BORON ADSORPTION AND DESORPTION STUDY: CORRELATION BETWEEN SOIL PROPERTIES, AVAILABLE BORON AND THE ADSORPTION ISOTHERM PARAMETERS

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ABSTRACT

Boron is one of the essential micronutrients to almost all the crops. Interest in boron research has been increasing due to its wide role and increasing deficiencies in many parts of the world. Boron adsorption and desorption study helps to have a detailed knowledge on boron availability, its adsorption and retention. Hence, the adsorption study was carried out using five major soil series which covers the major areas of Tamirabharani tract of TamilNadu, India. Varying concentrations of boron were added to the soils and their ability to adsorb as well the desorption with time has been studied. The study on the correlations between available boron and other soil properties were analyzed, which showed a high positive correlation with pH($r^2=0.87$), EC ($r^2=0.84$), Clay($r^2=0.78$), OC ($r^2=0.74$) and a negative correlation with silt($r^2=0.69$) and sand ($r^2=0.78$). The adsorbed Boron were fitted into Freundlich and Langmuir adsorption isotherm equations, which revealed that the Freundlich isotherm was best suited to Boron adsorption than Langmuir adsorption isotherm. The correlation between isotherm parameters of Freundlich and Langmuir with the soil properties were also studied. Boron desorption study revealed that the adsorption showed inverse relationship with boron desorption. Desorption of boron is initially rapid and it is slowed down as time proceeds.

KEYWORDS: Boron, Adsorption, Desorption& Isotherm equations

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1. INTRODUCTION

Boron is one of the essential micronutrients and its essentiality was first proven by Warrington. Various roles of boron in plant system includes sugar transport, protein and carbohydrate metabolism and so on. Boron is found to increase the quality parameters of most of the fruit crops and even reduction in chaffiness in cereal crops like rice and wheat. Since boron has important role in the reproductive growth of many crops, the study of availability is found essential. Boron deficiency has been reported at different parts of the world. Boron is the second most deficient nutrient in India. Nearly 33% of Indian soils are found to be boron deficient, whereas certain parts of the country face boron toxicity due to the high concentration of boron in the irrigation water as well as in the groundwater.

There is a narrow limit between boron deficiency and toxicity, and hence proper study and cautious fertilization program is absolutely essential. Adsorption and desorption studies are used to indicate the availability of any nutrient. Boron availability can also be studied by adsorption and desorption behavior of boron in soil. The study on boron has been lacking in India, especially in Tamil Nadu, and hence attracts a number of scientists to choose this field of study. The present study was conducted at Tamirabharani command area of Tamil Nadu, India where intensive agriculture(rice and

banana) is carried out without the application of micronutrients. The available Boron status of Tamrabharani command area is found to be in deficient status. Boron availability is influenced by number of soil properties like pH, EC, CEC, organic carbon and also the textural composition. Boron availability increases with increase in pH, and it is negatively influenced by sand content of the soil. Boron availability is also influenced by the organic matter, hydroxides of iron and aluminium and calcareousness. Available boron can be estimated by using various extractants like CaCl_2 , hot water, Mechlich's reagents etc. Besides all those, the hot water extracted Azomethane H method of boron estimation was found suitable. Various adsorption isotherm equations have been developed by different scientists, and the popular among them are Freundlich and Langmuir adsorption isotherms. Freundlich isotherm has been found more suitable than the Langmuir adsorption isotherm. The relationship between the isotherm parameters and the soil properties as well as the available boron, has been studied to evaluate the optimum dose of application of boron in relation to soil properties.

2. MATERIALS & METHODS

Figure 1: Map of the Study Area, Showing Series Location and Delineations.

