Sorption of boron in some foothill soils of north-west India

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Abstract: Boron (B) sorption studies in three foothill soils of Punjab varying in properties were conducted. The adsorption isotherms indicated that the adsorption of B increased with increasing concentration in the equilibrium solution. Linear relationship was observed in all the soils at all concentration ranging between 1 and 100 μg B mL^{-1} indicating that B adsorption data conform to Langmuir and Freundlich equations. The maximum adsorption maxima (b) was observed to be 80.00 mg B g^{-1} in Soil-I soil and the bonding energy (k) constant was maximum of 0.064 ml mg^{-1} in Soil-II. There was positive and significant correlation between adsorption maxima (b) and clay (r=0.99**) and CEC (r=0.99**) of soils. The soils which have higher affinity for B adsorption tended to desorb less amount of boron. Boron desorption by these soils was positively correlated with the sand (r= 0.54) and negatively with clay (r = -0.85) and CEC (r = -0.92). The maximum desorption maxima and constant related to B mobility (K$_d$) was observed to be 49.52 mg g^{-1} and 0.262 mL g^{-1} soil.

Additional words: *Adsorption, desorption, equilibrium*

Introduction

The availability of boron (B) depends upon adsorption-desorption processes, which are influenced by various physical and chemical characteristics of soils (Elrashidi and O'Connor 1982; Arora and Chahal 2005). Adsorption and desorption of B is an important phenomenon in soils that regulate its supply from soils for plant growth. A potential source of B in soil solution is that associated with solid phase in the adsorbed form. The soluble boron remains in dynamic equilibrium with the adsorbed forms and hence cannot be readily removed through leaching. Its deficiency in plants is most widespread in soils, which are coarse in texture, low in organic matter and high in pH and calcareousness (Das 2000). Also, B deficiency is common in highly leached acidic soils especially in humid regions. It becomes most available to plants in the pH range 5.0 to 8.5. The range between B deficiency and toxicity being narrow (0.5 to 1.0 mgkg^{-1}), it is difficult to maintain appropriate boron levels in soil solution (Gupta 1979). The foothill region of Shivaliks constitute nearly 10 per cent of the area of Punjab and lies in 30° 40' to 32° 30' N latitude and 75° 30' to 76° 48' E longitude. The area receives nearly 1100 mm of rainfall per annum, which is erratic in distribution. The area represents alluvium of Shivaliks and the soils are broadly classified as Ustifluvents, Ustipsamments and Ustochrepts (Kukal *et al.* 1993). Being at the foothills, these soils are leached leading to poor organic matter and nutrient, especially micronutrients. Because of its non-ionic nature, once B is released from soil minerals, it can be leached rapidly causing its deficiency (Gupta 1979). Boron deficiency in soils of Punjab is emerging due to intensive cultivation and

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leaching from coarse textured soils (Singh and Nayyar 1999; Arora and Chahal 2007a, b) and hence some crop show response to boron application in these soils. Therefore, the present study has been conducted to provide information on the behaviour of B in the foothill soils ascertaining the energies involved in B retention, which can help in predicting the availability of B to plants.

Materials and Methods
Physical and chemical properties

The three surface soils (Soil-I: Dhar, Soil-II: Chamror, Soil-III: Hoshiarpur) were collected from Gurdaspur and Hoshiarpur districts of Punjab representing alluvium-derived foothill region of Shivaliks and analysed for their physical and chemical properties following standard procedures. Soil pH and EC were determined in 1:2.5 (w/v) soil : water ratio (Jackson 1973). Mechanical analysis of the soil was carried out by International Pipette method as outlined by Day (1965). Organic carbon was determined by rapid titration method as described by Walkley and Black (1934). The cation exchange capacity (CEC) was determined by using neutral normal sodium acetate (Jackson 1973). Available B content was extracted by hot water method and B content in the extract was determined by the improved Azomethine-H method (Wolf 1974).

Sorption studies

Ten grams of surface soils (0-0.15m) were taken in 50 ml polypropylene centrifuge tubes in triplicate. Boric acid (H_3BO_3) solution 20 mL, in 0.01 M $CaCl_2$, varying in B concentrations from 1 to 100 mg L^{-1} was added to each soil and was shaken to equilibrate to a pre-determined equilibrium time of 24 hrs at 25 ± 1 °C. At the end of equilibration time, the tubes were centrifuged and the suspension was filtered through Whatman filter paper No. 42. The B concentration in the equilibrium solution was determined colorimetrically using Azomethine-H. The amount of B adsorbed was calculated by the difference between equilibrium B concentration and initial B added. The sorption of B in soils was then defined by adsorption equations viz. Langmuir and Freundlich adsorption isotherms:

Langmuir equation : $C/x/m = 1/b\,(C) + 1/k\,b$
Freundlich equation : $\text{Log}\,(x/m) = 1/n\,\log C + \log K$

Where, C is equilibrium concentration of B in soil solution (mg mL^{-1}), x/m is the amount of B adsorbed (mg g^{-1}) by soil, b is adsorption maxima (mg B g^{-1} soil) and K is a constant related to bonding energy (mL mg^{-1}). The Freundlich constant K and 1/n provides the estimate of adsorbent capacity and intensity.

