbon, large additions of boron could be made available without it becoming toxic to plants because of high adsorption capacity and bonding energy of the soils. These results suggest that low and high rate of boron fertilization have to be adjusted to fine textured soils to bring the same in the adequate level for optimum crop production depending upon the magnitude of the soil, clay and organic matter content of the soils.

5.2.1.2 Freundlich adsorption Isotherm

The boron adsorption data was fitted to the Freundlich equation. The linear form of the equation is given as under;

$$\text{Log } x/m = 1/n \log C + \log k$$

A plot of log (x/m) versus Log C gave a straight line as the data confirmed to the Freundlich equation. k can be obtained from the intercept and 1/n from the slope of the isotherm. K and 1/n provides the estimates ofadsorbent capacity and intensity of adsorption. The values of 1/n also indicated the degree of non-linearity between solution concentration and adsorption. Although Freundlich equation is empirical in nature, it could be used to explain the adsorption of compounds on soils and it is best suited for a heterogeneous system like soil-nutrient-water system (Krishnaswamy*et al.*, 1997).

The plot of boron adsorbed against equilibrium boron concentration on a log-log scale gave linear relationship in all the soils. The concentration ranged from 1 to 100 µg B ml^{-1}, indicating that boron adsorption data confirms to Freundlich equation. Many workers have reported boron adsorption data could be successfully described by Freundlich modelover the entire range of concentration (Saha and Singh,1997; Dekamedhi*et al.*, 1998; Arora and Chahal, 2010).

The results of present investigation also indicated that Freundlich equation was valid for a wider range of boron concentration than by the Langmuir adsorption equation. Freundlich model assumes multilayer adsorption and heterogeneity of the sites as compared to monolayer adsorption and homogeneity of sites in Langmuir equation. At higher concentration of applied boron, multilayer adsorption and/or precipitation reaction appears to have occurred thereby this resulted in a better fit of the data on the latter than the former model. These results are in agreement with those reported by Krishnaswamy*et al.* (1997), Saha and Singh (1997), Dekamedhi*et al.* (1998) and Arora and Chahal (2010).

Freundlich k values ranged widely among soils, ranging from1.73 to2.72 µg g^{-1}. Dekamedhi*et al.*(1998) also reported a range in k-values from 0.86 to 1.29 µg g^{-1} in Assam soils. Freundlich k values for adsorption ofboron in Tamil Nadu soils ranged from 0.18 to 1.96 µg g^{-1} (Krishnaswamy et *al.*, 1997), and the range of 1.08 to 1.91 µg g^{-1} of k values in Punjab soils was also reported by Arora and Chahal (2010).

The data of this study indicates by and large, the difference in k values was associated with the magnitude of variation in clay content of soils and have a highly significant relation with clay content (r= 0.906**). Max adsorption capacity appeared to increase with fineness of soil texture (Biggar and Fireman, 1960). The values of K are also in consonance with the results obtained by Krishnaswamy*et al.* (1997) and Arora and Chahal (2010).

The values of Freundlich constant 1/n are less than unity in all the soils indicating L-shape isotherm. The 1/n values ranged from 0.618 to 0.704 in the soils under study. The Freundlich 1/n values ranged from 0.703 to 1.203 in Assam soils (Dekamedhi*et al.*, 1998) and 0.661 to 0.734 in Punjab soils (Arora and Chahal, 2010). The Freundlich ‘n’ value, which has been designated as bonding energy related term (Huang, 1980) was found to be lowest for Calciorthent but equal for haplustert ,Haplustalfs, and Ustochrept soils (Saha and Singh 1997).

5.2.2 Desorption of boron by soils

It was necessary to determine whether the adsorbed boron of soils can be readily released. Desorption studies were undertaken by replacing the soil suspension after adsorption processes by 10 ml of 0.01 M $CaCl_2$ solution. The amount of desorbed boron in different soils equilibrated for 24 hour is shown in result chapter. The percentage of desorbed boron was higher at higher level of added boron. Similar results have been reported by Elrashidi and O’Connor (1982). The soils having higher affinity for boron adsorption tend to desorb less amount of boron. This indicated that adsorption and desorption of boron were almost inversely related. These results are in conformity with the finding of Saha and Singh (1997) and Elrashidi and O’ Connor (1982).

The initial adsorption of boron in soils is followed by slow changes that ultimately govern the rate of boron release from the soils. Moreover, the difference between magnitude of adsorption and desorption of boron depends on the time of contact of boron solution and intensity of boron bonding in soils. The perusal of data also revealed that the rate of boron desorption was slow at low saturation of solid phase matrix and at high saturation, the desorption of boron was fast, suggesting that soils having higher adsorption capacity, releases boron slowly and vice-versa.