Surface soil samples (10-20 cm depth) were collected from five major soil series of Tamirabarani tract viz., Manakara(Mkr), Killikulam(Kkm), Ezhuthaniyuthu(Etu), Vallanad(Vld) and Sivasubramanyapuram(Ssm). Various soil properties were determined, which includes texture by International pipette method, pH and EC by potentiometric and conductometric methods, CEC by Neutral normal ammonium acetate method and organic carbon by Walkley and Black method and organic

matter content was derived from organic carbon content. Available Boron content in the soil is estimated by using Hot water soluble Azomethane- H method (Gupta, 1967).

Adsorption and desorption behavior of boron in the soil was estimated by employing the method outlined by Elrashidi & O'Connor(1982) with few modifications. Ten grams of soil samples were added with 20ml of 0.01M CaCl₂ solution containing varying concentrations of boron viz., 0, 2.5, 5, 10, 20, 30, 40, 50 ppm of boron as boric acid. The contents were taken in centrifuge tubes and were shaken in wrist action shaker (occasional shaking) for 24 hrs and then centrifuged. Supernatant were collected and 10ml of supernatant was filtered through Whatman No. 40 filter paper and available Boron was estimated by spectrophotometric method using Azomethane H reagent. Amount of Boron adsorbed was identified by calculating the difference between the amount of B in initial solution and that in the final solution after shaking. The adsorption isotherms of Freundlich and Langmuir were used to describe the adsorbed Boron.

Freundlich Equation: $x = ac^{1/n}$

x - amount of adsorbed B (mg kg⁻¹ soil)

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: $x = \frac{kb c}{1 + kc}$

b - maximum monolayer B adsorption capacity (mg kg⁻¹ soil)

k - 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 transforming $c/x = c/b + 1/(kb)$. Maximum buffering capacity (MBC) of soils was also calculated as a product of adsorption maxima and affinity coefficient (Holford and Mattingly, 1976).

Desorption Study

The mixtures were re-suspended, centrifuged and 10ml of supernatant were removed for Boron estimation, at timely intervals. Boron desorbed was calculated as difference between amount of B at each step, and that in the previous step divided by 2 as dilution factor and expressed as percentage of adsorbed B at different added concentrations of Boron.

Statistical Analysis

Correlation analysis between various soil properties and available B is done. The Freundlich and Langmuir adsorption isotherm parameters were determined and their relationship with different soil properties was found out.

3. RESULTS

The initial soil properties of all major soil series were determined. The pH values varied from 6.6 in Sivasubramaniyapuram series to maximum of 7.84 in Killikulam series. The EC values ranged from 0.06 dS/min Sivasubramaniyapuram series to 0.4 dS m⁻¹ in Vallanad series (Table1). The cation exchange capacity of the soils is measured in terms of centi mole proton per kg and it varied from 10.68 to 13.25 (Table1). The textural fractions of all soil series were estimated, and it indicated that the Manakarai,

Killikulam and Sivasubramaniyapuram comes under sandy Clay loam and the series Ezhuthaniyuthu and Vallanad comes under sandy loam texture (Table 1). Available Boron content extracted through hot water and estimated using Azomethane-H method varied from 0.14 mg kg⁻¹ to 0.25 mg/kg (Table 1).

Correlation between the soil properties was determined. Soil pH is positively correlated with other soil properties considered, except the silt and sand percentage. Similarly, the EC values are also positively correlated with other soil properties except that of silt and sand percentage. The CEC of the soils was negatively correlated with sand percent alone. The organic carbon and organic matter content has negative correlation with sand fractions. From the textural class results, the negative correlation among different textural fractions can be visualized. There is a significant positive correlation between pH and EC ($r^2 = 0.97$), pH and Boron ($r^2 = 0.87$), OC and Clay ($r^2 = 0.97$), OM and Clay ($r^2 = 0.96$) and a significant negative correlation between CEC and Sand, and Boron and Sand percent (Table 2).

Available boron content of the soil formed positive correlations with pH, EC, CEC, OC, OM and Clay percent whereas it is negatively correlated with silt and sand percent (Table 2).

