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Adsorption: Desorption behaviour of boron in different soil series

S Suganya, PP Mahendran, P Saravana Pandian, A Subbiah and G Balasubramanian

S Suganya
Ph.D. Scholar, Department of Soils and Environment, Agricultural College and Research Institute, TNAU, Madurai, Tamil Nadu, India

PP Mahendran
Professor and Head, Department of Crop Management, Agricultural College and Research Institute, TNAU, Kudumiyanmalai, Tamil Nadu, India

P Saravana Pandian
Professor, Department of Soils and Environment, Agricultural College and Research Institute, TNAU, Madurai, Tamil Nadu, India

A Subbiah
Assistant Professor4, Grapes Research Institute, TNAU, Anaimalayanpatty, Rayappanpatty, Theni, Tamil Nadu, India

G Balasubramanian
Professor[5], Department of ENS, Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu, India

Corresponding Author:
S Suganya
Ph.D. Scholar, Department of Soils and Environment, Agricultural College and Research Institute, TNAU, Madurai, Tamil Nadu, India

Abstract
Boron adsorption is one of the most important factors in deciding the efficiency of B fertilization and its management in intensively cultivated soils. Studies on adsorption of boron were undertaken in major banana growing soils of Theni district representing two soil series *viz.,* Palaviduthi and Peelamedu and results revealed that the adsorption of added boron was in the order : Peelamedu > Palaviduthi. Higher the concentration of added B solution, greater was the variability in B adsorption. Freundlich and Langmuir adsorption equations fitted to the data, explained the adsorption behavior of the soils, yet based on prediction coefficients (R^2) Langmuir appeared to be the best fit for Palaviduthi and Peelamedu soil series, and Freundlich equations which showed lowest B adsorption. Freundlich constant 'a' and Langmuir constant 'b' were positively correlated with free $CaCO_3$, CEC and clay content. Desorption of added B was in the order: Palaviduthi > Peelamedu. Desorption of B increased with an increase in soil pH, whereas it decreased with an increase in organic C, clay and CEC.

Keywords: Boron, adsorption, desorption, Palaviduthi, Peelamedu, soil characteristics

Introduction
Boron (B) is an essential micronutrient required for crop growth and yield due to its major role in formation and maintenance of cell wall and cell membrane integrity. Coarse-textured acid soils of humid and per-humid regions, calcareous soils and those with low organic matter content are more prone to B deficiency. On the contrary, B toxicity is reported in arid and semi-arid areas owing to high levels of B in soils and addition of B through irrigation water (Keren and Bingham 1985) [12]. Management of this micronutrient is critical because the range between deficiency and toxicity for B in soil is much narrower as compared to other nutrients. For a better management of native soil B, a thorough knowledge of B adsorption-desorption mechanism in soil is necessary.

Some of the important reviews on B nutrition (Niaz *et al.,* 2007) [17] pointed out that the partitioning of B between soil solution and soil surfaces is affected by clay mineral types, clay content and specific surface area, mineralogy of the sand and silt fractions, sesquioxides, organic matter content, soil pH, ions on the exchange complex, and soil salinity. Boron adsorption reactions on oxides, clay minerals and soil materials have been described using various adsorption equations (Datta and Bhadoria, 1999) [2]. However, Langmuir or Freundlich equations were most commonly deployed to describe B adsorption on aluminum and iron oxides (McPhail *et al*., 1972) [14], clay minerals (Gu and Lowe, 1992) [9], calcite (Goldberg *et al.*, 2005) [7], humic acids (Gu and Lowe, 1990) [8] and soils (Mondal *et al*., 1993) [15].

Adsorption sites on organic matter, oxide minerals, clay minerals and carbonates act as a source and sink for B (Keren and Bingham, 1985; Datta and Bhadoria, 1999) [12, 2]. Adsorbed B is neither directly available nor toxic to the plants, thus adsorption complex plays a critical role in regulating soil solution B concentrations. After sorption of B on different soil surfaces, the release of sorbed B is of immense significance, as plants respond primarily to the B activity in soil solution.

