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Boron Adsorption in Soils with Different Characteristics

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This study was conducted to investigate boron adsorption characteristics of ten topsoils having different properties and the relationship between these characteristics and some physical and chemical properties of soils. Boron adsorption data in nine (except soil 6) of the ten soils fit to the linear Langmuir adsorption isotherm. On the other hand, boron adsorption was described with Freundlich isotherm over the entire boron concentration ranges. According to these results, Langmuir and Freundlich adsorption isotherms could be applied to determine the boron adsorption maximum (b) and capacity (K_f). The boron adsorption maximum (b) and capacity (K_f) were found to be greater for soils high in clay and lime on the soils with basic pH. Stepwise regression models performed predicted 98.6 and 94.0% of the variance in Langmuir b and Freundlich K_f values, respectively. From the correlation analyses results, it is possible to suggest that soil pH, clay, sand and lime contents are the most influential soil properties on boron adsorption and leaching in the studied region.

Key Words: Soil, Boron adsorption, Langmuir and Freundlich isotherms.

INTRODUCTION

Boron is an essential micronutrient for plant nutrition. Boron concentration ranges between deficiency and toxicity symptoms are narrow and both boron deficiency and toxicity levels cause yield decrement[1]. Boron deficiencies occur in coarse textured and acid soils in humid regions because of boron leaching from the soils[2,3]. Liming of acid soils in humid regions can decrease plant available boron concentration for increasing boron adsorption[3].

Boron distributions between solid and solution phases depend on boron adsorbability and desorbability characteristics of the different soils[1]. Boron availability to plants and adsorption in soils are affected by several factors such as soil pH[4], texture, moisture and temperature[5,6], clay minerals[1,7], calcium carbonate[4,8], organic matter[3,4] and oxides[3,9].

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The distributions of boron between solid and solution phases in soils have been described by using Langmuir and Freundlich isotherms[8, 10, 11]. A better conformity was described with Freundlich isotherms in a wide range of boron concentration, but certain deviations from Langmuir equation at higher boron concentrations occurred in many researches[11, 12].

Boron leaching was greater in the study area due to higher rainfall (1197 mm), and boron deficiency in plants was the common problem. Therefore, determining boron adsorption characteristics of the soils was crucial for boron management in the soils.

The aim of this study was to investigate (i) boron adsorption characteristics of ten top soils with different properties selected from Ordu province by using Langmuir and Freundlich adsorption isotherms and (ii) the relationship between these characteristics and some physical and chemical properties of soils.

EXPERIMENTAL

Soil samples were taken from ten topsoils (0–20 cm) with different properties in middle Black Sea region (Ordu province: 400°18′–410°08′ N, 360°52′–380°12′ E) of Turkey[13] where the mean annual precipitation is 1196.6 mm and air temperature 13.9°C. The soils were classified as Typic Haplustoll, Typic Argiustoll and Lithic Haplustoll according to Soil Survey Staff[14]. Soil samples were air-dried, sieved using 2 mm mesh size stainless steel sieve and stored in polyethylene bags until analyzed.

All the plastic and glassware were cleaned by soaking in dilute HCl (1 + 9) and were rinsed with deionized water prior to use. Particle size distributions of the soil samples were determined by using the hydrometer method[15]. Soil pH was determined in a 1 : 2.5 soil : water (w/v) extract[16] and organic matter (OM) content using the Walkley-Black method[17]. Carbonates were measured by calcimeter method[18]. Cation exchange capacity (CEC) was determined by saturating the soil samples with sodium acetate[19].