Desorption of boron was found to be maximum in Kulgam, Kangan and Shopian soils, indicating that these soils were more prone to release the applied boron which might be attributed to the lower content of clay and low CEC of the soils. Whereas, Sagipora, Tangmarg, Tral and Shalimar soils showed less desorption due to high amount of clay and higher adsorption sites. Saha and Singh (1997) also reported that the amount of boron sorbed by the soil was always higher during desorption than adsorption process at a given equilibrium solution concentration in the soils. The desorption of boron was almost same as the order of sand content and from these results it could be concluded that desorption of boron from these soils are mainly governed by texture. Boron desorption was positively and significantly correlated with sand content and negatively with clay. Similar results were reported by Peryer *et al.* (1985) from a leaching experiment on boron.

The data on boron desorption was applied to modified Langmuir equation which is commonly used for phosphate desorption (Sharma *et al.*, 1995). In this study, keeping in view the good applicability of this equation for describing P-desorption, an attempt has been made to apply Langmuir type equation for boron desorption. Desorbed boron (De) when plotted against B-desorbed/ B-adsorbed (De/S) for different soils, a linear relation was obtained. The straight line relationship showed that the desorption of boron in these soils as determined by 0.01 M $CaCl_2$ solution could be described by Langmuir type equation as given below;

$$De/S = 1/kdDm + De/Dm$$

Where,
S= Boron adsorbed (µg g^{-1})
De=Boron desorbed (µg g^{-1})
Dm= desorption maxima (µg g^{-1})
kd =Constant related to mobility of boron (ml g^{-1})

The Langmuir desorption parameters such as desorption maxima (Dm) and constant related to mobility of solid phase (kd) were worked out from the linear plots of De/S versus De. The plot was found to be linearly correlated for each of the soils. The desorption constants computed from these plots clearly indicates the differential behaviour of each soil sample in supplying boron to the plants. Desorption maxima (Dm) indicate the maximum desorbable capacity of the soils. More the Dm values, less is the potential of the soil to release boron for meeting the requirements of the crop. Similarly, kd values (a constant related to the boron mobility) are also indicative of boron supply to the crops. The smaller the kd value, the less the desorption of soil boron, thereby suggesting a need for boron fertilization (Sharma *et al.,* 1995). The data of desorption constants revealed that there are higher values for desorption maxima in fine textured soils. The mobility constant (kd) had almost inverse relationship with bonding energy of boron adsorption. This showed that the mobility of desorbed boron in heavy textured soils was at lower rate.

5.3 Kinetics of Boron adsorption-desorption

5.3.1 Kinetics of boron adsorption by soils

Batch studies were conducted to investigate the kinetics of boron adsorption process. $CaCl_2$ (0.01 M) solution containing 40 µg B ml^{-1} was added to each 10 g soil in 50 ml polyethylene centrifuge tubes. In all the soils, the boron adsorption was characterized by an initial fast reaction followed by a slow process. Similar reaction rates of boron adsorption have been reported by Krishnaswamy (1996) and Krishnaswamy *et al.* (1997). Rapid rate of reaction can be attributed to chemical reaction and slow reaction to diffusion of boron into micropores of organic and inorganic compounds (Krishnaswamy, 1996)

Adsorption of boron was almost complete after 48 hr in all the soils, though complete equilibrium was not attained until 72 hr. Bingham and Page (1971) showed that boron equilibrium was only attained under conditions of prolonged reaction periods. The prolonged time requirement is probably relatedto diffusion of boron from the outer solution into sites that are not readily accessible for adsorption reactions. Mezuman and Keren (1981) used 24 hrwhereas;

Elrashidi and O’Connor (1982) adopted 12 hr of equilibrium time for their experiments on boron adsorption by soils.

The concentration of boron in the equilibrium solution ranged from 27.5 to 36.1 µg ml^{-1} at the completion of the adsorption reaction. This is also consistent with the data reported by Elrashidi and O’Connor (1982).