For desorption studies, 20 ml B-free 0.01 M $CaCl_2$ solution was added to each soil after adsorption. The mixture was resuspended by vigorous agitation and equilibrated for 24 hours at 25 ± 1°C with intermittent shaking. The suspension was centrifuged and the B concentration in supernatant was determined colorimetrically using Azomethine – H method (Wolf 1974). This process was repeated three more times, resulting in a total of four desorptions for each sample. The data on the amount of B retained by the soil during desorption at the corresponding equilibrium concentration were fitted to Langmuir type equation, given as:

$$D_e/A_b = 1/\,K_d\,D_m + D_e/D_m$$

Where, A_b is B adsorbed (mg g^{-1}), D_e is B desorbed (mg g^{-1}), D_m is desorption maxima (mg g^{-1}) and K_d is constant related to mobility of boron (mL g^{-1}). The desorption parameters such as desorption maxima (D_m) and constant related to mobility of solid phase (K_d) were worked out from the linear plots of D_e vs D_e/A_b according to the Langmuir desorption relationship. Simple correlations were made to determine any relationship between various soil properties and B adsorption parameters.

Results and discussion
Soil properties

The soils varied in texture (sandy loam to sandy clay loam), pH from 6.3 to 8.1, EC from 0.15 to 0.24 dS m^{-1}, organic carbon content from 4.5 to 11.0 g kg^{-1} and cation exchange capacity from 8.54 to 10.65 cmol (p^+) kg^{-1}. Available B content varied from 0.35 to 0.44 mg kg^{-1} soil (Table 1). The soils had mixed mineralogy and the dominant minerals in the sand and silt fractions were quartz, micas and feldspars. Illite and kaolinite are the most abundant clay mineral in these soils (Sharma et al. 1997).

Boron adsorption studies

Boron adsorption capacity of the soils was different (Table 2) and the behaviour of B adsorption by different

soils was not uniform in whole concentration range. The results of B adsorption clearly showed that all the soils have affinity for its adsorption. The amount of B adsorbed for each soil was plotted against its equilibrium concentration to obtain the adsorption isotherm, indicating the effect of B concentration on its adsorption. The adsorption isotherms indicated that though the adsorption of B increased with its increasing concentration in the equilibrium solution, yet the percentage of adsorbed B decreased. This may be because of an increase in the ratio of adsorbate to adsorbent. Bloesch et al. (1987) also reported that adsorption of B increased with increasing concentration in solution.

Adsorption of boron was found to be higher in Soil-I and Soil-II and this may be attributed to the high amount of clay content and CEC of the soils. Soil-III had the lowest adsorption capacity for B which is likely due to its sandy loam texture and low CEC. Amount of B adsorbed was correlated positively with organic carbon (r =0.987), clay (r =0.708) and CEC (r =0.742) but negatively with sand content (r=-0.766). From these results, it could be inferred that adsorption of B was mainly governed by organic matter, clay content and CEC of the soil. Keren and Talpaz (1984) also observed increase in B adsorption on the clay particles was related to the increase in CEC of the clay with fineness.

In all the soils, the Langmuir adsorption isotherm showed linearity when equilibrium B concentration was plotted against C/x/m. The strength of retention decreases with increasing concentration of B in equilibrium solution as a result of precipitation reaction (Fig. 1). Similar linear type of relationship for B adsorption has also been reported by Krishnasamy et al. (1997) in soils representing Vertisol, Inceptisol, Entisol and Alfisol of Tamil Nadu.

The Langmuir constants from the isotherms for each soil are given in table 2. The maximum value of adsorption maxima (b) was observed to be 80.00 μg B g^{-1} for soil-I while minimum of 21.08 μg B g^{-1} for soil-III. The bonding energy constant (k) was maximum of 0.064 mL μg^{-1} in soil-II, and minimum of 0.017 mL μg^{-1} in soil-I. Singh (1964) also found higher k value of 71.43 mL mg^{-1} in light textured soils as compared to 55.05 ml mg^{-1} in heavy textured soils. Saha and Singh (1998) also reported the higher B capacity of Bhopal soil than Indore soil, might be due to the high clay content of the former soils. This is mainly due to high

clay, CEC and organic matter content of soils, which possessed positive correlation with b (r=0.999**, 0.997** and 0.654, respectively). Boron adsorption maxima was significantly correlated with organic carbon (r= 0.96*) in some soils of Assam (Dekamedhi et al. 1998).