The sieved three-gram of the soil samples were placed in 25 mL polypropylene centrifuge tubes, and 15 mL of 0.01 M $CaCl_2$ solution containing different concentrations of boron (ranging from 0, 2, 4, 8, 16, 32, 64, 128 $\mu g\ mL^{-1}$) were added to each centrifuge tubes. The suspensions were equilibrated by shaking for 24 h on a reciprocating shaker at 24 ± 2°C. After the centrifuge of the suspensions, the solutions were filtered through Whatman no. 42 filter paper. The boron in the filtrates was analyzed by he azomethine-H method[20] using Shimadzu UV-1208 Model spectrophotometer. The amounts of boron adsorobed by the soils were calculated by the mass balance equation (eqn. 1).

$$x/m = (C_o - C)\cdot V/W \qquad (1)$$

where x/m is the amount of boron adsorbed per unit mass of soil ($\mu g\ g^{-1}$); C_o is boron concentration in the initial stage ($\mu g\ mL^{-1}$); C is boron equilibrium concentration ($\mu g\ mL^{-1}$); V is the volume of solution added (mL) and W is the air-dried mass of soil (g).

Boron adsorbed by the soils was calculated as the difference between the initial and equilibrium boron concentrations. To describe boron adsorption characteristics of the soils, the linear form of Langmiur isotherm [eqn. (2)] and the logarithmic form of the Freundlich isotherm [eqn. (3)] were used.

$$C/(x/m) = 1/kb + C/b \tag{2}$$

where b is Langmuir adsorption maximum or adsorption capacity ($\mu g\ g^{-1}$) and k is the adsorption energy coefficient ($mL\ \mu g^{-1}$).

$$\log x/m = \log K_f + 1/n \log C \tag{3}$$

where K_f is the measure of a soil's ability to retain a solute or adsorption capacity ($\mu g\ g^{-1}$), 1/n is indicative of its affinity for the solute.

The Langmuir and Freundlich equation of each line was defined by regression analysis[21]. Correlations between Langmuir and Freundlich parameters (b, k and K_f, 1/n) and soil properties were calculated by using Pearson method with Minitab computer program.

RESULTS AND DISCUSSION

Some physical, chemical and mineralogical properties of the studied soils are given in Table-1. Soil lime, clay and organic matter contents ranged from 0.10 to 1.65%, 14 to 46% and 1.53 to 5.06%, respectively. Soil pH values varied between 4.15 and 7.75. These results provide evidence that the studied soils had very different physical and chemical properties. The higher plant-available boron concentrations were found in soils 2, 5 and 7 with greater lime, clay contents and pH values than those of the other soils (Table-2). Moreover, there was significant correlation between plant-available boron concentrations and soil variables such as lime ($p < 0.01$), clay ($p < 0.05$) and pH ($p < 0.05$) (Table-3). These findings are in agreement with results reported in literature[3, 4].

TABLE-1

SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE EXPERIMENTAL SOILS

Soil name and no.		Sand (%)	Loam (%)	Clay (%)	pH (1 : 2.5)	$CaCO_3$ (%)	O.M. (%)	CEC ($cmol\ kg^{-1}$)	Boron ($\mu g\ mL^{-1}$)
Uzundere	1	51	29	20	6.75	0.66	2.30	32	0.35
Çatalpinar	2	44	17	39	7.30	0.47	1.53	35	0.61
Gurgentepe	3	45	34	21	4.40	0.10	4.46	21	0.29
Bolluk	4	45	27	28	6.10	0.12	2.02	45	0.10
Çaltepe	5	23	31	46	7.70	1.65	5.06	55	1.60
Şeyhler	6	38	31	31	5.50	0.38	2.05	21	0.15
Durak	7	42	26	32	7.75	1.33	1.92	46	0.52
Sarihalil	8	36	30	34	4.50	0.40	2.42	40	0.06
Günören	9	57	29	14	4.15	0.24	4.54	28	0.01
Alinca	10	49	29	22	5.55	0.36	4.37	33	0.05

Soil subgroups: 1, 3, 4, 6: Typic Haplustoll; 2, 5, 7: Typic Argiustoll; 8, 9, 10: Lithic Haplustoll.
(Source: Partly taken from ref. 22)