Six different Kinetic models viz. Zero order, First order, Second order, Elovich, Power function and Parabolic diffusion were tested by least square regression analysis for describing boron adsorption in soils representing major soils of Kashmir. The model which had the highest coefficient of determination (R^2) and the lowest standard error of estimates (S.E) values was considered to be best fit.The Zero order, firstorder, second order and Power function kinetic equation could not describe the adsorption of boron by soils, as coefficient of determination (R^2) values were very low and S.E values were large. The amount of boron adsorbed by eight soils of Tamil Nadu was poorly described by Zero order, first order and third order reaction equations (Krishnaswamy*et al.*, 1997). The Parabolic diffusion was best of the other kinetic equations studied to describe the rate of boron adsorption as evidenced by the overall highest values of coefficient of determination (R^2) and lowest standard error of estimates (SE) over the entire time range. Such conformityhas alsobeen reported by Krishnaswamy*et al.* (1997), whilestudying boron adsorption kinetics of Tamil Nadu soils. Elovich kinetic model was as good as parabolic diffusion equation in describing boron adsorption kinetics in all the soils.

5.3.2 Kinetics of boron Desorption by soils

All the soils used for boron adsorption kinetics were also subjected to desorption study after 48 hours of adsorption study. The soils were pre-treated with 40 µg Bg^{-1} soil. The amount of desorbable boron was strikingly higher in the coarse textured soils as compared to the fine textured soils. The increase in desorbable boron with time can be attributed to the less number of exchange sites due to the low clay content to retain boron more tightly. Also desorbed boron when expressed in percentage of adsorbed content was lower in fine textured soils. This again suggests that boron was held more tightly and thereby more time for it’s desorption was taken from fine textured soils. The similar results were reported by Borkakati (1988) in Assam soils. The difference in desorbable boron resulted from more number of boron retentive sites as well as their ability to retain boron with great tenacity, because of the large variation in physical and chemical properties of these soils. Furthermore, the desorption of boron took relatively more time in fine textured soils. Similar results were reported by Borkakati (1988). The behaviour of boron desorption reaction with time is due to the nature of reaction because of variation in clay content and amount of organic matter and calcium carbonate content which have a substantial role in boron adsorption and release by soils.

The desorption reaction was initially fast and thereafter the desorption of boron became slow. The desorption reactions seemed to have completed in 48 hours in most of the soils and only in few soils the reaction was not complete even after 72 hr and therefore, the values of total desobable boron could not be ascertained. For the kinetic treatment of the data, the concentration of solution boron at the plateau of the curves was considered as the total desorbable boron (Bo) with the assumption that the desorption reaction at that stage was complete in these soils.

The data were then given the kinetic treatment using the integrated rate equation (Frost and Pearson, 1961) given as under;

$$\text{Log (Bo-C)} = \log \text{Bo}-(K/2.303)$$

The curves of the soils after plotting log (B_0-C) vs. time (t) indicate two distinct linear portions suggesting, thereby, the involvement of two types of pseudo-first order reactions in boron desorption. Griffin and Burau (1974) also studied the kinetics of boron desorption from different soils and postulated that the slope of the two linear portion of the curves represent different sites of boron retention by the soils, then the sites 1 and 2 corresponding to the upper and lower line i.e. to the steep and less steep slopes of the curves, belonged to fast and slow boron desorption reaction sites, respectively. In the present study, 73 and 82 percent of total desorbable boron could be attributed to the site-1 and only 18 and 27 per cent to site-2. These results are in agreement with those of Griffin and Burau (1974) who also reported about 90 and 10 per cent of the desorbable boron attributed to the site 1 and 2, respectively. The relative constancy of the percentages of desorbable boron at site 1 and 2 indicated that the desorption of boron has originated from two sites of retention on the same substance, possibly the hydroxyl Al and Fe compounds, as suggested by Sims and Bingham *et al.* 1971, Rhoades *et al.* 1970a, Griffin and Burau ,1974) and Keren and Gast (1983). Boron may also be adsorbed on the edges and inter layer regions of clay minerals by anion exchange and/or hydroxyl substitution. The dissolution of borate salts or precipitated boric acid may release a considerable amount of boron to site 1, in addition to the desorption from some specific adsorption sites. But, boron dissolved from the borate salt or acid could be expected to come in solution phase in first few minutes and during later periods, the desorption of boron may continue from the site-1. The soils representing major soils of Kashmir used under present investigation are dominated by illitic clay mineral (Wani and Rajkumar, 2008) which can be expected to control the adsorption and desorption of boron due to presence of large amount of tetrahedral aluminium (Hingston, 1964 and Fleet, 1965).

According to Couch and Grim (1968), $B\ (OH)_4^-$ is held at the edges of illitic crystal. They proposed that the first step in mechanism for boron retention by illite is a rapid chemical adsorption of $B\ (OH)\ _4^-$anion in the “frayed edge” of the illite flakes. The second step is a much slower diffusion of boron into the tetrahedral structural position in the crystal. Sims and Bingham (1968a) concluded that hydroxyl iron and aluminium compounds on the layer silicates dominated over clay mineral species in determining boron retention characteristics which in turn may be conditioned by clay mineral species.

