Adsorption and desorption processes of boron in calcareous soils

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ABSTRACT

Boron (B) availability is regulated by its equilibrium concentration that in turn is buffered by adsorption and desorption reactions. Ionic strength, pH, OM content, and the type and amount of minerals are the major factors affecting B sorption reactions. To evaluate the influence of calcium carbonate equivalent (CCE) and ionic strength on B chemical behavior, its adsorption and desorption isotherms were measured in eight calcareous soils differed in CCE (0–85%). Adsorption and desorption data were described by the Langmuir and the Linear adsorption equations, respectively. No statistically significant relation was found between model parameters and soil properties. However, in comparison, soils with higher reactive particles (clay and OM) and higher pH adsorbed more boron. Removing CCE from a soil sample (CCE = 18%) lowered B adsorption maximum by 35%. In contrast, increasing electrolyte concentration (0.01 M NaCl) to 0.1 and 0.5 M caused to increase B adsorption maximum by 30% and 75%, respectively. At the equi-molar concentration, $CaCl_2$ increased B adsorption stronger than NaCl. The positive effect of ionic strength was attributed to a better screening of surface charges and compaction of double layer thickness. Desorption data were deviated from adsorption isotherms only at equilibrium concentrations smaller than 2 mM. Analysis of boron solution speciation and adsorption–desorption data revealed that B is mainly adsorbed as spectroscopically proved outer-sphere complex in the studied soil samples. The experimental data and model prediction could be used to manage B bio-availability and to optimize remediation processes in calcareous soils.

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1. Introduction

Boron (B) is an essential microelement for plants that its uptake is regulated by B concentration in soil solution. Boron concentration in soil solution is buffered by the adsorbed B on mineral surfaces through adsorption and desorption reactions. Since the range between deficiency and toxicity limits of B for plants is very narrow, any change in B equilibrium concentration may turn to considerable influence on plant growth (Keren and Bingham, 1985). Thus, adsorption and desorption reactions are very important in the management of B bio-availability. In addition, accumulation of B in surface soils is a common problem in many calcareous soils irrigated with water containing high B. Application of any remediation plan in these soils needs information on the B adsorption and desorption reactions.

During last few decades, adsorption and desorption behavior of boron has intensively been studied in soil and on minerals. Ionic strength, pH, organic matter, and the type and amount of minerals have been identified as the most important factors influencing B reactions in soils and in other natural systems (Keren and O'Connor, 1982; Goldberg and Glaubig, 1988; Singh and Mattigod,

1992; Goldberg et al., 1993; Debussetti et al., 1995; Hobbs and Reardon, 1999; Sharma et al., 2006; Chen et al., 2009; Keren and Communar, 2009).

Adsorption isotherms of B exhibit a trend similar to most oxyanions, i.e. a Langmuir type of adsorption; however, its adsorption edges are rather specific, like silicon (Si). At low pH, adsorption is weak. It gradually increases and reaches to a maximum at pH range 7–9, depending on the type of soil and minerals. At higher pH range, its adsorption gradually decreases to a minimum value (Keren and Sparks, 1994; Debussetti et al., 1995). The first two parts of this trend originate from the solution speciation of B. However, decrease in adsorption at high pH is due to a drop in surface potential on minerals with pH-dependent charge. In addition to pH, ionic strength has a noticeable effect on B adsorption. This effect has been measured small for oxides but large for clay minerals and soils (Keren and O'Connor, 1982; Mattigod et al., 1985; Goldberg et al., 1993; Keren and Sparks, 1994). Keren and O'Connor (1982) and Keren and Sparks (1994) argued that negative electrical field associated with the planar surface of clay minerals affects on the B adsorption on edge surfaces. Therefore, an increase in ionic strength suppresses the negative electrical field of planner surface and allow for higher adsorption of B. Furthermore, different types of minerals in soil exhibit different charge and potential behavior that affects on the B adsorption (Keren and O'Connor, 1982; Keren

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and Sparks, 1994). The interaction of B with OM and its components, i.e. HA and FA, is more complicated than its interaction with clays and oxides (Keren and Communar, 2009). OM binds B stronger and larger than clay minerals (Yermiyahu et al., 1995) and at the same time, due to similarity in charge, they may compete with B for adsorption on minerals. This interaction lowers binding of B by minerals (Marzadori et al., 1991; Xu and Peak, 2007).

Although the importance of metal (hydr)oxides, OM and clay minerals on boron adsorption has been quantified, however the effect of calcium carbonates still needs to be clarified. Elrashidi and O'Connor (1982) reported that the presence of calcite is not statistically significant in B adsorption. In contrast, a negative correlation between B adsorption and carbonate minerals has been observed by Hingston (1964). On the other hand, Goldberg and Forster (1991) measured relatively high adsorption of B on calcite.

Adsorption data provide valuable information for interpretation of ion adsorption in soil and on soil minerals. However, from the perspective of plant nutrition and for evaluation of environmental remediation processes, desorption isotherms are more appropriate. This advantage arises from the fact that adsorption and desorption isotherms of ions usually do not coincide. The observed hysteresis is partly due to the heterogeneity in adsorption affinities and partly due to the pathways through which adsorption and desorption occur (Yin et al., 1997). To increase our understanding of boron adsorption and desorption behavior in calcareous soils, in this study we measured adsorption and desorption of boron in eight soils differed in calcium carbonate content. The effects of removing calcium carbonate, change in ionic strength, and the type of electrolyte solution on boron adsorption were also evaluated.