Boron adsorption in nine of the ten soil samples used fit to Langmuir adsorption isotherm over the entire concentration ranges (Table-2, Fig. 1). Langmuir parameters for the soil 6 were not calculated because of not fitting to linear Langmuir isotherm. On the other hand, boron adsorption data also conformed to the linearized Freundlich adsorption isotherm over the entire boron concentration ranges for all the soils (Fig. 1). Many investigators pointed out that boron adsorption in soils could be described by Langmuir and Freundlich isotherms$^{4, 7, 11, 23}$. The relationship between C/x/m *vs.* C and log x/m *vs.* log C were found significant for the soils investigated (Table-2). Langmuir parameters (b and k) and Freundlich parameters (K_f and 1/n) for B adsorption were given in Table-2. Adsorption maximum (Langmuir b) values varied from 25.5 to 76.9 µg mL^{-1}. The higher b values were found in soils 2, 5 and 7 having the greater lime, clay contents and pH values than those of the other soils.

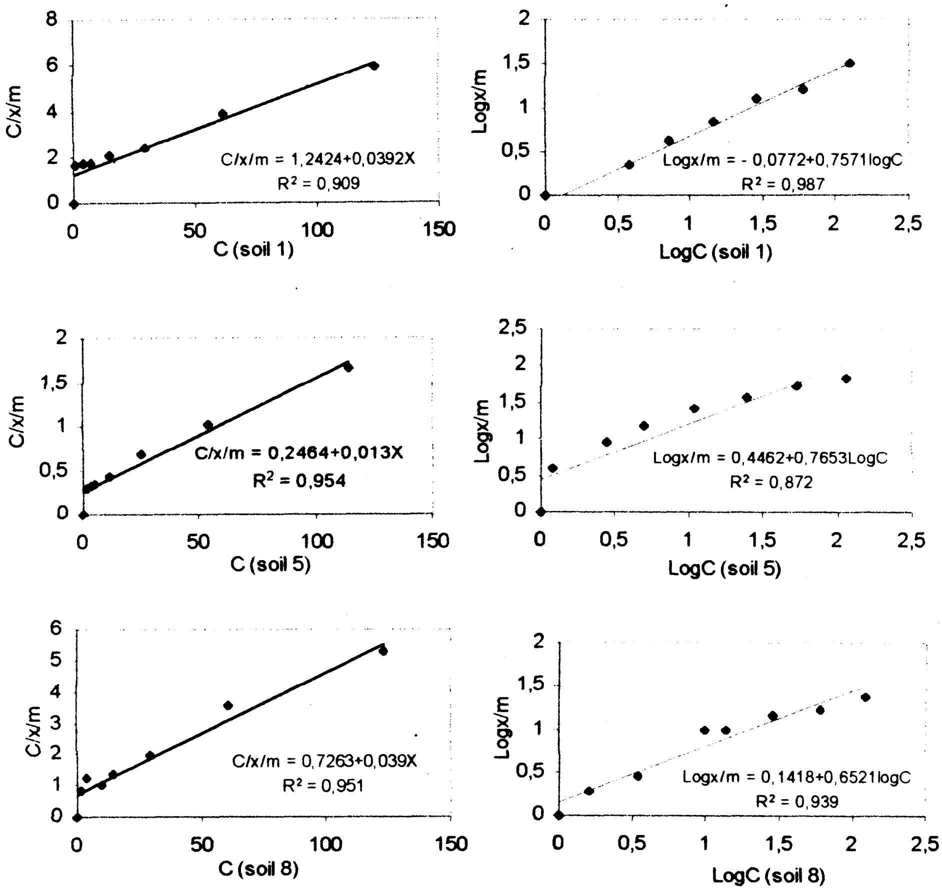

Fig. 1. Langmuir and Freundlich boron adsorption isotherms of the soils 1, 5 and 8.

