Environment and Ecology 36 (2A) : 708—714, April—June 2018
Website: environmentandecology.com ISSN 0970-0420

Adsorption–Desorption of Boron in Acid Soils of Odisha

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Received 24 February 2018 ; Accepted 19 March 2018 ; Published on 6 April 2018

Abstract Studies on adsorption of boron (B) was undertaken in seven different soils of Odisha representing different agroecological regions. The study showed that the adsorption of added B was in the order: *Vertisol* > *Inceptisol* > *Alfisols*. Soils within each order also differed in B adsorption. The two adsorption equations, namely Freundlich and Langmuir were fitted to the data. Based on prediction coefficients (R^2), Freundlich appeared the best fit for all the soils compared to Langmuir. Langmuir constant b is positively correlated with organic carbon, Silt and CEC. Desorption of added B was in the order : *Inceptisols* > *Vertisols* > *Alfisols*. Desorption of B decreased with an increase in pH, organic carbon, clay and CEC.

Keywords Boron, Adsorption, Desorption, Acid soils.

Introduction

Adsorption–desorption processes play a major role in governing the solubility of B in soil solution and consequently its availability to growing plant. Boron is one of the essential micronutrients required for normal growth of most plants. However, the range of B concentration in the soil solution causing either deficiency or toxicity in plant is narrow. So for a better management of native soil B, adsorption-desorption of B mechanism in soil is necessary (George and Sureshkumar 2016). The partitioning of B between soil solution and soil surfaces is affected by clay content, sand silt fractions, organic matter content, soil pH (Niaz et al. 2007). Adsorbed B is neither directly available nor toxic to the plants, thus adsorption complex plays a critical role in regulating soil solution B concentration. After sorption of B on different soil surfaces, the release of sorbed B is of great importance, as plants respond primarily to the B activity in soil solution.

According to All India Coordinated Research Project on Macro and Secondary nutrients and Pollutant Elements in soils and plants, B is the second most deficient micro-nutrient in Indian soils only next to zinc. Available B deficiency across the state exhibited 33% (Shukla et al. 2012) whereas in Odisha average boron deficiency covering 12 districts were 42% (Pal and Jena 2012).

Boron adsorption-desorption mechanism in soils, have great significance, emergence of B deficiencies in soils of arid and semi-arid regions were reported (Dwivedi et al. 2008) that were earlier considered adequate in B supply. The study related to pattern of boron may be helpful in predicting boron availability to plants. Very limited information regard-

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Table 1. Physico-chemical properties of soils used for B adsorption studies.

Sl. No.	Soil type	pH	EC (dS m^{-1})	OC (g kg^{-1})	HWB (mg kg^{-1} soil)	CEC [cmol (p^+) kg^{-1}]	Soil separates (%) Sand	Silt	Clay	Tex-ture	$CaCO_3$ (%)
1	Red soil	4.64	0.1	0.33	0.36	3.5	78.8	10.9	10.3	Sandy loam	5
2	Black soil	6.26	0.23	0.98	0.68	36.7	22.4	42	35.4	Silty clay loam	6.6
3	Brown forest soil	5.29	0.06	1.33	0.48	8.3	82.8	4.9	12.3	Sandy loam	0.4
4	Alluvial soil	4.98	0.06	0.11	0.53	4.9	79.7	4.9	15.4	Sandy loam	3.5
5	Laterite soil	4.5	0.06	0.13	0.32	1.94	84.8	4.9	10.3	Sandy loam	0.4
6	Red & yellow soil	6.89	0.28	0.55	0.52	8.3	75.7	8	16.3	Sandy clay loam	3
7	Red & black soil	6.3	0.13	0.26	0.56	8.5	73.7	6.9	19.4	Sandy loam	5.2

ing the soils of Odisha is available. Hence the present investigation was undertaken to study the adsorption–desorption mechanism of applied boron in soil and inter-relationship between soil characteristics and boron adsorption constants in soils.

Materials and Methods

Sampling sites

Seven soil samples (0–15 cm depth) belonging to different groups of soils were collected from different locations of Odisha using variability in physico-chemical characteristics as a the criteria for selection. The soil samples were collected from the farmers' field of different districts of Odisha, namely, Bargarh, Subarnapur, Kendrapara, Khordha, Nayagarh representing seven groups of soils. According to the soil groups, black soil, mixed red and black soil and brown forest soil may be classified under *Vertisols*. Alluvial soils under *Inceptisols* and red soil, laterite soil and mixed red and yellow soil under *Alfisols*.

