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Removal of organic matter and oxides of iron and manganese from soil influences boron adsorption in soil

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ABSTRACT

The influences of specific soil components such as organic matter and oxides of Fe and Mn on B adsorption characteristics are not understood well. In the present study, we compared B adsorption behavior of two acidic soils after removal of organic matter, and Fe- and Mn-oxides with that of untreated soil samples. The B adsorption capacity of the soils before and after removal of different components was low; the average values of maximum B adsorption obtained from nonlinear least square optimization of Langmuir adsorption isotherm being 20.61 mg kg^{-1} for Mallerbari soil and 27.15 mg kg^{-1} for Sikarpur soil. Removal of organic matter by NaOCl treatment from the soils increased B adsorption. This indicates that Fe- and Al-oxides and other available adsorption sites on the mineral surfaces are coated by organic matter and are activated only after removal of organic matter. Removal of Fe- and Mn-oxides, however, resulted considerable decrease in B adsorption in the soils. It is, therefore, suggested that B adsorbing surfaces in soil decrease on removal of Fe- and Mn-oxides, since these oxides are known to have good adsorptive capacity for B.

1. Introduction

Boron deficiency is commonly observed in light-textured acidic soils, in soils containing a high amount of calcium carbonate or oxides and hydroxides of Fe and Al and also in soils of low organic matter content (Keren and Bingham, 1985; Mandal et al., 2004). The deficiency is caused by leaching loss (because of high precipitation) and fixation of the element in unavailable forms. Soils of a vast area of land in India, particularly eastern and north eastern parts, suffer from such deficiency (Dwivedi et al., 1993; Sarkar et al., 2008a). To correct B deficiency its application to soil for optimum crop production is very common in the region. Boron applied to soil undergoes adsorption reactions and the adsorbed B in the soil solid surfaces equilibrates with its concentration in soil solution (Goldberg, 1993). Uptake of B by plant is determined directly by its concentration in soil solution (Keren et al., 1985) and indirectly by the amount adsorbed on the soil surfaces.

Although, it has been reported by many workers that B adsorption in soil is influenced by soil solution pH, organic matter, clay, sesquioxides, Mn-oxides and carbonates (Goldberg et al., 2000; Mondal et al., 1993; Sharma et al., 2006; Sims and Bingham, 1968), the role of soil components on B adsorption behavior is not consistent. Boron adsorption was found to be positively correlated with oxides and hydroxides of Fe and Al (McPhail et al., 1972; Sims and Bingham, 1968). Elrashidi and O'Connor (1982), however, did not find any relationship between B adsorption and Fe- and Al-oxide contents in soil. In another study taking 16 soils, Mondal et al. (1993) observed significant negative relation of Fe_2O_3 content in soils with adsorbed B. Sharma et al. (2006) and Yermiyaho et al. (1995) found an increase in B adsorption when organic matter was added to soil, while Diana et al. (2010) observed a decrease in B adsorption in soil with addition of organic matter. Contradictory results of B adsorption with removal of organic matter from soil have also been reported. Olson and Berger (1947) showed that B adsorption capacity of soil decreased with removal of organic matter from soil. On the contrary, Mezuman and Keren (1981) found no such changes and Marzadori et al. (1991) reported greater adsorption of B after removal of organic matter from the soils.

Solubility of B by various extraction techniques has been used to assess plant available B status of soils (Goldberg et al., 2002; Sarkar, 2008b). Sarkar et al. (2008a) found that the amount of B extracted by three different extractants (0.02 M hot-$CaCl_2$, 0.5 M potassium dihydrogen phosphate and 0.01 M tartaric acid) was positively correlated with organic C, and amorphous Al- and Fe-oxides but negatively correlated with Mn-oxide content of soils. These extractants are known to be capable of extracting B bound by organic matter, which retains the element through the formation of B-organic complexes (Gupta et al., 1985). Extraction of B bound by oxides of Fe and Mn is not known because these oxides at higher pH combined B through ligand exchange mechanisms, making it difficult to extract (Mandal and

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De, 1993). This information made us to hypothesize that soil organic matter rather than Fe-, Al- and Mn-oxides is the main reserve of available B, which is considered to be a good index of plant available B.

The available literature describing influences of specific soil components is inconsistent and relatively meager. The present experiment was, therefore, undertaken with the objective to evaluate the influence of removal of organic matter, amorphous and crystalline Fe-oxides and Mn-oxides on B adsorption behavior in soils.

2. Materials and methods

2.1. Preparation of soils

Two B deficient surface soil samples were collected from Mallerbari and Sikarpur located in northern West Bengal, India. The soils were both classified as coarse-loamy, mixed, hyperthermic Typic Fluvaquents. They were air dried, powdered, passed through a 2 mm nylon sieve, and analyzed for clay (international pipette method), pH (in 1:2.5 soil–water suspension), organic carbon, cation exchange capacity, Mn-oxides, free Fe-oxide, amorphous Fe-oxides, and Al-oxides and hydroxides (Table 1) following standard chemical methods (Sparks et al., 1996). Surface area was measured using the ethylene glycol monoethyl ether adsorption method of Cihacek and Bremner (1979). Individual sub-samples were then subjected to different treatments to remove various soil components such as organic matter, Mn-oxides, amorphous and crystalline Fe-oxides following standard procedures presented in Table 2.