TABLE-2
LANGMUIR AND FREUNDLICH PARAMETERS FOR BORON ADSORPTION OF ALL THE SOILS

Soil No.	Langmiur b	Parameters k	Freundlich Parameters			
			r	K_f	1/n	r
1	25.5	0.031	0.945†	0.84	0.757	0.993†
2	57.5	0.056	0.978†	2.37	0.729	0.947†
3	35.2	0.028	0.931†	1.16	0.702	0.994†
4	26.8	0.042	0.934†	1.34	0.635	0.981†
5	76.9	0.053	0.976†	2.81	0.765	0.934†
6	77.5	0.010	0.552^{ns}	0.87	0.843	0.982†
7	42.7	0.051	0.974†	1.76	0.723	0.960†
8	25.6	0.054	0.975†	1.39	0.652	0.969†
9	27.6	0.045	0.964†	1.07	0.725	0.972†
10	35.7	0.028	0.895*	1.06	0.723	0.990†

r: Correlation coefficient (correlation of C/x/m *vs.* C and log x/m *vs.* log C)

* Significant at $p < 0.01$,

† Significant at $p < 0.001$. ns: Not significant.

There was positive significant correlation between b values and lime ($p < 0.05$), clay ($p < 0.01$) contents and pH value ($p < 0.05$), but negative correlation ($p < 0.05$) between b values and the sand contents (Table-3). According to these results, soil pH, lime and clay contents play a major role in the B adsorption maximum in the studied soils. Boron adsorption maximum values were significantly positively correlated with pH[23, 24], lime[8] and clay contents[7, 25, 26].

TABLE-3
CORRELATION COEFFICIENT OF SOIL PROPERTIES RELATING TO ADSORPTION PARAMETERS

		Sand	Loam	Clay	pH	Lime	O.M.	CEC	B
Langmuir	b	–0.714*	–0.246	0.788**	0.654*	0.706*	0.246	0.540	0.925†
	k	–0.048	0.192	0.728*	–0.201	–0.108	–0.176	0.312	–0.249
Freundlich	K_f	–0.664*	–0.430	0.840**	0.655*	0.673*	0.0847	0.713*	0.854†
	1/n	–0.175	0.113	0.115	0.243	0.313	0.0536	–0.330	0.290
	B	–0.727*	–0.074	0.733*	0.703*	0.823†	0.270	0.620	1.000

* Significant at $p < 0.05$. † Significant at $p < 0.01$,

O.M.: Organic matter %, CEC: Cation exchange capacity, B: Plant available B.

Bound energy coefficent (Langmuir k) values were ranged from 0.028 to 0.056 (mL μg^{-1}), and any significant correlation was not obtained between k values and soil properties (except clay). This may be attributed to the multiple affecting factors or the presence of multiple adsorption sites such as clay, lime and organic matter contents.

Freundlich adsorption capacity (K_f) and affinity coefficient (1/n) were found between 0.87–2.81 and 0.635–0.843, respectively. Statistically significant correlations were observed between K_f values and clay ($p < 0.01$), lime ($p < 0.05$) contents and CEC ($p < 0.05$), whereas sand content negatively correlated ($p < 0.05$) with K_f value. Correlation analyses indicated that high pH, clay and lime contents seem to be responsible for the boron adsorption capacity as also reported for the Langmuir b values. It is pointed out that clay content, organic matter, CEC and specific surface have significant relation with the Freundlich K_f values, and fine-textured soils exhibited higher K_f values than coarse-textured soils[4, 27]. A similar finding for K_f values in soils has been also reported previously[11, 28]. Based on our results, there is no significant relationship between organic matter and K_f and b values, and this could be attributed to the large difference in organic matter contents (1.53–5.06%) of the soils or effect of soil organic matter on boron adsorption masked by the action of soil variables. The effect of organic matter on boron adsorption and desorption in soils has not been still clearly understood and there are opposite research results on this subject[10]. The lack of significant correlation between 1/n values and soil properties may be due to very different physical and chemical properties of the soils studied. Therfore, the lack of relationships between organic matter and Langmuir and Freundlich parameters does not mean that the organic matter does not affect boron sorption. As seen below, the best stepwise model predicting b and K_f contains soil organic matter content.