In India, studies on B in soils and plants are mostly confined to acid soils, for neutral to alkaline and non-calcareous soils are generally well-supplied with B. However, excessive uptake of macro and micro-nutrients under intensive cropping during past decades, and neglect of their replenishment in adequate quantities resulted in widespread deficiency of different nutrients including B. According to All India Coordinated Research Project on Micro and Secondary Nutrients and Pollutant Elements in Soils and Plants, B is the second most deficient micronutrient in Indian soils only next to zinc (Zn). Averaged across the states, 33 per cent soils exhibited B deficiency (Shukla *et al*., 2012) [19]. Understanding B adsorption-desorption mechanisms in the soils, therefore, assumes great significance, especially in the light of recent reports indicating emergence of B deficiencies in the soils of even arid and semi-arid regions (Dwivedi *et al*., 2008) [3] that were earlier considered adequate in B supply. Therefore, the present investigation was undertaken to monitor the fate of applied B in taxonomically different soils. The objective of this study was to understand the adsorption-desorption mechanisms of applied B in the soils, and role of different soil components in the whole process.

Materials and Methods

Study Area

The study was undertaken in banana growing soils of Theni district of Tamil Nadu. It is basically an inland district lying at the foot of Western Ghats and geographically lies between 9º30' and 10º12' north latitude and 77º10' and 77º42' east longitude. It is bounded by Dindigul district in the north, Madurai district in the east, Virudhunagar district in the south and Kerala state in the west. Theni district has 5 taluks and 8 blocks with a total geographical area of 2889.23 km. The climate of this region is semi-arid with an annual rainfall is 760.8 mm, mostly received from North East monsoon. The mean maximum, minimum and average air temperatures were 33.34, 23.55, 28.45^{0}C respectively. The soils of Theni district comprise of red, black and alluvial soil groups with rice, pulses, banana and other vegetables and millets as major crops.

Sampling sites

Based on the analytical results of the surveyed soil samples, two field experiments were taken up in boron deficient soils of Uthamapalayam and Cumbum blocks of Theni District, followed by it, confirmation trial were also conducted in different locations of Cinnamanur and Cumbum blocks. The first field experiment which was conducted at Annaimalayanpatty Village of Uthamapalayam block comes under the Palaviduthi soil series with the taxonomical class of *Typic Rhodustalf*, whereas the second field experiment comes under Peelamedu soil series which is located at Angurpalayam village of Cumbum Block at Theni District and the taxonomical class of the experimental soils was *Typic Haplustert.* The main criterion for selection of soil samples (0-15 cm depth) from Palaviduthi and Peelamedu soil series was due to their variability in its physicochemical characteristics. The various soil characteristics of two series are given in (Table 1).

Table 1: Details of soil samples collected for B adsorption-desorption studies

Details	Field experiment I	Field experiment II
A. Soil series	**Palaviduthi**	**Peelamedu**
B. Taxonomical class	***Typic Rhodustalf***	***Typic Haplustert***
Mechanical analysis		
Clay (%)	24.2	40.1
Silt (%)	10.2	12.1
Fine sand (%)	25.3	24.9
Coarse sand (%)	39.6	22.1
Textural class	**Sandy clay loam**	**Sandy clay**
B. Physico – chemical properties		
Soil reaction (pH)	7.51	8.70
Electrical Conductivity (dS m^{-1})	0.38	0.60
AEC (c mol (p^-) kg^{-1})	9.62	3.09
CEC (c mol (p^+) kg^{-1})	9.36	17.40
E. Chemical properties		
Total Sesquioxides (%)	17.85	6.45
Al_2O_3 (%)	11.40	3.59
Fe_2O_3 (%)	6.45	2.86
Organic Carbon (g kg^{-1})	3.88	3.64
Free $CaCO_3$ (%)	Nil	4.50
Hot water soluble - B (mg kg^{-1})	0.30	0.28

Soil Characterization

The soil samples were air dried, gently powered with wooden mallet and sieved through 2 mm plastic sieve. The processed soil samples were analyzed for pH, EC (Jackson, 1973) [10], texture (Piper, 1966) [18], Organic carbon (Walkley and Black method, 1934) [21], $CaCO_3$ (Piper method, 1966) [18], Iron and aluminium (Volumetric method), Sesquioxides (Gravimetric method) by Piper (1966) [18], AEC (Gillman, 1979) and CEC (Jackson, 1973) [10].