2. Materials and methods

The experimental soil samples were collected from different soil series (0–20 cm) representing eight soils with different amount of calcium carbonate equivalent (CCE). The collected samples were then air dried and passed through a 2-mm sieve, homogenized, and stored in plastic containers. The CCE content was determined by titration method. The reactive fraction of CCE (CCE_r) was measured using the ammonium oxalate method. Organic carbon (OC) and particle size distribution were determined by the wet oxidation method of Walkley and Black and hydrometer method, respectively (Page et al., 1982; Klute, 1986). The amount of amorphous and crystalline iron and aluminum in experimental soil samples were determined by ammonium oxalate and dithionite–citrate–bicarbonate (DCB) methods (Coffin, 1963; Schwertmann, 1973).

The adsorption experiments were carried out in batch systems. Soil samples (8.12 g) were added to 50 mL polypropylene centrifuge tubes and equilibrated with 25 mL of 0.01 M $CaCl_2$ solution, containing varying concentration of H_3BO_3. Initial concentration of B ranged from 0 to 10 mM. The centrifuge tubes were equilibrated for 20 h on an end-over-end shaker (180 rpm) in a constant temperature room (25 ± 1 °C). The suspensions were then centrifuged (4000g for 15 min, 25 °C) and the aliquot of clear supernatants were taken and filtered through Whatman No. 42 filter paper. The supernatants were analyzed for B concentration using the colorimetric azomethine-H method (Bingham, 1982), in which B forms a stable complex with azomethine-H at pH 5.1. The solution pH was buffered with glacial acetic acid and ammonium acetate. After stabilization of developed color (15–30 min), absorbance was measured at 420 nm. The equilibrium pH was measured in the remixed remained of the suspensions. No change in pH was observed compares to the control sample.

Boron desorption isotherms were measured in soils 2, 3, and 4 for five initial B concentration. The centrifuged residues of adsorption experiments were weighted to determine the amount of oc-

cluded solution, and then re-suspended in 25 mL of boron-free 0.01 M $CaCl_2$. The tubes were shaken for 20 h, centrifuged, and then clear supernatants were removed. This sequence of operations was repeated for four times. Boron concentration was measured in supernatants separately for each desorption step. The desorbed B was calculated for each step taking into account the amount of B remained in the occluded solution.

To examine the effect of ionic strength, boron adsorption isotherms were measured in soil 6 in 0.01, 0.10, and 0.50 M NaCl solutions. Furthermore, for evaluation of the importance of carbonate minerals on B adsorption, carbonates were removed from soil 6 using a modification of the procedure described by Kunze and Dixon (1986). The soil sample was washed three times with 0.5 M Na-acetate solution, adjusted at pH = 5 by the addition of glacial acetic acid, then washed twice with deionized water, air dried, and passed through a 2-mm sieve. B adsorption in the treated soil was determined similar to the procedure described above.

The native adsorbed B in soil samples was estimated from the equilibrium concentration of B in blank samples using the parameterized adsorption isotherm equations. In addition, adsorption isotherm of phosphate was measured in soil 6 assuming a similar adsorption mechanism for boron and phosphorus. In this experiment, 3.12 g soil sample was added to 50 mL polypropylene centrifuge tubes and equilibrated with 25 mL of 0.01 M $CaCl_2$ solution, differing in P concentration (0–0.65 mM). After equilibration and centrifuging, both B and P concentrations were measured in the supernatants.

2.1. Computations and modeling

The amount of adsorbed ions was calculated by the difference between the initial and final equilibrium concentration. In the desorption experiments, the B concentration retained by the soil in the suspension after each desorption step was calculated according to (Yin et al., 1997):

$$\Gamma_i = \Gamma_{i-1} - (c_i - c_{i-1}/n)/w \tag{1}$$

where Γ_i and Γ_{i-1} are the concentrations of B remaining in the soil at the end of the ith and $(i-1)$th desorption steps (mmol kg^{-1}), c_i and c_{i-1} are B concentrations in the solution at the end of the ith and $(i-1)$th desorption steps (mM), n is dilution factor, and w is the solid concentration in the suspension (kg L^{-1}).

Experimental adsorption and desorption data were respectively described with the Langmuir (Eq. (2)) and the Linear (Eq. (3)) adsorption isotherm equations.

$$\Gamma = \Gamma_{max} \frac{K_L c}{1 + K_L c} \tag{2}$$

$$\Gamma = K_d c + \delta \tag{3}$$

where Γ represents the amount of boron adsorbed (mmol kg^{-1}), c equilibrium concentration of the B in solution (mM), Γ_{max} maximum adsorption capacity of soil for B (mmol kg^{-1}), and K_L (L mmol^{-1}) and K_d (L kg^{-1}) approximations of adsorption energy, and δ is a measure of irreversible adsorbed B (mmol kg^{-1}).

3. Results and discussion

3.1. Chemical and physical properties of soils

Some properties of the experimental soil samples including soil particle size distribution, total calcium carbonate equivalent (CCE), reactive calcium carbonates (CCE_r), OC, and amorphous and crystalline iron and aluminum (hydr)oxides are presented in Table 1. The CCE content in soil samples was varied from 3% to 85%, indicat-