Soil characterization

Physical and chemical characteristics of the soils were determined following standard procedures. The pH and EC were determined in 1:2 soil : water suspension and in supernatant of the same soil : water ratio respectively. Mechanical analysis, organic carbon (OC) hot water extractable B, cation exchange capacity (CEC) and free $CaCO_3$ were determined following standard methods (Page et al. 1982).

Boron adsorption studies

Five gram of soil sample and 20 ml of 0.01 M $CaCl_2$ solution (containing increasing concentrations of B viz 2.5, 5, 10, 20, 30, 40, 50 mg B L^{-1} as H_3BO_3) was taken in duplicate in 50 ml polypropylene centrifuge tubes and the contents were shaken for 23 h on a shaker. The suspension was centrifuged and a 10 ml aliquot of the clear supernatant was taken and filtered through Whatman No. 42 filter paper. Boron was determined in the filtrate using azomethine – H method. The difference between the amount of B in the initial solution and that in the filtrate was taken as the amount of B adsorbed by the soil from the equilibrating solution.

The following adsorption equations were used to describe B adsorption in the soils. Freundlich equation : $x = ac^{1/n}$

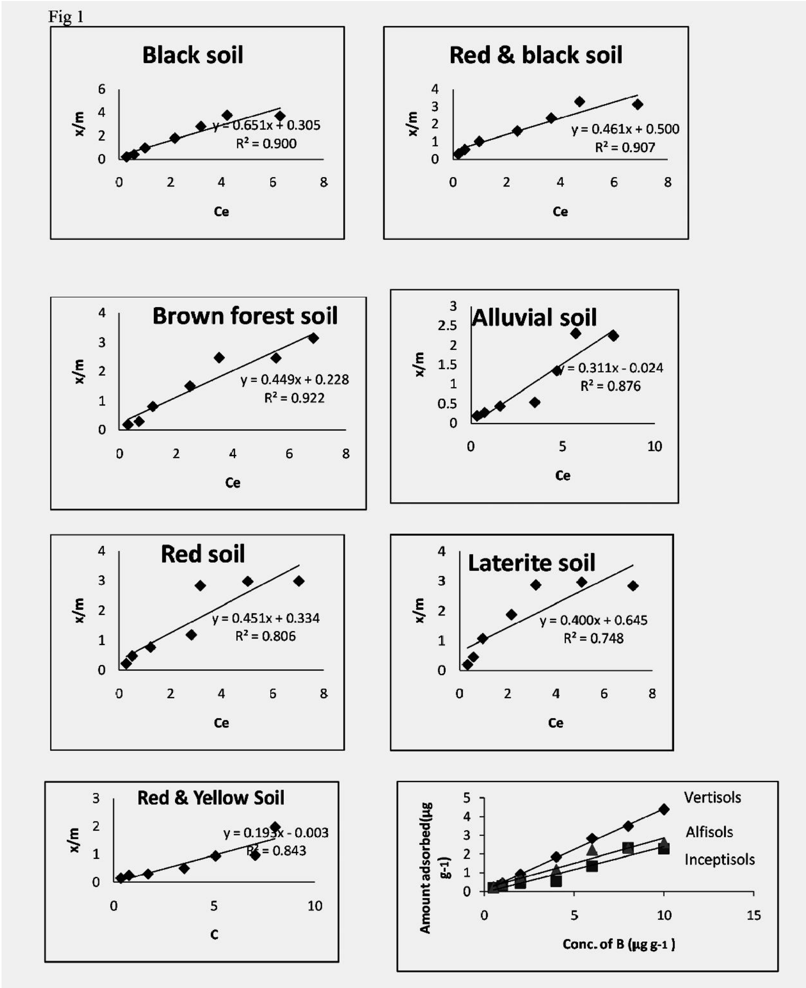

Fig. 1. Boron adsorption at varying equilibrium B concentration in different soils.

Where x is the amount of adsorbed B (mg kg^{-1} soil) and c the equilibrium B concentration (mg L^{-1}). Two parameters a and 1/n, were calculated using the linear transformation log x =log a + 1/n log c

Langmuir equation : $x = k\,b\,c / (1 + kc)$

Where b is the maximum monolayer B adsorption capacity (mg kg^{-1} soil) and k the affinity coefficient that reflects the relative rate of adsorption and desorption of B at equilibrium and it is thus, related to binding energy (L mg^{-1}). The parameters b and k were calculated using the linear transformation as $c/x = c/b + 1/kb$

Maximum buffering capacity (MBC) of soil was also calculated as a product of adsorption maxima (b) and affinity coefficient.