The study thus suggested the possibility of cropping up of boron deficiency in the soils which have already desorbed about 90 % of its leachable boron in soils belonging to the high rainfall areas and are being intensely cultivated with high yielding varieties and the use of boron free chemical fertilizers.

The data of boron desorption was also fitted to various Kinetic models like zero order, first order, second order, power function, Elovich and parabolic diffusion was tested by least square regression analysis for describing boron desorption from the soils. The models which had highest coefficient of determination (R^2) and the lowest standard error of estimates (SE) values was considered to be the best fit. The results are in consonance with the findings of Peryuea *et al.* (1985) and Sharma *et al.* (1989).

The perusal of the data showed that Elovich kinetic equation was best among different models as evident by the overall highest values of coefficient of determination (R^2) and lowest standard error of estimates (SE) values over the entire range of time. The requirement of short reaction time (Aharoni and Ungarish, 1976) for fitting data to the Elovich equation may be one of the reasons for higher SE values observed in the present study. The Power function model was found to be equally good in describing boron desorption kinetics in all the soils. Sharma *et al.* (1989) also indicated that power function, pseudo-first order and Elovich Kinetic models adequately described boron release from salt affected soils of Punjab.

5.4 Response of Berseem to Boron and its critical limits in soils and plants

5.4.1 Response of Berseem

A greenhouse experience was conducted to study the response of berseem to boron application at 0, 1.0 and 2.0 mg B kg^{-1} soil. The boron deficiency symptoms on berseem plants grown on control treatments were observed at 45 days after seeding. The deficiency symptoms ranged from mild to severe. The symptoms were almost similar to those described by Bergman (1992).

First Cutting

The mean dry matter yield of Berseem in control treatment was 1.480 g pot^{-1} which increased to 2.057 g pot^{-1} with application of 1.0 mg B Kg^{-1} soil, showing 27.78 per cent increase over control treatment. Further application of 2.0 mg B Kg^{-1} soil increased the mean dry matter yield by 3.90 per cent over the control. The difference in dry matter yield in different soils might be due to variation in available boron status of soils. Similar increase in dry matter yield with application of boron to clovers was reported by Sherell (1983) and Dear and Lipsett (1987). The soils differ in their response to boron applied. The mean Brays per cent dry matter yield of 76.90 % was observed in these soils. The rest of the yield may be attributed to boron application. Some soils respond more to boron application than the others. Such response was also reported by Datta *et al.* (1994) for soybean crop at Chotanagpur. The variation in dry matter yield of berseem in different soils was mainly due to variation in the boron contents of plants and secondly due to the level of soil available boron.

The mean boron concentration was 19.47 µg g^{-1} and it increased to 21.707 and 27.950 µg g^{-1} when boron was applied at 1.0 and 2.0 mg B kg^{-1} soil, respectively. There was successive increase in boron concentration with boron application. Increase in boron concentration with increasing levels of boron was also observed by Datta *et al.* (1994). Malewar *et al.*(1999a) and Sherell (1983). Characteristic symptoms of boron deficiency were observed in the berseem when plants were deficient in boron contents. These soils, which responded more to boron application, were poor in boron status.

The boron uptake in plants increased significantly and successively with the application of increasing rates of boron application. The mean increase in boron uptake with 1.0 and 2.0 mg B kg^{-1} over control were 36.81 and 81.58 per cent over control, respectively. The marked variation in boron uptake by plants in different soils was due to the variation in dry matter yield as well as their boron concentration. Sakal *et al.* (1991) also reported significant increase in total boron uptake with the increasing levels of boron application in all the varieties of mustard tested on calcareous soils of Bihar.

Second cutting

The data on dry mater yield of berseem at second cutting taken at 30 days after first cutting is presented in Table 4.24. The mean dry matter yield in the control treatment was 3.483 g pot $^{-1}$ and it increased to 3.977 g pot $^{-1}$ with 1.0 mg B Kg^{-1} and 4.293 g pot $^{-1}$ with 2.0 mg B Kg^{-1}. The Bray's per cent yield in different soils varied between 70.41 to 94.07 per cent. None of the soils have Bray's dry matter yield more than 100 %, indicating no toxic effect of boron content of these soils. The soils were low to high in available boron, thus such type of mixed response was observed. The response of boron application to various field crops has earlier reported by Sinha *et al.* (1991). The variation in dry matter yield of berseem in different soils was, therefore, mainly due to variation in the boron content of plants.

