RESEARCH

Effect of pH on boron adsorption in some soils of Paraná, Brazil

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Temporary B deficiency can be triggered by liming of acid soils because of increased B adsorption at higher soil pH. Plants respond directly to the activity of B in soil solution and only indirectly to B adsorbed on soil constituents. Because the range between deficient and toxic B concentration is relatively narrow, this poses difficulty in maintaining appropriate B levels in soil solution. Thus, knowledge of the chemical behavior of B in the soil is particularly important. The present study investigated the effect of soil pH on B adsorption in four soils of Paraná State, and to correlate these values with the physical and chemical properties of the soils. Surface samples were taken from a Rhodic Hapludox, Arenic Hapludalf, Arenic Hapludult, and one Typic Usthorthent. To evaluate the effect of pH on B adsorption, subsamples soil received the application of increasing rates of calcium carbonate. Boron adsorption was accomplished by shaking 2.0 g soil, for 24 h, with 20 mL of 0.01 mol L^{-1} NaCl solution containing different concentrations (0.0, 0.1, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0, and 4.0 mg B L^{-1}). Sorption was fitted to non-linear form of the Langmuir adsorption isotherm. Boron adsorption increased as concentration increased. Boron adsorption was dependent on soil pH, increasing as a function of pH in the range between 4.6 and 7.4, although the bonding energy has decreased. Maximum adsorption capacity (MAC) of B was observed in the Arenic Hapludalf (49.8 mg B kg^{-1} soil) followed by Arenic Hapludult (22.5 mg kg^{-1}), Rhodic Hapludox (17.4 mg kg^{-1}), and Typic Usthorthent (7.0 mg kg^{-1}). The organic matter content, clay content, and aluminum oxide content (Al$_2$O$_3$) were the soils properties that affecting the B adsorption on Paraná soils.

Key words: Langmuir isotherm, maximum adsorption capacity, liming, boron fertilizer.

INTRODUCTION

In tropical conditions, B deficiency in soil poses a serious limitation to the development of several economic-interest crops, due to natural soil's low fertility, removal by crops and inappropriate or excessive use of acidity corrective that contribute to its insolubilization. It should be noted also that the adequate management of B in soil-plant system is usually difficult because the range between B deficiency and toxicity is relatively narrow. Thus, knowledge of the chemical behavior of B in the soil is particularly important.

The availability of B depends upon adsorption-desorption processes, which are influenced by various physicochemical properties of soils (Arora and Chahal, 2005). The extent of B adsorption in soils depends on solution pH, soil texture and mineral composition (Communar and Keren, 2006). Of these, the soil pH has been reported as the main factor affecting the B adsorption in the soil (Saltali et al., 2005; Soares et al., 2008), mainly by influencing in the control of the predominant B species in solution and attributes related to its adsorption such as charge balance on colloids surface. Other factors, such as the clay content, Al and Fe (hydr)oxides, clay minerals, calcium carbonate and organic matter of soil also influence B sorption in agricultural soils (Arora et al., 2002; Goldberg et al., 2005; Arora and Chahal, 2007; Goldberg et al., 2008; Shafiq et al., 2008; Arora and Chahal, 2010).

Boron adsorption increases with increasing pH and reaches a maximum around pH 9.0 and decreases with further increase in pH (Goldberg, 1997). The maximum development of adsorption sites occurs at a pH equivalent to the dissociation constant (pKa) of boric acid, approximately 9.2. At below pH 7.0, B(OH)$_3^0$ predominated, but because the affinity of the clay from this species is relatively low, the amount of adsorption is small. As the pH increased, the B(OH)$_4^-$ concentration increased rapidly. The amount of adsorbed B increased rapidly because of the relatively strong affinity of the clays. Further, increase in pH resulted in an enhanced OH$^-$ concentration relative B(OH)$_4^-$, and B adsorption decreased rapidly due to the competition of OH$^-$ for the adsorption sites (Goldberg et al., 2005).