Adsorption experiment was carried out with all major soil series by using different concentrations of boron. When no boron was introduced, adsorption ranged from 0.08 mg kg⁻¹ to a maximum of 0.20 mg kg⁻¹. The boron adsorption of soils increased with increasing concentrations. When a maximum of 50 mg kg⁻¹ of boron were introduced, a maximum of 28 mg kg⁻¹ was adsorbed. Percentage of adsorption varied from 48% to a maximum of 84%. The maximum adsorption was observed in Sivasubramaniyapuram series with a average of 64% adsorption of applied boron and minimum adsorption was found with Vallanad series with an average of 57% adsorption. (Figure 3)

Correlation between the considered soil properties and the constants of Freundlich and Langmuir Adsorption isotherm was carried out. Among the Freundlich constants, the Intercept(a) was positively correlated with most properties with the exception of silt and sand percent and the slope(1/n) formed negative correlation with all other properties, except silt percent. The Langmuir constants b, k, b*k formed positive correlations with all other properties except silt and sand percent (Table 4).

The R² values of Freundlich adsorption isotherm were 0.77 to 0.88, which showed a high suitability of application of Freundlich isotherm to boron adsorption (Table 5). The maximum bonding energy of 1.20 (L mg⁻¹) was found with Sivasubramaniyapuram series which showed higher percentage of adsorption earlier. The R² values of Langmuir adsorption isotherm were 0.12 to 0.28, which indicated the lesser suitability of its application to boron adsorption. Based on Langmuir adsorption the adsorption maxima was higher for Ezhuthaniyuthu with 98 (mg g⁻¹) and lower for 72.58 (mg g⁻¹). According to Langmuir isotherm, maximum bonding energy was observed for Killikulam series, which is on par with Sivasubramaniyapuram series. The maximum buffering capacity was found with Sivasubramaniyapuram series followed by Killikulam series (Table 6).

The desorption study revealed that the desorption was minimum with Sivasubramaniyapuram series with an average among time as 9.69 mg kg⁻¹ followed by Killikulam series with 9.73 mg kg⁻¹ and maximum desorption was found with vallanad series with the average of 10.6 mg kg⁻¹ (Table 7). In general, among all the series the desorption was maximum initially, and it slowed down as time proceeds. The series with maximum adsorption showed lower desorption and vice-versa. (Figure 3&4).

Table 1: Soil Properties of Major Soil Series of Tamirabharani Tract of Tamil Nadu Chosen for Adsorption Study

Series Name	pH	Ec (dS ⁻¹ m ⁻¹)	CEC (c mol ⁺ (p ⁻)kg ⁻¹)	Clay %	Silt %	Fine sand %	Coarse sand %	Organic carbon (%)	Organic matter (%)	Soil available Boron ⁻¹ (mg kg ⁻¹)
Manakarai	7.04	0.08	11.63	31.40	12.40	31.70	24.50	0.54	0.936	0.15
Killikulam	7.84	0.19	13.25	32.56	13.03	33.23	21.18	0.53	0.918	0.23
Ezhuthaniyuthu	7.58	0.10	10.10	19.83	13.28	40.53	26.28	0.50	0.866	0.17
Vallanad	7.16	0.40	10.68	19.50	13.20	40.10	25.70	0.59	1.020	0.14
Sivasubramaniyapuram	8.61	0.06	11.30	29.38	15.95	37.03	27.53	0.48	0.831	0.25

Table 2: Relationship Among Different Soil Properties and Soil Available Boron

	pH	EC	CEC	OC	OM	Clay	Silt	Sand	Boron
pH	1								
EC	0.97	1							
CEC	0.385	0.48	1						
OC	0.336	0.256	0.382	1					
OM	0.336	0.256	0.369	0.999	1				
Clay	0.389	0.349	0.602	0.967	0.964	1			
Silt	-0.336	-0.255	0.004	0.863	0.864	-0.752	1		
Sand	-0.044	-0.104	-0.891	-0.279	-0.271	-0.477	-0.216	1	
Boron	0.868	0.839	0.514	0.739	0.732	0.777	-0.687	-0.783	1