The mean boron concentration in the control treatment was 19.404 µg g^{-1} and increased to 21.620 to 27.440 µg g^{-1} with the application of 1.0 and 2.0 mg B kg^{-1} soil, respectively. The boron uptake by second cutting of berseem was 68.829 µg pot^{-1} in control treatment which increased to 87.155 µg pot^{-1} and 118.776 µg pot^{-1} with the application of 1.0 and 2.0 mg B kg^{-1} soil, respectively. The boron uptake in different soils varied significantly to as low as 50.69 µg pot^{-1} in Tral soils to as high as 167.860 µg pot^{-1} in Shopian soils. There was a considerable variation in boron uptake in different soil. The marked variation in boron uptake by plants in different soils was due to the variation in dry matter yield as well as their boron concentration. Datta *et al.* (1994) reported that soybean differ in the response to boron application.

The data on effect of boron application on dry matter yield, boron concentration and boron uptake by berseem at two cuttings i.e. after 60 days of growth and second at 30 days thereafter, are presented in Table 4.21-4.26. This shows the increased yield with the application of 1.0 mg B Kg^{-1} soil and 2.0 mg B Kg^{-1} soil, respectively, over control. Significant response to the application of 1.0 mg B kg^{-1} soil showed that this much boron was sufficient to raise the soil available boron level of these soils significantly to meet the requirement of berseem crop. Response of clovers to boron application has been reported to some of the workers (Dible and Berger, 1952; Sherell 1983; Gestring and Soltanpour 1984; Dear and Lipsett, 1987; Pal *et al.,* 1989).

5.4.2 Relationship of different soil extractants with crop yield and boron uptake

The coefficient of correlation between plant parameters and boron extracted by different methods indicated that water soluble extracted boron had the highest correlation with Bray's per cent yield of berseem (r^2=0. 884**), followed by hot water extracted boron (r^2=0.854**). There was non-significant coefficient of correlation with AB-DTPA extractable boron. Water soluble gave the highest coefficient of correlation with Bray's per cent yield at second cutting. Steenberg (1954) has presented a valuable discussion of the factors affecting nutrient concentration in plants and given reasons for preferring the nutrient uptake as a measure of the nutrient status of the plants and of the medium in which it grows. Thus the correlations between available boron and boron uptake may be more reliable than correlation coefficients between the available boron and crop yield. Keeping this in view, the correlations between the Bray's per cent boron uptake by berseem and boron extracted with different extractants from the soil were worked out. It is clear from the results that methods which are highly correlated with Bray's per cent yield and Bray's per cent boron uptake by berseem are 0.01 M $CaCl_2$, hot water and water. Very good correlation between boron extracted by 0.01 M $CaCl_2$ and relative dry matter yield of soybean have been reported by Datta *et al.* (1994). The effectiveness of boron extracted by 0.01 M $CaCl_2$, hot water and 0.05 N HCl has been also reported by Gestring and Soltanpour, 1984; Datta *et al.* (1994) and Dwivedi *et al*. (1993);

5.4.3 Critical levels of boron in soils and plants.

The critical level of boron in soils and plants was determined by plotting Bray's per cent dry matter yield against soil boron and plant boron concentration, respectively, adopting graphical method of Cate and Nelson (1965).

The critical limit for available boron extracted by hot water was 0.48 at first cutting and 0.49 mg kg^{-1} soil at second cutting, respectively. Hot water showed better correlation with plant parameters. Several workers have reported different values of hot water and 0.01 M $CaCl_2$ extracted boron for different crops grown on different soils. Malewar *et al.* (1999) reported 0.52 mg B kg^{-1}as the soil critical level for cauliflower using hot water as extractant. Datta *et al.* (1994) compared hot water and 0.01 M $CaCl_2$ extractants for boron and showed that the critical levels of soil available boron extractable with hot water and 0.01 M $CaCl_2$ were 0.46 and 0.65 mg kg^{-1} soil, respectively for soybean. Boron extracted by both the extractants was also significantly correlated with Bray's % yield, plant boron and boron uptake. Work done at Pusa and Jabalpur (Takkar *et al.*, 1989) also indicated good correlation between hot water extractable boron and crop yield. Boron extracted by 0.01 M $CaCl_2$ + 0.01 M mannitol showed better correlation with plant parameters. Similar results were reported by Tsadilas *et al.* (1997). They reported soil boron content corresponding to boron toxicity in kiwifruit as 0.80 $\mu g\ g^{-1}$ for 0.01 M $CaCl_2$ + 0.01 M mannitol extractant. Data *et al.* (1994) in the green house study observed with 0.05 N HCl extractable boron was not related with Bray's % yield for soybean, although it was correlated significantly with plant boron and boron uptake.