The agricultural practice that is most often used to raise soil pH is liming. Thus, it is expected that the acidity correction in soil until pH 6.0, as recommended for most crops, increases the B adsorption in the soil. In clayey

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Rhodic Hapludox of Mato Grosso State, Brazil, Rosolem and Bíscaro (2007) found that the application of 9.0 Mg ha^{-1} lime incorporated in the 0-20 cm layer increased seven times the maximum amount of adsorbed B in the first year.

Various models can describe adsorption reactions. Boron adsorption by soils has been described using empirical models such as Langmuir and Freundlich adsorption isotherm equations (Goldberg, 2003). Both of these equations contain two adjustable parameters and assume that adsorption occurs at constant solution pH. A sorption isotherm takes into account intensity, quantity and capacity factors, which are important for predicting the amount of soil nutrient required for maximum plant growth. As the amounts of nutrients required by a soil are affected by clay minerals, cationic exchange capacity, organic matter, soil texture and other properties, which need not to be measured in order to determine soil requirements using sorption technique (Goldberg, 1997).

The present study investigated the effect of pH on B adsorption in different soils of the western region of Paraná State, and to correlate these values with some physical and chemical properties of the soils.

MATERIALS AND METHODS

Surface samples (0-0.2 m) from four representative soils of the western region of Paraná State were selected for B adsorption studies (Table 1). The physical and chemical properties of the soils were determined by adopting standard procedures, and some characteristics are shown in Table 2. Soil pH was measured potentiometrically in

Table 1. Classification of the soils.

Soil	Brazilian soil classification[†]	Soil taxonomy[††]
1	Red Latosol	Rhodic Hapludox
2	Red Nitosol	Arenic Hapludalf
3	Red-Yellow Argisol	Arenic Hapludult
4	Regolithic Neosol	Typic Usthorthent

[†]According to Embrapa (2006).
[††]USDA Soil Taxonomy (Soil Survey Staff, 2010).

Table 2. Some physical and chemical properties of the soils.

	Soils			
Soil properties	Hapludox	Hapludalf	Hapludult	Usthorthent
pH H_2O (1:2.5)	4.6	4.7	4.9	5.1
ΔpH[†]	-0.4	-0.6	-0.7	-1.9
Clay, g kg^{-1}	580.0	740.0	720.0	510.0
Sand, g kg^{-1}	210.0	90.0	160.0	190.0
Organic matter, g kg^{-1}	22.4	32.5	9.6	15.2
Soluble B, mg kg^{-1}	0.2	0.4	0.4	0.5
Exchangeable Al, $mmol_c$ kg^{-1}	2.0	3.0	2.5	0.0
ECEC, $mmol_c$ kg^{-1}[††]	78.8	130.0	98.0	130.0
SiO_2, g kg^{-1}	210.0	234.0	206.0	261.0
Fe_2O_3, g kg^{-1}	170.0	198.0	162.0	196.0
Al_2O_3, g kg^{-1}	180.0	223.0	197.0	153.0
Ki[†††]	2.0	1.8	1.7	2.9

[†]$\Delta pH = pH$ KCl - pH H_2O used as an estimate of the charge balance.
[††]ECEC: Effective cation exchange capacity.
[†††]Ki: Weathering index calculated by the molar ratio SiO_2/Al_2O_3.

H_2O and 1 mol L^{-1} KCl suspensions (1:2.5 soil:solution ratio), and the difference $\Delta pH = pH$ KCl – pH H_2O was used to estimate the sign of the net charge (Mekaru and Uehara, 1972). Organic matter was quantified by oxidation with potassium dichromate in the presence of sulfuric acid, followed by titration with ammonium Fe(II) sulfate (Embrapa, 1997). Boron was extracted with water heated in a domestic microwave oven (power 700 W for 4 min and then in the power 490W for 5 min) and determined by spectrophotometry with azomethine-H (van Raij et al., 2001). Basic cations (Ca^{2+}, Mg^{2+}, and K^+) were extracted by ionic exchange resin in a soil:solution ratio of 1:20, and shaken for 16 h on a reciprocating shaker at 120 oscillations min^{-1} (van Raij et al., 2001) and determined by atomic absorption spectrophotometry. Exchangeable Al was extracted by 1 mol L^{-1} KCl solution and determined by titration with 0.025 mol L^{-1} ammonium hydroxide. Effective cationic exchange capacity (ECEC) was estimated by the summation method (ECEC = Ca + Mg + K + Al). The Fe and Al contents, associated to the secondary minerals, were extracted using a 9 mol L^{-1} H_2SO_4 solution (1:20 soil:solution ratio), and Si was removed with NaOH from the residue of the acid attack. Contents of Fe and Al were determined using flame atomic absorption spectrophotometry and Si was quantified by gravimetry, and expressed in the form of oxides to calculate the weathering index by the molar ratio Ki = (%SiO_2/60)/(%Al_2O_3/102). The particle size analysis was performed by the pipette method (Embrapa, 1997), based on decantation speed of different soil particles after dispersion in 0.015 mol L^{-1} $(NaPO_3)_6$ NaO/1 mol L^{-1} NaOH by overnight shaking.