The results indicated that in sandy soils having low organic matter, added B fertilizer might be expected to be readily available to plants due to the inability of the soil to adsorb B in large amounts. In the fine textured soils, having high amount of clay content and/or organic matter, large additions of B may not be toxic to plants because of the high adsorption capacity and bonding energy of the soils. The results suggested that low and high rate of boron fertilization have to be adjusted to coarse and fine textured soils, respectively for optimum utilization.

A plot of boron adsorbed against equilibrium boron concentration on a log-log scale gave linear relationship in all the soils at all the concentration range from 1 to 100 μg B mL^{-1} (Fig. 2) indicating that boron adsorption data conform to Freundlich equation. Many workers have reported that B adsorption data could be successfully described by Freundlich model over the entire concentration range (Elrashidi and O'Connor 1982; Saha and Singh 1997; Dekamedhi et al. 1998). The results of the present investigation also indicated that Freundlich equation was valid for wider range of B concentrations.

Freundlich K values ranged widely among the soils. The value was maximum of 5.45 μg g^{-1} for soil-II while minimum of 1.39 μg g^{-1} in soil-I (Table 2). Dekamedhi et al. (1998) reported a range in K values from 0.86 to 1.29 and 1.23 to 2.19 μg g^{-1} in Haplaquepts and Fluvaquepts groups of Assam, respectively. Freundlich K values for the adsorption of boron for eleven soils of Tamil Nadu ranged from 0.18 to 1.96 mg B kg^{-1} (Krishnasamy et al. 1997).

The differences in the values of K were associated with variation in clay content of the soil as indicated by significant relation of the K values with clay content (r=0.703*). The values of Freundlich constant (1/n) are less than unity in all the soils indicating L-shaped isotherm (Fig. 2). The maximum value of 1/n was obtained in soil-I (0.862) and minimum of 0.572 in soil-II. The Freundlich constant (1/n) values ranged from 0.703 to 1.230 in Haplaquepts and 0.611 to 0.703 in Fluvaquepts of Assam (Dekamedhi et al. 1998).

Table 1. Some physical and chemical properties of soils

Properties	Soil – I	Soil – II	Soil – III
pH (1:2.5)	6.30	8.10	7.40
EC (dS m^{-1})	0.20	0.24	0.15
Organic carbon (g kg^{-1})	11.0	10.4	4.5
Clay (%)	28.60	16.90	14.60
Sand (%)	46.80	34.60	56.20
CEC [cmol (p$^+$) kg^{-1}]	10.65	9.02	8.54
Avail. B (mg kg^{-1})	0.40	0.44	0.35
Texture	Sandy clay loam	Loam	Sandy loam
Taxonomy	Typic Dystochrept	Typic Eutrochrept	Typic Ustochrept

Boron desorption in soil

The percentage of desorbed boron was higher at higher level of added B in all the soils. The coarse textured soils tended to desorb higher amount of B as compared to fine textured soils. The soils which have higher affinity for B adsorption, like soil-I, tended to desorb less amount of B (34.5 per cent), whereas soil-III desorbed 57.8 per cent of the adsorbed boron. This indicated that adsorption and desorption of B were inversely related as observed by Saha and Singh (1997) and Elrashidi and O'Connor (1982).

The initial adsorption of B in soils is followed by slow changes that ultimately govern the rate of B release from the soils. The rate of B desorption was slow at low saturation of solid phase matrix whereas at high B saturation, the rate of desorption was fast. The results suggested

that soils having higher adsorption releases B slowly into the soil solution.

Desorption of B was found to be maximum in soil-III which indicated that this soil was more likely to release the applied B which may be attributed to the lower clay and CEC values of the soil, whereas, the soils I and II showed less desorption of B as these soils have high amount of clay and organic matter and thus higher adsorption sites.

The data of B desorption showed that amount of B desorbed by these soils correlated positively with the sand content (r= 0.544) and negatively with clay (r= -0.852) and CEC (r= -0.921). In a leaching experiment Peryea *et al.* (1985) observed that heavy textured soils released lower per cent of adsorbed B than coarse textured soils.