Boron Adsorption Studies

Ten gram soil sample and 20 mL of 0.01 *M* $CaCl_2$ solution (containing increasing concentrations of B *viz.*, 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, 14.0, 16.0, 18.0 and 20.0 mg B L^{-1} as H_3BO_3) was taken in 50 ml polypropylene centrifuge tubes, and the contents were shaken for 23 hours. 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 (John *et al*., 1975) [11]. The difference between the amount of B in the initial solution and that in the filtrate (after shaking) was taken as the amount of B adsorbed by the soil from the equilibrating solution_as per the procedure described by Elrashidi and O'Connor (1982) [4].

Freundlich equation: $x = a\,c^{1/n}$

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 is the affinity coefficient that reflects the relative rate of adsorption and desorption of B at equilibrium and it is, thus, an affinity term related to bonding energy (L mg^{-1}). The parameters b and k were calculated using the linear transformation c/x = c/b + 1/(kb). Maximum buffering capacity (MBC) of soils was also calculated as a product of adsorption maxima and affinity coefficient.

Boron Desorption Studies

The soils with the treatment of different added B concentrations in the adsorption study were used for desorption of B. Desorption was initiated with the removal of 10 ml of supernatant from equilibrated solution, and addition of 10 ml of B-free 0.01 *M* $CaCl_2$ solution. The mixtures were re-suspended through vigorous agitation and equilibrated for 23 hours. The suspensions were centrifuged, and 10 ml of supernatant solution was removed for B determination. The amount of B desorbed was calculated from the difference between equilibrium B concentration at the desorption step and the equilibrium B concentration previous to the desorption step divided by 2 (dilution factor). Desorption of B in different soils was expressed as the percentage of B adsorbed at different added B concentrations.

Results and Discussion

Surface samples representing two different soil series *viz.*, Palaviduthi and Peelamedu were used for the boron adsorption studies and the results are presented in table 2 and 3. The results clearly showed that both the soils had affinity towards B adsorption. The amount of B adsorbed for the both the soils were plotted against the equilibrium boron concentration to obtain the boron adsorption isotherms. The adsorption isotherms indicated that the adsorption of boron increased up to a level and it got decreased gradually. Results further showed that the adsorption capacity of different soil series was not identical and had a varied concentration range that was found to be maximum in Peelamedu soil series as compared to Palaviduthi series.

Palaviduthi soil series

It was inferred from adsorption and desorption behaviour of soils (table 2) that the amount of B adsorbed increased with the increase in the concentration of B upto 80 µg ml^{-1} beyond which it got declined. Regarding added B, the percentage of adsorption was ranged from 3.69 to 37.75 per cent. The highest percentage of adsorption of B was registered while adding 80 µg ml^{-1} and it got declined gradually. This might be due to the precipitation of borate by Fe_2O_3 and Al_2O_3 as the sesquioxide content of the experimental soil is 19.47 per cent. Similar type of relationship for B adsorption has also been reported by Krishnasamy *et al.* (1997) [13] in Alfisol of Tamil Nadu.

The adsorption data were fitted into two adsorption isotherms viz., Langmuir and Freundlich equations (Table 4a and 4b). Regarding Langmuir adsorption isotherm, the B sorption maxima (b) was observed as 27.78 mg kg $^{-1}$, bonding energy (K) was 5.14 and maximum buffering capacity was 142.78 mg kg^{-1}. The highest relationship was observed in Langmuir equation (R^2 = 0.94**) which was highly correlated to equilibrium B concentration (C) and B adsorption (x/m).

In Freundlich adsorption isotherm, the constants *viz.*, k and 1/n values were recorded as that of Langmuir equation. The concentration exponent (1/n) values were 0.17, K was 1.12 and R^2 was 0.17*. The highest positive relationship with equilibrium B concentration (C) and B adsorption (x/m) was exhibited that the amount of adsorbed B had a positive relationship and highly significant in Langmuir compared to Freundlich isotherm. The maximum B desorption of 16.67 µg g^{-1} was registered in 80 µg ml^{-1} of added B beyond which it got declined. The percentage of B desorption ranged from 15.89 to 54.27 and it was significantly increased while adding B upto 80 µg ml^{-1}.