To evaluate the effect of soil pH on B adsorption, four subsamples received the application of 0, 1, 2, 4, and 8 Mg ha^{-1} calcium carbonate. These subsamples were incubated at field capacity until constant pH for 40 d. After this period, soil samples were air-dried, crushed, and sieved to pass a 2-mm mesh screen. Soil pH was determined with an electrode on a 1:2.5 (w/v) soil-to-water solution.

Adsorption experiments were carried out in triplicate using a batch technique. About 2.0 g of soil was shaken, in polyethylene tubes, for 24 h at 25 ± 1 ºC, with 20 mL 0.01 mol L^{-1} NaCl solution containing B concentrations of 0.0, 0.1, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0, and 4.0 mg L^{-1} as boric acid, equivalent to 0, 1, 2, 4, 8, 12, 16, 20, and 40 mg B kg^{-1} soil, respectively. After shaking, the soil solution was filtered through Whatman nr 42 filter paper (Soares and Casagrande, 2009). Boron concentration in the filtrate was determined by the Azomethine-H method using a spectrophotometer at 420 nm wave length as described by van Raij et al. (2001).

The amount of B adsorbed, $[B]_{ads}$, and the adsorption percentage, $\%B_{ads}$, were calculated by the following ratios, respectively:

$$[B]_{ads} = [(C_0 - C_{eq})V]/m \qquad [1]$$

$$\%B_{ads} = [(C_0 - C_{eq})/C_0] \times 100 \qquad [2]$$

where $[B]_{ads}$ is the amount of adsorbed B after equilibrium (mg B kg^{-1} soil); C_0 and C_{eq} are the initial added and equilibrium concentrations (mg B L^{-1}), respectively; V = solution volume (mL); and m = mass of the soil sample (g). The amount of B originally present in soil samples (Table 2), although small, was discounted in the calculation of the amount of adsorbed B.

Adsorption isotherms ($[B]_{ads}$ vs. C_{eq}) were fitted from the experimental results, and the B adsorption was compared with that estimated by the non-linear form of the Langmuir isotherm:

$$B_{ads} = (KC_{eq}MAC)/(1 + KC_{eq}) \qquad [3]$$

where K is the constant related to bonding energy of B to the soil (L mg^{-1}) and MAC is the maximum adsorption capacity of soil (mg B kg^{-1} soil). Langmuir isotherm was fitted to the B adsorption results by the Fitfunc program (Barrow, 1987), which uses the non-linear optimization of the least squares and does not require the linearization of the isotherm, that avoids both the introduction of changes in the error distribution and the acquisition of influenced parameters (K and MAC) (Soares et al., 2005).

The experiment was designed to be completely randomized. Comparison among soils was made based on the maximum adsorption values. Simple linear correlation analysis was performed to detect the physical and chemical properties of soil that correlated with the constant of Langmuir adsorption (MAC and K) and adsorption after addition of 2.0 mg L^{-1} B (Alleoni and Camargo, 2000).