Table 3: Amount of Boron Adsorbed with Different Concentration of Added Boron

Boron Concentration (mg L ⁻¹)	Adsorbed Boron (mg kg ⁻¹)				
	Manakarai	Killikulam	Ezhuthaniyuthu	Vallanad	Sivasubramaniyapuram
0	0.10	0.18	0.12	0.08	0.20
2.5	1.30	1.33	1.26	1.24	1.20
5.0	3.21	3.25	3.25	3.31	3.47
10.0	7.23	7.37	5.17	5.22	8.37
20.0	15.1	14.9	15.0	14.8	14.9
30.0	18.1	17.9	16.9	16.8	18.5
40.0	22.6	22.4	21.3	21.0	23.1
50.0	27.2	26.9	25.6	25.3	27.8

Table 4: Correlation coefficients (r-values) between Adsorption Equation

Parameters and Soil Characteristics

Soil properties	Freundlich constants		Langmuir Constants		
	A	1/n	b	k	bxk
pH	0.45	-0.54	0.49	0.48	0.52
EC	0.4	-0.51	0.51	0.57	0.58
CEC	0.5	-0.19	0.88	0.97	0.94
OC	0.98	-0.82	0.78	0.52	0.65
OM	0.97	-0.82	0.77	0.5	0.64
Clay	0.98	-0.77	0.91	0.71	0.82
Silt	-0.85	0.99	-0.46	-0.21	-0.33
Sand	-0.31	-0.13	-0.78	-0.72	-0.77

Table 5: Freundlich Adsorption Isotherm Constants for Major Soil Series of Tamirabharani Tract

Series name	R ²	Intercept (a)	Slope(b)	Bonding Energy (L mg ⁻¹)
Manakarai	0.88	0.283	0.920	1.09
Killikulam	0.88	0.304	0.895	1.12
Ezhuthaniyuthu	0.88	0.200	0.921	1.09
Vallanad	0.88	0.202	0.913	1.10
Sivasubramaniyapuram	0.77	0.395	0.830	1.20

Table 6: Langmuir Adsorption Isotherm Constants for Major Soil Series of Tamirabharani Tract

Series Name	R ²	Slope (1/n)	Intercept (a)	Adsorption Maxima (mg g ⁻¹) (b)	Bonding Energy (L mg ⁻¹) (k)	Maximum Buffering Capacity
Manakarai	0.2	0.530	0.012	85.02	0.022	1.89
Killikulam	0.28	0.508	0.014	72.58	0.027	1.97
Ezhuthaniyuthu	0.14	0.670	0.010	98.09	0.015	1.49
Vallanad	0.16	0.671	0.011	90.62	0.016	1.49
Sivasubramaniyapuram	0.12	0.496	0.012	81.82	0.025	2.02

Table 7: Amount of B desorbed from the Soils in 0.01M CaCl₂ Solution with respect to time in Major Soil Series of Tamirabharani Tract

Time (hours)	Boron desorbed (mg kg ⁻¹)				
	Manakari	Killikulam	Ezhuthaniyuthu	Vallanad	Sivasubramaiyapuram
1	8.90	8.60	9.15	9.22	8.08
2	9.21	9.11	10.01	10.32	9.60
4	10.40	10.01	10.98	11.06	10.21
6	10.60	10.42	11.02	11.12	10.26
8	10.80	10.53	11.18	11.19	10.31

Figure 2: Freundlich Adsorption Isotherm for various Soil Series.

Figure 3: Langmuir Adsorption Isotherm for various Soil Series.

Figure 4: Average Percentage of Adsorption by various Soil Series.

4. DISCUSSIONS

Sand percent of the soil formed negative correlation with all of the soil properties analyzed, as higher sand content has a negative impact on most soil properties. The positive correlation obtained between pH and OC has been supported by Kundu et. al., (2016).