Boron extracted with AB-DTPA extractant was not significantly correlated with any of the plant parameters.

The critical value of boron in berseem plant at two cuttings was found to be 23 and 19 µg g^{-1} on dry weight basis, respectively. At first cutting of berseem, boron content was highly significantly correlated with relative yield (r= 0.884**). Whereas at second cutting the boron concentration was also significantly correlated with Bray's per cent yield (r= 0.913**). Similar positive and significant correlation of Bray's per cent yield with boron content of soybean and blackgram plants was obtained by Sakal *et al.* (1985) and Datta *et al.* (1994) respectively.

SUMMARY AND CONCLUSION

The present investigation deals with the different forms of boron in relation to physical and chemical characteristics of soils, boron adsorption-desorption behavior, kinetics of its adsorption-desorption and its availability to berseem. The salient findings of these investigations are summarized as under:

Different forms of boron in relation to soil properties:

The average WS-B content in the soils was 0.35 mg kg^{-1}soil. It was positively and significantly correlated with clay (r=0.572**), silt (r=0.374*) and CEC(r=0.620*) and negatively with organic carbon. Hot water soluble boron content ranged from 0.10 to 1.27 mg kg^{-1} soil with a mean content of 0.46 mg kg^{-1}soil. Sagipora soil had higher content of this form. Calcium carbonate was negatively and non-significantly correlated with hot water soluble boron. Correlation with organic carbon (r= -0.362*) and sand (r= -0.783**) was negatively significant. Silt and CEC were significantly correlated.

The mean content of $CaCl_2$ extractable boron was 0.63 mg kg^{-1} soil. Kangan soil had least amount (0.30 mg B kg^{-1}) whereas; Sagipora soil had highest content of this form (1.44 mg B kg^{-1}). The correlation of $CaCl_2$extractableboron with pH (r= 0.742**) and EC (r= 0.593**) was positive and significant. Organic carbon was negatively and significantly correlated (r= -0.432*) with this form of boron. The mean content of acid soluble (0.05 N HCI) boron was 0.64 mg kg^{-1}soil. Maximum content of this fraction was present in Sagipora soil (1.24 mg B kg^{-1}). This form was also negatively and significantly correlated with sand (r=-0.677**) and organic carbon (r=-0.148) content. Calcium carbonate was significantly and negatively correlated with acid soluble boron, while clay (r==0.564**) and CEC (r= 0.359) showed positively correlation. Leachable boron varied from 0.57 to 1.74 mg B Kg^{-1} soil with a mean value of 0.93 mg B kg^{-1}. Organic carbon was negatively (r=-0.140) correlated with leachable boron. Silt, clay and $CaCO_3$ content showed positive but non-significant correlation (r=0.203, 0.362 and 0.327, respectively). Ammonium bicarbonate-DTPA extractable boron varied from 0.77 to 1.94 mg B kg^{-1} soil in different soils. The AB-DTPA boron content was significantly correlated with pH (r= 0.874**), EC (r= 0.684**), clay (r=0.580**) and silt fraction (r= 0.399*)with this form. Organic carbon was negatively and significantly correlated with AB-DTPA extractable boron. Mean total boron content varied from 40.72 to 50.55 mg kg^{-1} in soils with overall mean of 45.46 mg kg^{-1} soil. Total boron was positively correlated with silt (r= 0.498*), clay (r=0.563*), CEC (r= 0.766**), pH (r= 0.686**) and EC (r= 0.421*) while negatively significant correlation was observed with sand content (r= -0.928**) and negatively non-significant correlation with organic carbon content(r=-0.219).

Regression equation showed that 82, 70, 77, 97, 85 and 84 per cent variations in water soluble, hot water soluble, $CaCl_2$ extractable, acid extractable, leachable and AB-DTPA extractable forms of boron were governed by various soil properties.

All the forms of boron were significantly correlated with each other in these soils. Most commonly used form of boron i.e. hot water soluble boron was highly significantly correlated (r= 0.897**) with 0.01 M $CaCI_2$ extractable boron. Ammonium bicarbonate-DTPA extractable boron was significantly correlated with all the other forms of boron.

Boron adsorption and desorption by soils.

Boron adsorption

Boron adsorption increased with increase in concentration of adsorbate. The adsorption isotherms were of L- shaped almost in all the soils. Boron adsorption was positively and significantly correlated with the clay (r= 0.906**) and CEC (r= 0.726**). Sagipora soil adsorbed maximum amount of boron. Boron adsorption for the Khag, Bandipora and Sagipora soils conform well to the Langmuir adsorption equation over the entire concentration range. In case of

Sagipora soil, relationship for boron adsorption was linear up to 60 µg B ml^{-1} in the equilibrium solution. Langmuir equation was applicable only up to limited concentration. The band k values were 34.843 µg B g^{-1} soil and 0.086 ml µg^{-1}, respectively.