Boron desorption studies

The soils with treatments of different added boron concentration in the adsorption study were used for desorption of boron. Desorption was initiated with addition of 20 ml of boron free 0.01 M $CaCl_2$ solution. The mixtures were agitated and equilibrated for 23 h.

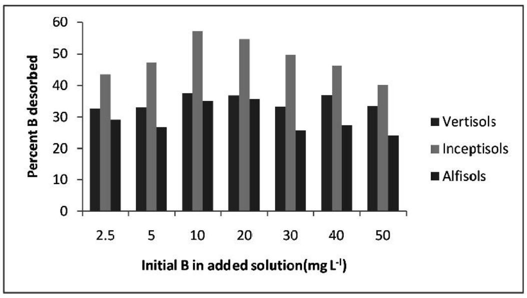

Fig. 2. Boron desorption at varying initial B concentration in added solution in different soils.

The suspension was centrifuged and 10 ml of supernatant was removed for boron determination. Amount of boron desorbed was calculated from the difference between equilibrium boron concentration at the desorption step and the equilibrium boron concentration previous to the desorption step.

Statistical analysis

Statistical analysis including simple and multiple correlation coefficients were done to determine relationships between soil properties and boron adsorption parameters using statistical analysis system (SAS version 9.2).

Results and Discussion

Characteristics of the soils

The soils used for adsorption – desorption study varied widely in their characteristics (Table 1). The pH of black soil and mixed red and black and mixed red and yellow soil were slightly acidic to neutral range. The rest soils exhibit moderately acidic range (pH 4.5 to 5.29). All the soils were non-saline as EC ranged between 0.06 to 0.28 dSm^{-1}. Soil organic carbon ranged between 0.11 g kg^{-1} in alluvial soil to 1.33 g kg^{-1} in brown forest soil. Hot water extractable boron varied from 0.32 mg kg^{-1} in laterite soil to 0.68 mg kg^{-1} in black soil. The clay content of black soil was 35.4% and the rest soils range between 10.3% to 19.4%. The black soils had greater CEC i.e. 36.7 cmol (p^+) kg^{-1} compared with other soils which range between 1.94 to 8.5 c mol (p^+) kg^{-1}. Soil texture varied from sandy to silty clay loam. As per soil order *Vertisols* had higher pH, CEC, $CaCO_3$ and clay content followed by *Inceptisols* and *Alfisols*.

Adsorption of boron in soils

Adsorption of boron in brown forest soil was the highest and it followed the order : brown forest soil > mixed red and black soil > black soil > alluvial soil > mixed red and yellow soil > red soil>laterite soil. As per soil order the adsorption of boron was highest in *Vertisols* followed by *Alfisols* and *Inceptisols* (Fig. 1). Relatively greater boron adsorption in *Vertisols* might be due to higher CEC and clay content compared to other soils. Among *Vertisols*, black soils and mixed red and black soil, adsorption maxima were achieved at 40 mg kg^{-1}. Any further increase in strength of added solution did not bring perceptible increase in boron adsorption in these soils.

In *Alfisols*, boron adsorption maxima achieved

Table 2. Different adsorption equation constants for boron adsorption in various soils of Odisha. *a and 1/n are intercept and slope respectively, b, k and MBC (b × k) are the maximum monolayer adsorption capacity (mg kg^{-1} soil) affinity coefficient (L mg^{-1}) and maximum buffering capacity respectively.