After the organic matter had been removed, the treated soil residues were resuspended in 50 ml of deionized water and the pH rose to about 10, restored to the original soil pH by the addition of dilute CH_3COOH (the use of HCl was avoided because locally high acid concentrations led to some loss of $CaCO_3$). The suspensions were shaken for 4 h, centrifuged, and the residues again resuspended in 50 ml of deionized water. These suspensions were gently shaken overnight. The pH was re-adjusted by repeating this operation several times until the final pH of the residues was the same as that of the original soil. In the case of removal of components other than organic matter, pH of the treated soils was also adjusted to the values of original soils by repeated addition of either dilute NH_4OH or CH_3COOH, so that it varies little during adsorption. The treated soils were washed several times with deionized water, air dried, ground and passed through 2 mm nylon sieve and used along with the untreated soils for B adsorption study.

2.2. Adsorption studies

Ten gram soil samples (original as well as treated) were placed in a 100 ml polypropylene centrifuge tube and 20 ml solution containing varied levels of B in 0.03 M KNO_3 medium was added and the resulting suspensions were allowed to attain equilibria for 24 h at room temperature (25 °C) with occasional shaking followed by centrifugation (15000 *g* for 15 min), decantation and filtration. The filtrate was analyzed for B following the spectrophotometric method using azomethine-H (Parker and Gardner, 1981). Additionally, one such sample for each concentration without soil was carried through the same procedure to account for possible contamination or other sorption losses. The B concentration in solution in each case had been arrived by dissolving boric acid, which yields monomeric solution of $B(OH)_3$ at a concentration of <0.025 M. Dilute KNO_3 solution was used instead of deionized water and dilute $CaCl_2$ solution to avoid a positive error in B determination by spectrophotometric method using azomethine-H due to presence of suspended or dissolved material in the water extract, which imparts yellow color to the solution (Sarkar et al., in press) or a possible B retention in presence of high content of soluble Ca^{2+} in the form of Ca-borate minerals.

Table 1
Some important properties of the experimental soils.

Soil properties	Mallerbari	Sikarpur
pH (1:2.5 soil:water)	4.8	4.8
Clay (g kg^{-1})	117	174
Organic C (g kg^{-1})	12	25
Cation exchange capacity (cmol p^+ kg^{-1})	8.0	22.2
Free Fe-oxides (g kg^{-1})	14.7	0.1
Amorphous Fe-oxides (g kg^{-1})	8.6	3.8
Mn-oxides (g kg^{-1})	0.5	0.9
Al-oxides (g kg^{-1})	0.6	4.4
Al-hydroxides (g kg^{-1})	122	189
Surface area (m^2 g^{-1})	45	62

2.3. Treatment of data

The amount of B adsorbed in each sample was calculated from the difference in the initial and final B concentration taking into account the amount of B found in the supernatant solution in no B control treatment. The adsorption data thus generated were fitted to the Langmuir adsorption isotherm.

$$S = \frac{bKC}{1 + KC}$$

where $C =$ equilibrium B concentration (mg l^{-1}), $S =$ B adsorbed (mg kg^{-1}), $b =$ maximum B adsorption (mg kg^{-1}) and $K =$ constant related to bonding energy (l mg^{-1}). To obtain b and K, the Langmuir adsorption isotherm was fit to nonlinear least square regression. This was done by using Microsoft Excel spreadsheet as prepared and described by Bolster and Hornberger (2007). The spreadsheet was designed to generate goodness-of-fit in terms of model efficiency (E). An E value of 1 indicates a perfect fit to the data. The relative influence of removal of different soil components such as organic matter, amorphous Fe-oxides, crystalline Fe-oxides and Mn-oxides on B adsorption has been assessed by comparing the adsorption parameters obtained from the original soils before and after removal of different components.

All determinations were made in triplicate and results are given as means. Statistical analyses of regression and comparisons of the means by Duncan's multiple range test at the $p \leq 0.05$ level were performed using SAS 9.2 (SAS Institute, 2008).

3. Results and discussion

3.1. Soil properties

The soils of Mallerbari and Sikarpur were sandy loam in texture and acidic in reaction (Table 1). Sikarpur soil contained relatively higher amount of clay, organic C, Mn-oxides, Al-oxides and hydroxides and had higher cation exchange capacity and surface area than those of Mallerbari soil, while the amount of Fe-oxides and hydroxide was higher in latter than those in former soil.

3.2. Adsorption isotherm

Boron adsorption by the original and treated soils was plotted as function of equilibrium B concentration in soil solution (Fig. 1). Although the values were higher but the percent increase in adsorption of the added amount showed a declining trend with increase in concentration. The adsorption data of both original and treated soils showed good fit to the nonlinear least square Langmuir adsorption isotherm. The E values were closer to 1 and varied from 0.980 to 0.998 and 0.987 to 0.996 for treated and original soils of Mallerbari and Sikarpur, respectively (Table 3). Conformity of B adsorption by untreated soils to the Langmuir isotherm was reported by the others (Elrashidi and O'Connor, 1982; Goldberg et al., 2008; Keren and Communar, 2009; Mondal et al., 1993). Similar conformity of B adsorption data to Langmuir model in soil removed of organic matter (Marzadori et al.,