RESULTS AND DISCUSSION

Soil characterization

The initial and after liming soil pH value ranged from 4.6 to 6.8 in the Rhodic Hapludox, from 4.7 to 7.3 in the Arenic Hapludalf, 4.8 to 6.5 in the Arenic Hapludult, and from 5.9 to 7.4 in the Typic Usthorthent. All samples had a negative balance of charge ($\Delta pH < 0$) probably due to the contribution of organic matter (Table 2). Organic carbon (OC) content was higher than 15 g kg^{-1} for the majority of samples, except for the Arenic Hapludult. Arenic Hapludalf and Arenic Hapludult were very clayey (> 600 g kg^{-1} clay), while Rhodic Hapludox and Typic Usthorthent were clayey (350-600 g kg^{-1}) (Table 2).

Boron adsorption by soils

The Langmuir model (hyperbolic Langmuir adsorption isotherms) fitted well to the values of adsorbed B by soils, across the range of B concentrations and pH values ($R^2 \geq 0.96$ at $P < 0.01$) (Figure 1). These results were expected since there is no record of deviations from the Langmuir equation at concentrations below 30 mg B L^{-1} (Alleoni and Camargo, 2000). The use of lower concentrations is best suited to represent the B amount contained in Brazilian soils (Alleoni et al., 1998). These authors whilst investigating weathered Brazilian soils used B concentrations in the solution ranging from 0

to 16 mg L^{-1} and found that B adsorption in soils were well fitted by the Langmuir isotherm. Other authors also pointed out the ability of the Langmuir isotherm to estimate the B adsorption by soils at different pH values (Communar and Keren, 2006; Shafiq et al., 2008; Goldberg et al., 2008; Arora and Chahal, 2010; Steiner et al., 2012).

Soil samples of Rhodic Hapludox, Arenic Hapludalf, and Arenic Hapludult showed type C (Constant) of isotherm, according to the classification of Soares and Casagrande (2009), and used by several authors (Soares et al., 2005; 2008; Steiner et al., 2012), which indicates the high adsorption affinity (Figure 1). In this type of curve, the number and energy of sites available for adsorption remain constant throughout the whole concentration range and expansion of the available surface area may occur in proportion to the amount adsorbed, until all the adsorption sites are occupied. This may be related to the low initial B concentrations (0 to 4 mg B L^{-1}) used in the study. Similar results were found by Soares et al. (2005; 2008), by using the same B concentrations. Soil samples Typic Usthorthent showed isotherms of type L (Langmuir), especially in the lower pH values (Figure 1d), with lower energy adsorption, characterized by low inclination due to the adsorption sites available decreasing as the adsorbent surface becomes saturated (Soares and Casagrande, 2009). From the inclination of adsorption isotherm is verified that there was an increase in B adsorption at lower concentrations. With the increased B concentration, more sites were taken and the occurrence of the reaction was more difficult, decreasing the curve inclination.