Peelamedu series

The data on B adsorption (table 2) revealed that the amount of adsorbed B was increased with the increase in the concentration of B up to 100 µg ml^{-1} beyond which adsorption got declined. The percentage of B adsorption was ranged from 5.10 to 38.40 per cent. The highest percentage of adsorption B was recorded with the concentration of 100 µg ml^{-1} beyond which it declined gradually.

As per Langmuir adsorption isotherm, the B sorption maxima (b) observed was 35.71 (mg kg $^{-1}$), bonding energy (K) 5.60 and maximum buffering capacity was 199.97 (mg kg $^{-1}$) and the highest relationship was observed in Langmuir equation (R^2 = 0.96**) which was highly correlated to equilibrium B concentration (C) and B adsorption (x/m).

In the case of Freundlich adsorption isotherm, the constants *viz*., k and 1/n values have exhibited the same trend as that of Langmuir isotherm. The highest concentration exponent (1/n = 0.07), K (1.10) and the regression coefficient (R^2 = 0.05*) were registered in Peelamedu series. In Peelamedu series, the amount of B desorbed was recorded as 16.65 µg g $^{-1}$ while adding B @ 100 µg ml^{-1}, further addition of B resulted in decreased B desorption range. The percentage of B desorption was found to range from 13.37 to 42.89. The rate of desorption of B increased in a linear manner while adding B from the range of 0 to 100 µg ml^{-1}.

Adsorption of boron was found to be higher in Peelamedu soil series which may be attributed to the presence of calcium carbonate (4.50%), on B addition the formation of calcium octa borates takes place which is so strong and has very less solubility percentage as the Ksp value is 0.000012 @ 25 to 35ºC besides high amount of clay content of the soil are the reasons behind the B adsorption whereas, the Palaviduthi soil series had less adsorption capacity for B which was likely due to its sandy clay loam texture along with presence of iron and aluminium oxides. Amorphous Al_2O_3 and Fe_2O_3 (17.85%) provide sites for boron adsorption (Bingham, 1973) [1]. The mechanism of B adsorption on iron and aluminium oxide minerals is considered to be ligand exchange with reactive surface hydroxyl groups (Goldberg *et al.*,1993) [6] which results in the formation of iron and aluminimu borates whose solubility is moderate to high [Ksp value of $FeB(OH)_4^+$ = 3.70 and $AlBO_3$ = 1.54 @ 25-35 ºC].

As regards of B desorption in Palaviduthi soil series (fig.1), the maximum B desorption of 16.67 µg g $^{-1}$ was registered in 80 µg ml^{-1} concentration of added B beyond which it got declined. The percentage of B desorption ranged from 15.89 to 54.27 and it was significantly increased while adding B upto 80 µg ml^{-1}.In Peelamedu series the amount of B desorbed was recorded as 16.65 µg g $^{-1}$ while adding B @ 100 µg ml^{-1}, further addition of B resulted in decreased B desorption range (fig.2). The percentage of B desorption was ranged from 13.37 to 42.89. The rate of desorption of B increased in a linear manner while adding B from the range of 0 to 100 µg ml^{-1}. Singh (1964) [20] also found higher k value in light textured soils as compared to heavy textured soils.

In general, coarse textured soils tended to desorb higher amount of B as compared to fine textured soils. Accordingly, the fine textured soils more particularly Peelamedu soil series had higher affinity for B adsorption and hence it tended to desorb less amount of B (42.89 %), whereas Palaviduthi soil series (Alfisols) desorbed 54 per cent of the adsorbed boron. This indicated that adsorption and desorption of B were inversely related as observed by Saha *et al.* (1998) and Elrashidi and O'Connor (1982) [4].

Desorption of B was found to be maximum in Palaviduthi soil series which indicated that this soil was more likely to release the applied B which may be attributed to the lower clay and higher AEC of soil [9.62(c mol (e$^-$) kg^{-1})], whereas, soils of Peelamedu soil series showed less desorption of B as these soils have high amount of clay and free calcium carbonates and thus higher adsorption sites. The results suggested that, the rate of boron fertilization have to be adjusted to coarse and fine textured soils, respectively for optimum utilization. Similar results were given by Saha *et al.* (1998).