Sl.		Langmuir equation				Freundlich equation		
No.	Soil type	b	k	MBC	R^2	a	1/n	R^2
1	Red soil	7.230	0.110	0.790	0.397	0.632	1.340	0.933
2	Black soil	26.180	0.030	0.840	0.131	0.724	1.152	0.877
3	Brown forest soil	18.690	0.030	0.580	0.117	0.632	1.129	0.942
4	Alluvial soil	8.080	0.040	0.340	0.052	0.378	1.258	0.883
5	Laterite soil	5.910	0.170	1.020	0.601	0.711	1.310	0.857
6	Red & yellow soil	3.260	0.080	0.261	0.241	0.285	1.320	0.881
7	Red & black soil	4.900	0.290	1.440	0.798	1.005	1.525	0.988

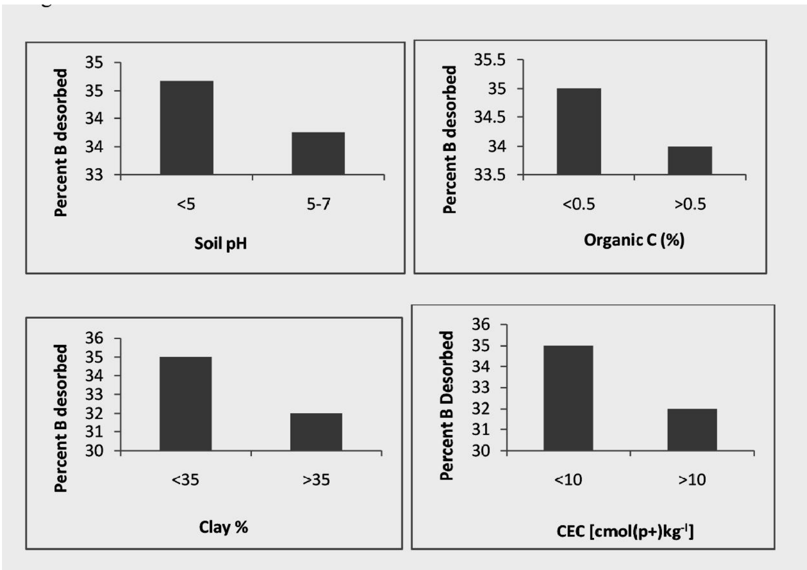

Fig. 3. Percent desorption of B as influenced by (a) soil pH, (b) organic C, (c) clay content and (d) CEC across the soil orders.

at varied concentration boron concentration ranged between 10–50 mg kg^{-1}. In red soil, maximum adsorption achieved at 30 mg kg^{-1}, whereas in laterite soils, adsorption maxima attained at 10 mg kg^{-1} and in red and yellow soil, it appeared to have reached at 50 mg kg^{-1}. Adsorption of boron in *Inceptisols* was least compared with that in *Vertisols* and *Alfisols*. These soils exhibited adsorption maxima at initial solution boron concentration of 20–30 mg kg^{-1} and thereafter an increase in the strength of added solution did not bring perceptible increase in B adsorption in these soils.

The variation in overall amount of boron adsorption depend on variation in mineralogical and chemical properties of soils. Lower boron adsorption in *Alfisols* as observed in the present case may be due to their acidic range of pH (Table 1). In acid soils boron adsorption is usually controlled by oxides and oxy-hydroxides of iron, aluminum and soil pH. Lower the soil pH smaller is the B adsorption in soil as soluble B at low pH values exist mainly as boric acid $(OH)_3$, which is easily lost by leaching resulting in B deficiency in acid soils especially coarse – textured soils of high rainfall areas.

Comparative evaluation of adsorption equation

Two adsorption equation namely Freundlich and Longmuir were fitted to explain the adsorption behavior of these soils.

Table 3. Corelation coefficient (r) between adsorption equation parameter and soil characteristics. *Significant at p = 0.05.

Sl.	Soil	Freundlich eqn		Langmuir eqn		
No.	characteristics	a	1/n	b	k	b*k
1	pH	– 0.04	0.15	0.09	0.07	– 0.05
2	EC	– 0.24	0.02	0.11	–0.12	– 0.20
3	OC	0.01	–0.70	0.78*	–0.54	– 0.21
4	Sand	–0.20	0.34	–0.74	0.28	– 0.12
5	Silt	0.18	–0.40	0.76*	–0.33	0.10
6	Clay	0.22	–0.24	0.67	–0.19	0.14
7	CEC	0.19	–0.44	0.81*	–0.34	0.07
8	$CaCO_3$	0.25	0.25	0.22	0.10	0.25

Table 4. Effect of soil characteristics on prediction of Freundlich and Langmuir constants.