Boron adsorption by soils was very dependent on soil pH, increasing as a function of pH in the range of 4.6 and 7.4 (Figure 1 and Table 3). The increase of 2.4 pH units (i.e., 4.9 to 7.3) resulted in a mean increase of 411% (4.4 to 22.5 mg B kg^{-1} soil) in the maximum amount of B adsorbed in the Arenic Hapludult (Table 3). For Rhodic Hapludox, Arenic Hapludalf and Typic Usthorthent the increased of 2.2 (pH 4.9 to 6.8), 2.7 (pH 4.7 to 7.4) and 1.9 (pH 5.1 to 7.0) pH units resulted, respectively, in a mean increase of 115%, 108%, and 53% in the maximum amount of B adsorbed (Table 3). Rosolem and Bíscaro (2007) also found a higher adsorbed B value of 24.2 mg kg^{-1} at higher pH (5.6) compared to 9.5 mg kg^{-1} at lower pH (4.5). Various studies have reported that one of the most important factors affecting the adsorption of B in soils is pH (Saltali et al., 2005; Soares et al., 2008; Chen et al., 2009). Boron adsorption by soils increases in the pH range between 3.0 and 9.0, and decreases in the range of 10.0 to 11.5, giving a typical bell curve with an adsorption peak of about 9.0, very close to the boric acid pKa of 9.2 (Goldberg, 1997). The increased with an increasing pH, which can be explained by the increased number of active adsorption sites and greater proportion of borate ion $[B(OH)_4^-]$ in relation to boric acid $[B(OH)_3]$ (Goldberg et al., 2005). However, Rosolem and Bíscaro
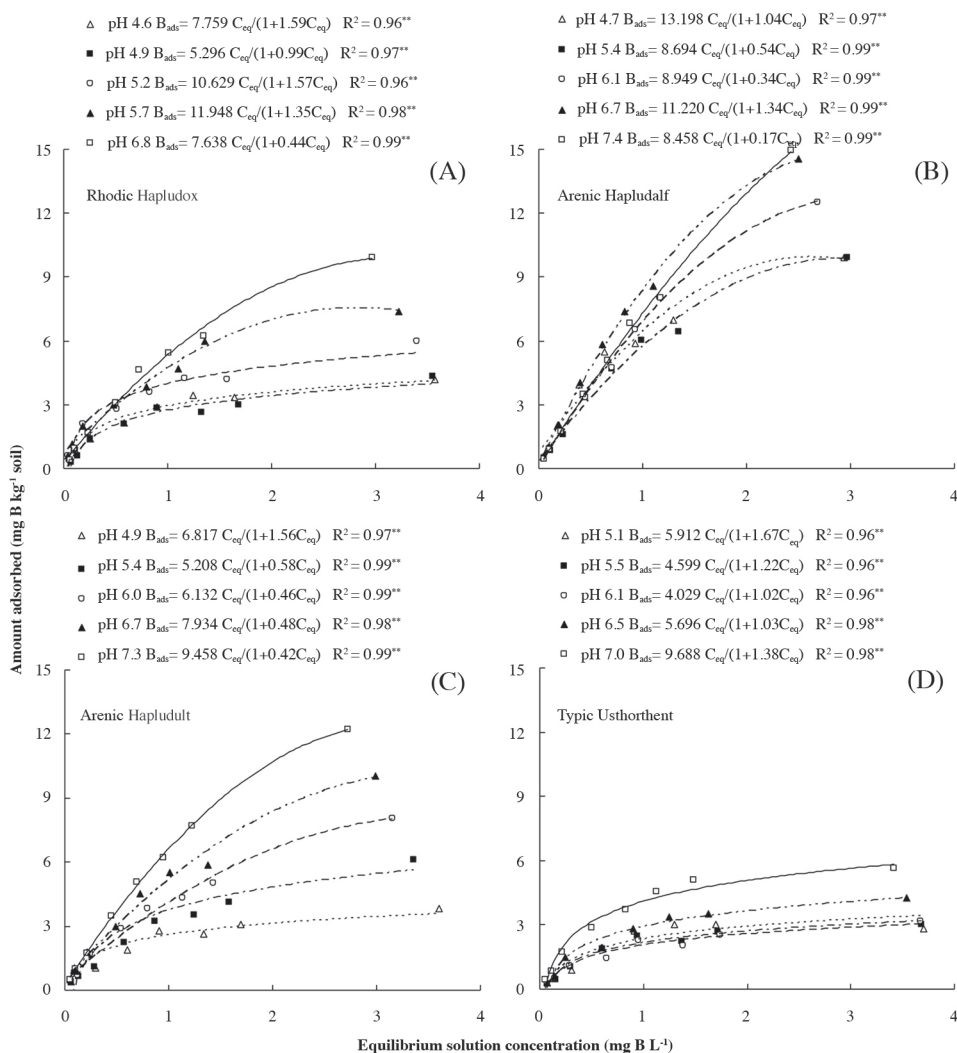
$$\text{pH } 4.6 \quad B_{ads}= 7.759\, C_{eq}/(1+1.59C_{eq}) \quad R^2=0.96^{**}$$
$$\text{pH } 4.9 \quad B_{ads}= 5.296\, C_{eq}/(1+0.99C_{eq}) \quad R^2=0.97^{**}$$
$$\text{pH } 5.2 \quad B_{ads}= 10.629\, C_{eq}/(1+1.57C_{eq}) \quad R^2=0.96^{**}$$
$$\text{pH } 5.7 \quad B_{ads}= 11.948\, C_{eq}/(1+1.35C_{eq}) \quad R^2=0.98^{**}$$
$$\text{pH } 6.8 \quad B_{ads}= 7.638\, C_{eq}/(1+0.44C_{eq}) \quad R^2=0.99^{**}$$