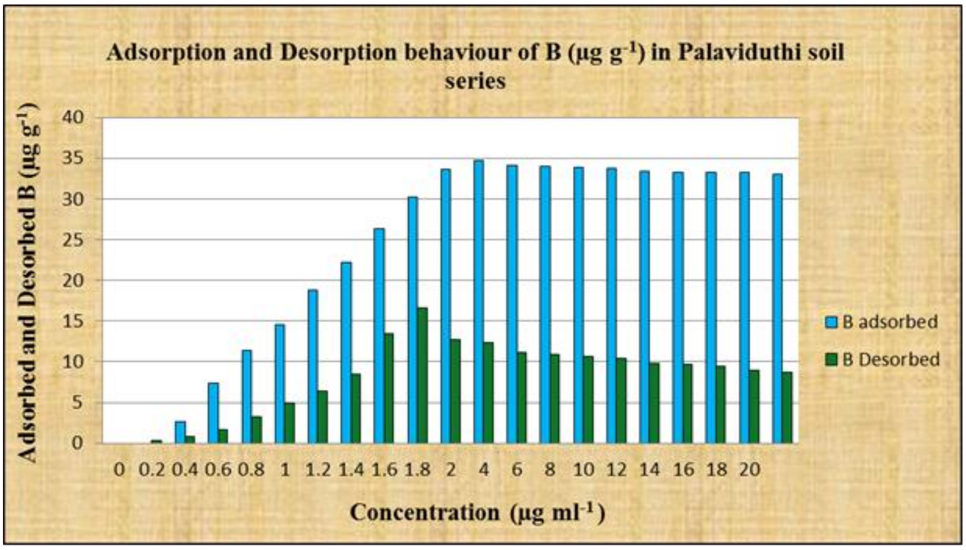

Fig 1: Adsorption and Desorption behaviour of B (µg ml^{-1}) in Palaviduthi soil series

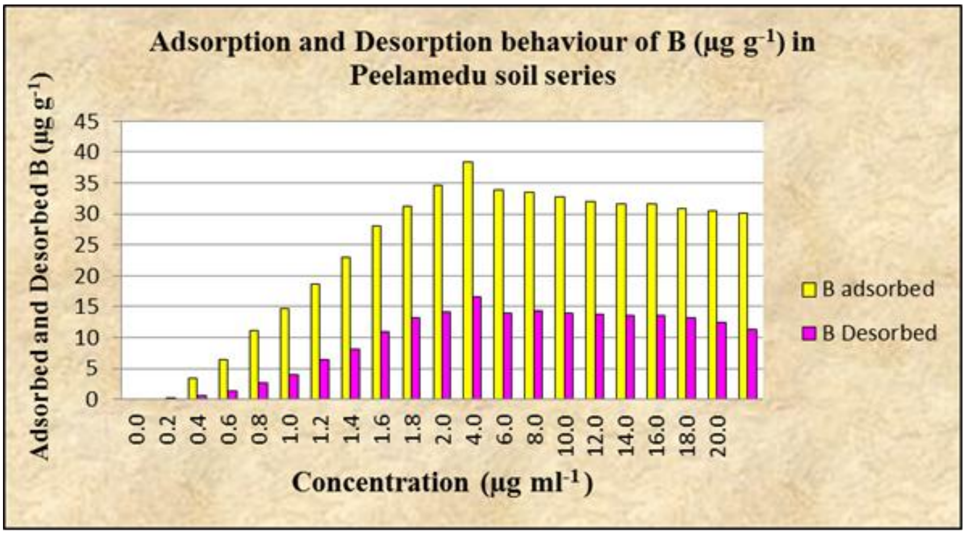

Fig 2: Adsorption and Desorption behaviour of B (µg ml^{-1}) in Peelamedu soil series

Conclusion

Sorption and desorption of B in soil were greatly affected by soil properties, namely, CEC, AEC, Clay, $CaCO_3$, pH and Organic carbon. This implies that retention, mobility and availability of applied B will vary in different soils. Adsorption of B was highest in Peelamedu, followed by Palaviduthi while B desorption was maximum in Palaviduthi comparing to Peelamedu soil series with respect to addition of boron. Boron adsorption parameters may be useful in modeling the plant B uptake from applied pool in different soils. Such information on the fate of applied B would be helpful in optimizing B application rates in different soils.