A linear relation was obtained in all the soils when

Table 2. Langmuir and Freundlich coefficients for B adsorption in soils

Soils	Langmuir constants			Freundlich constants		
	B (mg B g^{-1})	k (mL mg^{-1})	R^2	1/n	K (mg g^{-1})	R^2
Soil - I	80.00	0.017	0.995	0.862	1.397	0.994
Soil - II	28.12	0.064	0.992	0.572	5.457	0.916
Soil - III	21.08	0.058	0.990	0.641	1.895	0.984

Table 3. Boron desorption coefficients for different soils

Soils	D_m (mg g^{-1})	K_d (mL g^{-1})	R^2	Regression equation
Soil – I	49.52	0.262	0.964	Y = 0.0202x + 0.1525
Soil – II	35.44	0.137	0.986	Y = 0.0282x + 0.1586
Soil – III	32.46	0.211	0.972	Y = 0.0308x + 0.1456
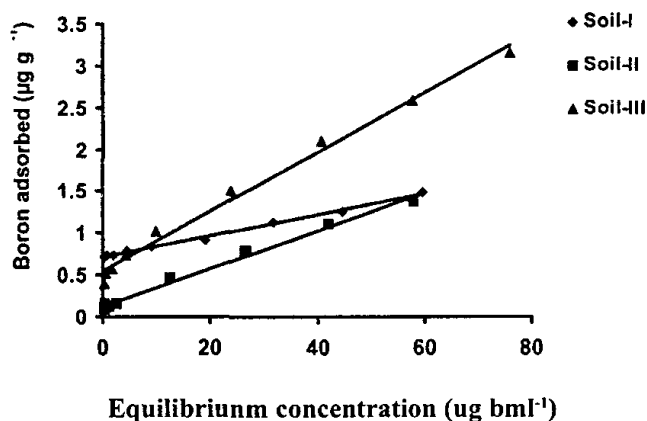
Fig. 1. Linear Langmuir isotherm for B adsorption on soils

desorbed B (D_e) was plotted against B desorbed/ B adsorbed (D_e/A_b) (Fig. 3). The Langmuir desorption parameters such as desorption maxima (D_m) indicating the maximum desorbable capacity of soils and constant related to mobility of solid phase (K_d) were worked out from the linear plots.

The fine textured soils had higher desorption maxima as compared to coarse textured soils. The values of D_m var-
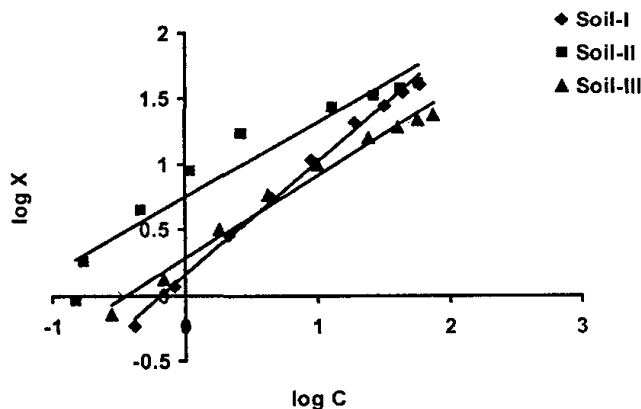

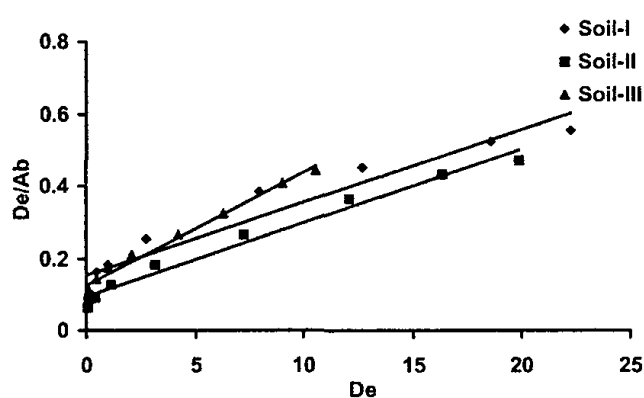**Fig. 2.** Linear Freundlich isotherm for B adsorption on soils

Fig. 3. Linear Langmuir isotherm for B desorption by soils

ied from 32.46 to 49.52 µg g^{-1} and K_d, a constant related to B mobility ranged from 0.137 to 0.262 mL g^{-1} in the soils studied (Table 3). 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 slow.

Conclusion

The soils not only varied in their capacity to retain B but also in the energy with which they absorb it. Adsorption of B conformed to Freundlich adsorption isotherms. Clay and CEC of the soils were significantly correlated with adsorption capacities (K values) of Freundlich equation. Langmuir adsorption isotherm was linear at all the concentrations in all the soils. The fine textured soils had higher desorption maxima and more mobility of adsorbed B as compared to coarse textured soils. The low and high rate of B fertilization have to be adjusted to coarse and fine textured soils respectively for optimum crop production.

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