(A) Rhodic Hapludox

$$\text{pH } 4.7 \quad B_{ads}= 13.198\, C_{eq}/(1+1.04C_{eq}) \quad R^2=0.97^{**}$$
$$\text{pH } 5.4 \quad B_{ads}= 8.694\, C_{eq}/(1+0.54C_{eq}) \quad R^2=0.99^{**}$$
$$\text{pH } 6.1 \quad B_{ads}= 8.949\, C_{eq}/(1+0.34C_{eq}) \quad R^2=0.99^{**}$$
$$\text{pH } 6.7 \quad B_{ads}= 11.220\, C_{eq}/(1+1.34C_{eq}) \quad R^2=0.99^{**}$$
$$\text{pH } 7.4 \quad B_{ads}= 8.458\, C_{eq}/(1+0.17C_{eq}) \quad R^2=0.99^{**}$$

(B) Arenic Hapludalf

$$\text{pH } 4.9 \quad B_{ads}= 6.817\, C_{eq}/(1+1.56C_{eq}) \quad R^2=0.97^{**}$$
$$\text{pH } 5.4 \quad B_{ads}= 5.208\, C_{eq}/(1+0.58C_{eq}) \quad R^2=0.99^{**}$$
$$\text{pH } 6.0 \quad B_{ads}= 6.132\, C_{eq}/(1+0.46C_{eq}) \quad R^2=0.99^{**}$$
$$\text{pH } 6.7 \quad B_{ads}= 7.934\, C_{eq}/(1+0.48C_{eq}) \quad R^2=0.98^{**}$$
$$\text{pH } 7.3 \quad B_{ads}= 9.458\, C_{eq}/(1+0.42C_{eq}) \quad R^2=0.99^{**}$$

(C) Arenic Hapludult

$$\text{pH } 5.1 \quad B_{ads}= 5.912\, C_{eq}/(1+1.67C_{eq}) \quad R^2=0.96^{**}$$
$$\text{pH } 5.5 \quad B_{ads}= 4.599\, C_{eq}/(1+1.22C_{eq}) \quad R^2=0.96^{**}$$
$$\text{pH } 6.1 \quad B_{ads}= 4.029\, C_{eq}/(1+1.02C_{eq}) \quad R^2=0.96^{**}$$
$$\text{pH } 6.5 \quad B_{ads}= 5.696\, C_{eq}/(1+1.03C_{eq}) \quad R^2=0.98^{**}$$
$$\text{pH } 7.0 \quad B_{ads}= 9.688\, C_{eq}/(1+1.38C_{eq}) \quad R^2=0.98^{**}$$

(D) Typic Usthorthent

Amount adsorbed (mg B kg^{-1} soil)

Equilibrium solution concentration (mg B L^{-1})

Figure 1. Boron adsorption isotherms for four soils of the western region of Paraná State, Brazil, as affected by pH values. **P < 0.01.

(2007) found that even with the applying of relatively high rates of lime, the B adsorption by soil is only significant in the year that the liming was carried out, so that over time a greater amount of B remains in the soil solution under conditions of being readily absorbed by plants or even being lost by leaching. Similarly, Chen et al. (2009) observed that soil re-acidification caused an increase in B desorption, increasing the element's content in solution. Indicating that B adsorption by soils submitted to liming is characterized by a rapid and reversible chemical reaction between the adsorbed and soluble B.

The values of maximum adsorption capacity (MAC) and bonding energy constant (K) estimated by the Langmuir isotherm (Table 3) were similar to those found in studies using a range similar to the B concentration added to the soil. The K ranged from 0.2 to 1.7 L mg^{-1}, while the MAC ranged from 3.5 to 49.8 mg B kg^{-1} soil. The wide variation in these parameters can be attributed

to differences in the physical, chemical and mineralogical properties of the soils. In highly weathered soils, Alleoni et al. (1998) and Alleoni and Camargo (2000) found lower K values (0.1-1.2 L mg^{-1}) and MAC (2.5-15.8 mg kg^{-1}). On the other hand, in acric soils of São Paulo, Brazil, Soares et al. (2008) found higher K values (0.2 to 2.1 L mg^{-1}) and MAC (32.5 to 128.6 mg kg^{-1}), which in turn were very close to the results reported by Shafiq et al. (2008) for calcareous soils of Pakistan.