Table 2: Sorption behaviour of boron in Palaviduthi soil series

B added (µg ml^{-1})	Initial concentration (µg ml^{-1})	Equilibrium concentration (µg ml^{-1}) (C)	B adsorbed (µg g^{-1}) (X/M)	% adsorbed	C/X/M	B Desorbed (µg g^{-1})	% Desorbed
0.00	0.00	0.00	0.00	0.00	0.000	0.30	0.00
10	0.2	0.07	2.60	26.00	0.027	0.82	20.77
20	0.4	0.03	7.42	37.10	0.004	1.61	17.92
30	0.6	0.03	11.38	37.93	0.003	3.19	25.57
40	0.8	0.04	14.60	36.50	0.005	4.89	31.58
50	1.0	0.06	18.76	37.52	0.003	6.39	32.57
60	1.2	0.09	22.20	37.00	0.004	8.43	36.71
70	1.4	0.08	26.40	37.71	0.003	13.42	49.77
80	1.6	0.09	30.20	37.75	0.003	16.67	54.27
90	1.8	0.12	33.60	37.33	0.004	12.68	36.90
100	2.0	0.26	34.72	34.72	0.008	12.30	34.62
200	4.0	2.30	34.10	17.05	0.067	11.11	31.76
300	6.0	4.30	33.98	11.33	0.127	10.86	31.14
400	8.0	6.31	33.84	8.46	0.186	10.61	30.53
500	10.0	8.31	33.78	6.76	0.246	10.43	30.05
600	12.0	10.33	33.44	5.57	0.309	9.84	28.59
700	14.0	12.33	33.32	4.76	0.370	9.63	28.06
800	16.0	14.34	33.28	4.16	0.431	9.49	27.68
900	18.0	16.34	33.22	3.69	0.492	9.01	26.28
1000	20.0	17.35	33.00	5.30	0.327	8.70	15.89

Table 3: Sorption behaviour of boron in Peelamedu soil series

B added (µg ml^{-1})	Initial concentration (µg ml^{-1})	Equilibrium concentration (µg ml^{-1}) (C)	B adsorbed (µg g^{-1}) (X/M)	% adsorbed	C/X/M	B Desorbed (µg g^{-1})	% Desorbed
0.00	0.00	0.000	0.00	0.00	0.000	0.18	0.00
10	0.2	0.028	3.44	34.40	0.008	0.64	13.37
20	0.4	0.080	6.40	32.00	0.013	1.32	17.81
30	0.6	0.040	11.20	37.33	0.004	2.68	22.32
40	0.8	0.060	14.80	37.00	0.004	4.03	26.01
50	1.0	0.070	18.60	37.20	0.004	6.45	33.71
60	1.2	0.050	23.00	38.33	0.002	8.12	34.52
70	1.4	0.001	27.98	39.97	0.000	11.04	38.81
80	1.6	0.040	31.20	39.00	0.001	13.22	41.79
90	1.8	0.070	34.60	38.44	0.002	14.18	40.46
100	2.0	0.080	38.40	38.40	0.002	16.65	42.89
200	4.0	2.307	33.86	16.93	0.068	14.02	40.87
300	6.0	4.327	33.46	11.15	0.129	14.42	42.56
400	8.0	6.360	32.80	8.20	0.194	14	42.13
500	10.0	8.398	32.04	6.41	0.262	13.83	42.60
600	12.0	10.417	31.66	5.28	0.329	13.61	42.42
700	14.0	12.423	31.54	5.26	0.394	13.65	42.71
800	16.0	14.456	30.88	5.15	0.468	13.21	42.20
900	18.0	16.471	30.58	5.10	0.539	12.49	40.26
1000	20.0	17.690	30.11	7.70	0.383	11.32	24.11

Table 4: Langmuir and Freundlich constant for boron adsorption

A). Langmuir constant

Soil series	Langmuir constants		Maximum buffering capacity	Regression equation	R^2
	Sorption maximum (mg kg^{1})	Bonding energy (K)			
Palaviduthi	27.78	5.14	142.78	Y= 0.007+0.036x	0.94**
Peelamedu	35.71	5.60	199.97	Y= 0.005+0.028x	0.96**

B). Freundlich constant

Soil series	Freundlich constant		Regression equation	R^2
	K	1/n		
Palaviduthi	1.12	0.17	Y= 3.052+ 0.170x	0.17*
Peelamedu	1.10	0.07	Y= 3.014+0.078x	0.05*

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