The Soil pH showed a significant positive correlation ($r^2 = 0.86$) with available boron content of soil, and this result is supported by many workers of boron adsorption which includes Kumari et. al., (2017) Mathur & Sudan, (2011), Sarkar et. al., (2008), Elrashidi & O'Connor, (1982), Tili et. al., 2019, Sarkar et. al., 2008, whereas Tili et. al., (2019) concluded that available Boron is positively correlated with pH upto a pH of 9 and decreases thereafter. On a contrary, certain authors like Hara & Tamai, (2012), Arora & Chahal (2005) and Kundu et. al., (2016) indicated negative correlation between available Boron and soil pH. The

obtained significant positive correlation between EC and Boron is in line with the conclusions of Arora & Chahal, Tili et. al., (2019) and Mathur & Sudan (2011). This may be due to the fact that increasing salt concentrations of soil increases boron availability. Clay content in soil has a major effect on available Boron. A high positive correlation ($r^2 = 0.78$) between clay content and available boron was obtained. This conclusion may be attributed to the greater capacity of clay fractions to retain and release boron into soil solution. This positive relationship has been proved by Hara & Tamai, Tili et. al., and Shorrocks.

The Cation exchange capacity increases the boron availability and hence a positive relationship has been obtained ($r^2 = 0.51$), and this is supported by Arora & Chahal. Increase in organic carbon increased the availability of most of the soil properties and also with boron. This is proven by high positive correlation ($r^2 = 0.73$) between organic carbon and available Boron. This is evident with the results of various workers like Mathur & Sudan (2011), Kundu et. al., Sarkar et. al., Raza et. al., and Elrashidi & O'Connor. A negative correlation between silt and boron content was obtained which is in contrary with the results of Tili et. al., who concluded positive relationship between silt and available Boron. Sand percentage had a negative relationship with other soil properties especially with available Boron ($r^2 = 0.78$).

Boron adsorption formed a positive relationship with pH and similar results were obtained with Tili et. al., and Datta & Bhadoria. High organic carbon content showed higher adsorption of boron. Boron adsorption increases with increasing cation exchange capacity. Adsorption of boron increases with clay content as adsorption increases with increasing fineness of soil fractions and decreases with increasing sand content. This is in accordance with the results obtained by Tili et. al., and Datta & Bhadoria. The adsorption of boron increased with increasing concentrations of added boron. Boron desorption is in inverse relation with adsorption of boron. Moreover boron desorption forms positive correlation with Organic carbon as well as CEC.

The adsorption isotherm parameters like Freundlich 'a', Freundlich '1/n', Langmuir 'b, k, b*k' were correlated with soil properties. Freundlich 'a' formed positive correlation with all other properties except silt and boron. The positive correlation of Freundlich 'a' with clay and CEC has been proved by Chaudhary & Shukla (2004). Freundlich '1/n' formed negative correlation with all other properties except silt percentage. The negative correlation between organic carbon and 1/n is in contrary with Chaudhary & Shukla (2004), who concluded a positive relationship. All the isotherm parameters formed positive correlations with other soil properties except with silt and sand percentage. This is in accordance with Chaudhary & Shukla (2004), who showed a positive relationship between Langmuir adsorption isotherm parameters and CEC. Freundlich isotherm parameters formed higher r^2 values (0.77 to 0.88) with the studied soil series than Langmuir parameters (0.12 to 0.28). This proves that Freundlich adsorption is best suited for boron adsorption than Langmuir adsorption isotherm. This is also in line with the conclusions of Chaudhary & Shukla (2004).

5. CONCLUSIONS

Soil available boron (Hot water soluble) content is positively correlated with certain soil parameters like pH, EC, OC, Clay and CEC, whereas it is negatively correlated with silt and sand percentage. Boron adsorption increased with increasing concentrations of boron upto 50ppm, and it also depends on certain parameters like pH EC CEC Clay etc., Desorption of boron is rapid initially, and it slows down with time. The Freundlich adsorption isotherm is best suited to explain boron adsorption than Langmuir adsorption isotherm.

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