The maximum value of MAC, that is, 49.8 mg B kg^{-1} soil, was observed in the Arenic Hapludalf followed by 22.5 in Arenic Hapludult, 17.4 in Rhodic Hapludox, and 7.0 in Typic Usthorthent (Table 3). The lowest adsorption capacity of B observed for the Typic Usthorthent due to lower clay content (510 g kg^{-1}), the lower degree of weathering reported by weathering index (Ki) greater than 2.46, and the highest proportion of negative charges (-1.9 ΔpH) compared with the other soils (Table 2). Among

Table 3. Maximum adsorption capacity (MAC) of B, bonding energy of B to the soil (K) and percentage of B adsorption (%Ads) after addition of 2.0 mg B L^{-1} in four soils of the western region of Paraná State, Brazil, with different pH values.

| Soil | Soil pH | Langmuir constants | | %Ads |
		MAC	K	
		mg B kg^{-1} soil	L mg^{-1}	%
	4.6	4.9	1.6	28
	4.9	5.4	1.0	36
Rhodic Hapludox	5.2	6.8	1.6	41
	5.7	8.9	1.4	52
	6.8	17.4	0.4	63
	4.7	12.7	1.0	34
	5.4	16.1	0.5	41
Arenic Hapludalf	6.1	26.3	0.3	53
	6.7	33.0	0.3	58
	7.4	49.8	0.2	62
	4.9	4.4	1.6	36
	5.4	9.0	0.6	41
Arenic Hapludult	6.0	13.3	0.5	51
	6.7	16.5	0.5	64
	7.3	22.5	0.4	78
	5.1	3.5	1.7	26
	5.5	3.8	1.2	33
Typic Usthorthent	6.1	4.0	1.0	34
	6.5	5.5	1.0	39
	7.0	7.0	1.4	43

Table 4. Correlation coefficients of simple linear regression analysis between parameters of Langmuir adsorption isotherms (MAC and K) and adsorption after addition 2.0 mg B L^{-1} and some soil properties.

| Soil properties | Langmuir isotherm constants | | | | Adsorption after addition of 2 mg B L^{-1} |
	MAC at natural pH	MAC at higher pH	K at natural pH	K at higher pH	
Soil pH	–0.49	0.77	0.48	–0.40	0.45
ΔpH	0.45	0.58	–0.45	–0.96**	0.39
Clay	0.66	0.83*	–0.69	–0.85*	0.61
Organic matter	0.89*	0.81*	–0.87*	–0.60	0.89*
Soluble B	–0.18	–0.24	0.17	0.71	–0.13
Ex. Al	0.66	0.72	–0.68	–0.98**	0.61
ECEC	0.44	0.31	–0.44	0.39	0.50
SiO$_2$	0.04	–0.18	–0.02	0.77	0.12
Fe$_2$O$_3$	0.51	0.29	–0.48	0.38	0.57
Al$_2$O$_3$	0.84*	0.96**	–0.86*	–0.88*	0.81*
Ki	–0.51	–0.70	0.53	0.68	–0.45

ΔpH = pH KCl – pH H$_2$O used as an estimate of the charge balance; Ex. Al: Exchangeable aluminum; ECEC: effective cation exchange capacity; SiO$_2$, Fe$_2$O$_3$ and Al$_2$O$_3$: silicon, iron and aluminum oxides, respectively; Ki: weathering index calculated by the molar ratio SiO$_2$/Al$_2$O$_3$.

the chemical properties of soil, pH and clay content are factors that most influence B adsorption (Chaudhary and Shukla, 2004; Saltali et al., 2005).

The percentage of B adsorption (%Ads) by soils after addition of 2.0 mg B L^{-1} increased with increasing of soil pH (Table 3). The percentage of adsorbed B ranged of 26 to 36% at lower pH value and 43 to 78% at higher pH value. A mean increase around of 33% B adsorption after application of calcium carbonate was observed in soil from São Paulo by Alleoni and Camargo (2000).