Langmuir constants	Reression equation	R^2
b	$Y = 13.118 - 0.91 clay - 0.37\ CaCO_3 + 3.91\ OC + 1.19\ CEC$	0.87
	$Y = - 2.66 + 0.51\ clay - 0.03\ CaCO_3 + 10.80C$	0.78
	$Y = - 18.25 - 1.25\ clay - 0.61\ CaCO_3 + 1.54\ CEC$	0.85
Freundlich equation		
a	$Y = 0.38 - 1.69\ OC + 0.1\ EC - 0.01\ CEC + 0.02\ clay + 0.03\ CaCO_3$	0.32

Freundlich adsorption equation

Freundlich 'a' value which is somewhat indicative of adsorption capacity was invariably higher for *Vertisols* compared to other soils (Table 2). The mean values of prediction coefficients (R^2) for Freundlich equation were 0.663 > 0.543 > 0.378 for *Vertisols*, *Alfisols* and *Inceptisol*, indicating that the Freundlich equation could provide relatively better prediction of B adsorption in *Vertisols* compared with other soils under study. Freundlich equation has successfully been used in a variety of soils by several workers (Arora and Chahal 2010). The advantage of Freundlich model is that it assumes unlimited sorption sites, thus correlating better with a heterogeneous soil medium having variable chemical and physical properties. At higher adsorption level, a multilayer adsorption and/ or precipitation reaction appears to have occurred, resulting in a better fit of data with Freundlich than with Langmuir equation. Higher values of Freundlich constant 'a' and also higher prediction coefficients (R^2) for *Vertisols* showing highest B adsorption are thus explainable (Table 2).

Langnuir adsorption equation

Adsorption maxima 'b' varied from 3.26 to 26.18 mg kg^{-1} and affinity coefficient i.e. bonding energy 'k' from 0.03 to 0.29 L mg^{-1} in different soils. The mean R^2 values for *Vertisols*, *Inceptisols* and *Alfisols* were 0.349, 0.052 and 0.413 respectively. Apparently, the mean R^2 values of Langmuir equation were lower than those of Freundlich equation for *Vertisol*, *Inceptisols* and *Alfisols*. Maximum buffering capacity (MBC) i.e. 'b × k' was also highest for *Vertisols*, followed by *Alfisols* and *Inceptisols*.

Relationship of B adsorption parameters with soil characteristics

Boron adsorption in soil depends on boron concentration soil pH, texture, organic matter, CEC and clay. In present case, Langmuir 'b' known as maximum monolayer adsorption capacity showed significant ($p < 0.05$) positive correlation with OC, silt and CEC content, with r values ranging between 0.76 to 0.81 (Table 3). However Freundlich 'a' value which indicated adsorption capacity of soil, has no significant correlation with any of the soil properties (Table 4).

Earlier studies revealed significant correlation of adsorption maxima of B and affinity coefficient relating to bonding energy with CEC of soils (Chaudhary 2002, Arora and Chahal 2010). As pH of soils under study varied from 4.64 to 6.89, majority of boron was present as undissociated H_3BO_3 during adsorption. There is little scope for boron to be adsorbed in these soils due to electrostatic force of attraction. The mechanism of B adsorption on soil constituents i.e. clay and organic matter has been considered to be ligand exchange in several studies.Multiple regression analysis revealed that clay, $CaCO_3$, CEC and OC could explain the variability in Langmuir 'b' to the extent of 87%.

Desorption of B in different soil

Desorption of B computed as percent of adsorbed B at varying added B concentration in different soils is illustrated in Fig. 2. The B desorption at any of the added the B concentration was highest in *Inceptisols* (40—57%), followed by *Vertisols* (33–37%) and *Alfisols* (24–36%). Similar result were found by Dey et al. (2013) Across the soil orders and initial B concentration, magnitude of B desorption decrease in increase in soil pH, organic carbon, clay and CEC (Fig. 3). An inverse relationship between B desorption and soil pH, OC, clay and CEC indicated that these soil characteristics retarded the release of adsorbed B. Similar results were obtained earlier that clay and organic carbon individually explained 40.7% and 28.5% variability in B desorption in some acid soils of India. Arora and Chahal (2010) also reported that B desorption from soils was positively and significantly correlated with sand content and negatively correlated with clay content and CEC.

Conclusion

Sorption and desorption of B in soils were greatly affected by soil properties, namely CEC, organic carbon and clay. This implies that retention, mobility and availability of applied B will vary in different soils. Adsorption of B was highest in *Vertisols*, followed by *Inceptisols* and *Alfisols*. Boron adsorption parameters may be useful in modeling the plant B uptake from applied pool in different soils. Such information would help in optimizing boron application rates in different soils.

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