All the other soils, gave curvilinear relationship indicating two sites of B adsorption, which may be attributed to the inconsistent energy of adsorption in these soils except S2 and S7. At the first site monolayer adsorption and at the second site multilayer adsorption and/or precipitation reaction of boron are dominated. The adsorption maxima, b1 and b2 varied from 9.718 to 34.843 µg B g^{-1}soil and 32.468 to 47.170 µg B g^{-1} soil, respectively. The bonding energy constant k1 and k2 values ranged between 0.064 to 0.313 and 0.028 to 0.076 ml µg^{-1}, respectively for these soils. Bonding energy was strikingly influenced by soil texture. The clay content markedly influenced the adsorption capacity of the soil. The b1 values were significantly correlated with clay content (r= 0.565**) and CEC (r= 0.506**).

Freundlich equation gave a straight line relationship over the entire range of equilibrium solution of 1 to 100 µg B ml^{-1} added. The Freundlich equation assumes multilayer adsorption and heterogeneity of soils as compared to monolayer adsorption and homogeneity of sites in Langmuir equation. Freundlich k values or the adsorbent capacity increased strikingly with the increase in clay. It was maximum of 2.722 for Sagipora soil and minimum of 1.738 for Kulgam soil. The values of 1/n, the intensity of adsorption were less than unity for all the soils, with maximum of 0.704 for Kulgam and minimum of 0.624 for Anantnag soil.

Desorption of boron by soils

Boron desorption in soils was far less than the boron adsorbed. The results denote that adsorbed boron was not readily released in the solution. The per cent desorbed boron (of the adsorbed) was higher at higher levels of added or pre-sorbed boron. Boron desorption by soils was positively and significantly correlated with sand and negatively with clay.

Boron desorption was maximum in Kulgam and minimum in Sagipora soil. Boron desorption obeyed the Langmuir type equation over the entire concentration range. The desorption maxima (Dm) was higher in fine textured soils as compared to coarse textured soils. The Sagipora soil having maximum value of Dm indicating that this soil has less potential to release boron for meeting the boron requirements of the crop. The values of constant related to boron mobility (kd) ranged between 0.163 to 0.412 ml g^{-1} soil.

Kinetics of boron adsorption -desorption

Adsorption kinetics

Boron adsorption reaction was initially fast followed by slower process. Adsorption of boron by these soils was almost complete after 48 h in all the soils, although the complete equilibrium was not attained until 72 h has elapsed. Boron concentration in the equilibrium solution ranged from 27.5 to 36.1µg ml^{-1} at the completion of the adsorption reaction. Maximum boron was adsorbed by Sagipora and minimum by Khag soil.

Boron adsorption was applied to different kinetic models and it was found that zero order, first order, second order andpower function rate equation failed in describing the boron adsorption kinetics in almost all the soils. The Parabolic diffusion kinetic equation was the best in described the rate of B adsorption as evidenced by the overall highest values of R^2 and lowest value of standard error (SE). The Elovich equation was also found to be suitable for describing the rate of boron adsorption by the soils.

Desorption kinetics

The soils were pretreated with 40 µg Bg^{-1}soil and desorbed with 0.05 M mannitol solution as a function of time. The total desorbable boron was higher in coarse textured soils as compared to the fine textured soils. Maximum desorable boron of 13.58 µg g^{-1} soil was in Kangan, while minimum of 9.55 µg g^{-1} in Sagipora soil.

Furthermore, the desorption of boron took relatively less time (24 to 48 h) in coarse textured soils in comparison to 48 to 72 h in fine textured soils. The integrated rate equation when applied to the desorption data, indicated two distinct linear portion expressed as site 1 and site 2 indicating two types of pseudo first order reactions in boron desorption. The two sites represented two boron retention sites, the first belonging to the fast and the second to the slow boron desorption reactions. About 73 to 82 per cent of the total desorbable boron was attributed to the first site that belonged to the most readily desorbable boron fraction and the rest meager amount of 18 to 27 per cent to the second site, which retained boron tightly.

Boron desorption data were also fitted into other kinetics models like zero order, first order, second order, Elovich, power function and parabolic diffusion equations. The Elovich kinetic equation was found to be successful in describing boron desorption data in these soils. The Power function model was equally good in describing boron desorption kinetics in all the soils. The Parabolic diffusion kinetic model could not describe the boron desorption satisfactorily.