The bonding energy (K) decreased with the pH in most soils (Table 3). These findings indicate that at higher pH values the B is adsorbed more weakly. This decrease on bonding energy can be explained by the increased surface charge of soil particles with increasing pH, increasing the

repulsion of B and then reducing the bonding energy of these particles.

Effect of soil properties on B adsorption

The values of adsorbed B did not present a significant correlation with most of the soil chemical properties – i.e., pH, charge net balance (ΔpH), soluble B, exchangeable aluminum, effective cation exchange capacity (ECEC), silicon (SiO$_2$) and iron (Fe$_2$O$_3$) oxides and weathering index (Ki) (Table 4). The absence of correlation between these soil properties can be explained by the fact B retention as a function of soil pH has a maximum value between 8.0 and 9.0 (Goldberg et al., 2008), and the pH reached only 7.4. Knowing this, the isolated effect of soil pH on the B retention seems to be relatively small in acid soils. Alleoni and Camargo (2000) studied soils with pH varying from 3.5 to 5.5, and also did not obtain correlation with adsorbed B in soils of São Paulo State. It is important to note that, in the acid range, B is predominantly in the form of boric acid and not in its ionic form B(OH)$_4^-$ (Goldberg, 1997). The absence of correlation between the maximum B adsorption and ECEC can be explained due to this variable depends on other soil properties – e.g., organic matter and clay content. The ECEC cannot theoretically contribute to adsorption of negatively charged species, such as B(OH)$_4^-$.

The correlation coefficient between adsorbed B and organic matter was highly significant (r = 0.81* to 0.89*; Table 4). This finding corresponds to the results obtained by other researchers (Arora et al., 2002; Van et al., 2005; Sharma et al., 2006; Arora and Chahal, 2010). Organic matter is an important soil factor affecting the availability of B. Humus extracted from a soil retained significant amounts of B and was considered to play an important role in B adsorption (Yermiyahu et al., 1995). Datta and Bhadoria (1999) reported that organic C exerted a beneficial effect on the B retention capacity of soils, which could be due to the formation of a complex between dihydroxy-organic compounds and B. The presence of organic materials can also occlude the B reactive adsorption sites on clays and soils (Yermiyahu et al., 2001). A possible mechanism for B sorption on organic matter is ligand exchange. Moreover, it has been suggested that the formation of the B-diol complexes was associated with the breakdown products of soil organic matter.

A highly significant correlation (r = 0.83*) was found between clay content and the B adsorption maximum at higher pH (Table 4). According to Saltali et al. (2005) adsorbed B is dependent on soil texture, and increases with increasing clay content. Therefore, in fine-textured soils with a high amount of clay and organic C content, additions of B could be made without it becoming toxic to plants because of high adsorption capacity.

Aluminum oxide content was significantly correlated with the MAC of B (Table 4). This finding corresponds

to the results obtained by other researchers (Alleoni and Camargo, 2000). The higher correlation coefficients are expected with Al oxides than with Fe oxides, due to the high affinity of B with the OH groups of Al (hydr) oxides and the higher specific surface (Goldberg and Glaubig, 1985).

The K can provide insights into the mechanism most likely involved in B adsorption. The values of K at higher pH were significantly correlated with organic matter content (r = -0.87*) and aluminum oxide contents (r = -0.86*; Table 4). At higher pH the values of K correlated negatively with charge net balance (r = -0.96**), clay content (r = -0.85*), exchangeable aluminum (r = -0.98**) and aluminum oxides (r = -0.88*; Table 4). These findings indicate that the higher the value of these properties lesser is the bonding energy of B to the soil.

CONCLUSIONS

The amount of adsorbed B by soils increased with increasing applied concentration of this element. Boron adsorption increased with increasing soil pH. The bonding energy decreased with the pH in most soils, indicating that at higher pH values the B is adsorbed more weakly. Maximum adsorption capacity of B in the Arenic Hapludalf is due to higher clay and organic matter contents. The organic matter content, clay content, and aluminum oxide content (Al_2O_3) were the soils properties that affecting the B adsorption on Paraná soils.

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