A stepwise selection procedure was performed to evaluate the interactions between various variables and to find empirical equation, which best predicits b and K_f values using soil pH, CEC, clay, sand, loam, lime and O.M. contents. To select the best model, the maximum determination coefficient (R^2) improvement technique and the highest probability levels (p) were used. The best models for the Langmuir b contain a combination of pH, CEC, clay, sand and OM contents as independent variables (Table-4).

The CEC, clay, sand and OM contents appeared as the independent variables in Freundlich K_f prediction models. Stepwise regression analysis of these variables yielded R^2 values of 0.986 and 0.940% to predict b and K_f values, respectively. The adding of the other variables into regression equations had only minor improvement in the variation for predicting values of b and K_f. The stepwise regression equations including soil variables in the best models accounted for 98.6% (Langmuir b) and 94.0 (Freundlich K_f) variation in boron sorption by the soils. According to these results, boron adsorption capacity (Langmuir b and Freundlich K_f) can be predicted from multiple stepwise regression equation, when the pH, CEC, clay, sand and OM contents of soils are known. Stepwise regression analyses suggest that interactions between various soil variables have a higher effect on the behaviour of boron in the soils compared with the effect of individed soil variables. Therefore, a combination of the variables including in the best models can be evaluated as the important factors responsible for boron sorption and leaching reactions on the soils studied as also reported in literature[2, 11, 28].

TABLE-4
STEPWISE REGRESSION EQUATIONS RELATING LANGMUIR b AND FREUNDLICH K_f TO SOIL PROPERTIES

Stepwise regression equations	R^2	P
$b = 0.922 + 1.35$ clay %	0.622	0.012*
$b = -19.6 + 1.49$ clay % $+ 5.2$ OM %	0.787	0.010†
$b = -44.0 + 1.0$ clay % $+ 6.7$ OM % $+ 5.7$ pH	0.901	0.006†
$b = -142.2 + 2.3$ clay % $+ 9.3$ OM % $+ 4.7$ pH $+ 1.34$ sand %	0.962	0.004†
$b = -112.7 + 2.2$ clay % $+ 8.8$ OM % $+ 6.1$ pH $+ 0.97$ sand % $- 0.48$ CEC **(the best model)**	0.986	0.006†
$b = -112.4 + 2.3$ clay % $+ 8.7$ OM % $+ 5.6$ pH $+ 1.0$ sand % -0.51 CEC $+ 11.8$ lime %	0.987	0.040*
$K_f = -0.17 + 0.057$ clay %	0.705	0.002†
$K_f = -0.7 + 0.06$ clay % $+ 0.13$ OM %	0.775	0.005†
$K_f = -5.9 + 0.12$ clay % $+ 0.26$ OM % $+ 0.07$ sand %	0.922	0.001†
$K_f = -5.8 + 0.12$ clay % $+ 0.24$ OM % $+ 0.067$ sand % $+ 0.01$ CEC **(the best model)**	0.940	0.003†
$K_f = -5.7 + 0.11$ clay % $+ 0.23$ OM % $+ 0.068$ sand % $+ 0.008$ CEC $+ 0.12$ lime %	0.944	0.013*
$K_f = 0.57 + 0.11$ clay % $+ 0.24$ OM % $+ 0.066$ sand % $+ 0.008$ CEC $+ 0.08$ lime % $+ 0.02$ pH	0.944	0.054^{ns}

* Significant at $p < 0.05$. † Significant at $p < 0.01$. ns: Not significant.

O.M: Organic matter %. CEC: Cation exchange capacity.

Conclusion

Boron adsorption data fit both Freundlich and Langmuir (except for soil 6) adsorption isotherms in the soils investigated. Soil pH, clay and lime contents were significantly positively correlated with B adsorption parameters (b and K_f), whereas sand content had a negative correlation. It is possible to suggest that soil variables in the best models play an important role in the behaviour of B in the soils. Boron adsorption maximum (b) and capacity (K_f) could be predicted from the best stepwise regression equation and B status and behaviour in the soils would also be evaluated by using the b and K_f values predicted in the soils investigated.

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