Pot experiment

Ten bulk surface soil samples of major soils of Kashmir were used in a pot experiment. Boron was applied at the rate of 0, 1.0 and 2.0 mg B kg^{-1} soil through borax with three replications. Berseem (*Trifolium alexandrinum)* was raised in polythene lined earthen pots and was harvested at 60 and 90 days of growth. Six extractants for boron viz. water, hot water, 0.01 M $CaCl_2$, 0.05 N HCI, 0.01 M

$CaCl_2$ + 0.01 M mannitol and 0.1 M NH_4HC0_3 + DTPA were tested for predicting boron availability to berseem.

Dry matter yield of berseem increased significantly with the application of 1.0 mg B kg^{-1} and 2.0 mg B kg^{-1} soil with respect to control. At first cutting, the mean increase in yield with the application of 1.0 mg B kg^{-1} soil was 2.057 g pot^{-1} and it was 27.78 per cent over control treatment. Boron concentration and uptake increased significantly with boron application. The total boron concentration in berseem plant in control treatment varied from 12.3 to 35.4 µg g^{-1}, whereas, its concentration with the application of 2.0 mg B g^{-1} soil varied from 22.9 to 38.8 µg g^{-1} at first cutting. At second cutting, boron concentration in plant varied from 12.1 to 36.0 µg g^{-1} with zero boron level and with the application of 2.0 mg B kg^{-1} soil it ranged between 20.8 and 37.3 µg g^{-1} dry weight. The mean percent increase in boron uptake with the application of 1.0 and 2.0 mg B kg^{-1} was 45.98 and 61.03 µg pot^{-1} over control (33.61 µg pot^{-1}), respectively at 60 days of growth. At second cutting, boron uptake increased from 68.83 µg pot^{-1} in control to 87.16 and 118.78 µg pot^{-1} with the application of 1.0 and 2 0 mg B kg^{-1} soil.

The amount of boron extracted from the soil by various extractants was in the order of AB-DTPA> $CaCl_2$ + mannitol> 0.05 N HCl > 0.01 M $CaCI_2$>hot water >water. All the extractants used for available boron estimation were found to be significantly correlated with each other. Most commonly used hot water for extracting available B was significantly correlated with all the other extractants. Correlation was highly significant with AB-DTPA (r=0.958**) followed by 0.01 M $CaCl_2$ (r= 0.897*) 0.05 N HCl (r=0.881**), and 0.01 M $CaCl_2$ + 0.01 M mannitol (r= 0.811**). Among the different extractants, boron extracted with 0.01 M $CaCl_2$ gave the highly significant coefficient of correlation with Bray's per cent yield (r= 0.854**) at first cutting and r= 0.886* at second cutting of berseem, respectively.

The critical levels of available boron estimated by water, hot water, 0.01 M $CaCl_2$, 0.05 N HCI and 0.01 M $CaCl_2$ + 0.01 M mannitol, below which berseem will respond to B application, were of the order of 0.34, 0.48, 0.70, 0.62 and 0.74 mg kg^{-1} soil, respectively for the first cutting. For the second cutting, the soil critical level was estimated as 0.34, 0.49, 0.71, 0.63 and 0.74 mg kg^{-1} soil using water, hot water, 0.01 M $CaCI_2$, 0.05 N HCI and 0.01 M $CaCI_2$+ 0.01 M mannitol, respectively.

The critical levels of boron in berseem plant at first and second cutting were found to be 23.00 and 19.00 µg g^{-1}, respectively.

CONCLUSION

1. There was no particular trend regarding distribution of different forms of boron because of different physico-chemical characteristics of soils.
2. Boron adsorption data was satisfactorily described by both Langmuir and Freundlich adsorption isotherms over the entire concentrations used. Adsorption of boron was mainly governed by the clay content and CEC of soils.
3. Desorption of boron was found maximum in soils having low clay content and lesser CEC.
4. Parabolic Diffusion and Elovich model was found to be the best fit for studying the adsorption kinetics in different soils. While as Elovich and Power Function was found to be best fit for desorption kinetics
5. Berseem was used as an indicator crop for boron. Some soils were quiet responsive to application of boron as compared to others. The variation in dry matter yield of berseem in different soils was mainly due to variation in the boron content of plants and secondly due to level of soil available boron.
6. Critical limit for available boron extracted by hot water was 0.48 mg kg^{-1} of soil and showed better correlation with different plant parameters. The critical value for boron in berseem plant at two cutting was found to be 23 and 19 mg kg^{-1} on dry weight basis respectively.

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