Boron adsorption by maize cell walls

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Abstract

Boron adsorption by cell walls isolated from corn (*Zea mays*) roots was investigated as a function of solution pH and ionic strength. Adsorption increased with increasing solution pH from pH 4.5 to 10, exhibited an adsorption maximum at pH 10–10.5, and decreased with increases in pH above 10.5. Boron adsorption increased with increasing solution ionic strength indicating the formation of strong inner-sphere surface complexes. A surface complexation model, the constant capacitance model was well able to describe the B adsorption data, optimizing two B surface complexes and the dissociation constant for the surface functional group, XOH. The large absolute value of the dissociation constant is consistent with phenolic functional groups.

Introduction

Boron is an important micronutrient element essential for plant growth, yet its primary functions remain unclear (Matoh, 1997). Boric acid crosslinks two chains of pectic polysaccharide through borate-diester bonding forming a network of pectic polysaccharides in the cell walls (Loomis and Durst, 1991; Matoh, 1997). Boron forms particularly stable complexes with compounds having *cis*-diol configurations, such as those found in phenolic and pectic substances (Cakmak and Römheld, 1997). Since the majority of cell wall B is associated with pectin, B influences cell wall structure through this interaction (Hu and Brown, 1994).

Ion exchange behavior of plant cell walls has been modeled using mass action expressions for H^+, K^+, Ca^{2+}, and Mg^{2+} sorption (Bush and McColl, 1987) and Donnan theory for Na^+, Ca^{2+}, La^{3+}, and Cl^- exchange (Richter and Dainty, 1989a, b). The constant capacitance model, a surface complexation model, has been used to describe H^+ and Cu^{2+} adsorption on maize and soybean root cell walls (Allan and Jarrell, 1989). The diffuse layer model, another surface complexation model, has been used to describe metal ion sorption by bacterial cell walls (Daughney and Fein, 1998; Daughney et al., 1998; Fein et al., 1997; Fowle and Fein, 1999, 2000; Yee and Fein, 2001) and lignocellulose extracted from wheat bran (Ravat et al., 2000a, b). The advantage of surface complexation models is that they define surface species, chemical reactions, mass balances, and charge balances and their molecular features can be given thermodynamic significance (Sposito, 1983).

Surface complexation modeling of B adsorption on Al and Fe oxides, the clay minerals, kaolinite, montmorillonite, and illite, and a set of 32 diverse soil samples has been successful using the constant capacitance model (e.g., Goldberg and Glaubig, 1985, 1986; Goldberg et al., 2000; Goldberg, 1999). In these studies, B adsorption behavior was investigated as a function of solution pH. In these model applications, B was assumed to adsorb specifically forming strong inner-sphere surface complexes. Inner-sphere surface complexes contain no water between the adsorbing ion and the surface functional group. The surface complexation models have not yet been applied to anion adsorption on cell wall materials.

Boron is a micronutrient element that can be toxic to plants at elevated concentrations. In arid regions

additions of B via the irrigation water often lead to toxicity symptoms and yield reduction. Boron tolerant genotypes are able to maintain lower B concentrations in their shoots than susceptible genotypes (Nable et al., 1997). Since the cell wall is the main binding site for B in plants, we believe that the B adsorption capacity of plant cell walls may well play a role in controlling B tolerance of plant species. The objectives of the present study were: (1) to determine B adsorption on maize cell walls as a function of solution pH and solution ionic strength; (2) to test the ability of the constant capacitance model to describe B adsorption on these walls.

Materials and methods

Maize cell walls were isolated using a modification of the method of Allan and Jarrell (1989). Maize seeds were laid out on cheese cloth supported by wire mesh screens (28 by 16 in.) over a tank of aerated nutrient solution. The plant roots were harvested between 14 and 21 days. Each screen produced between 750 and 1000 g of plant material. The root material was washed in deionized water to remove dirt and debris. The washed material was then coarse cut with scissors and put into a Waring blender with small amounts of deionized water and homogenized into a pinkish pulpy mash. The homogenized root material was filtered through cheese cloth to remove as much liquid as possible. The root material was then frozen in liquid nitrogen and crushed into a powder in a mortar. The powder was then remixed with deionized water to create a root slurry. The root mash/slurry was placed into a Parr Cell Disruption Bomb Model 4635* (Parr Instrument Co., Moline, IL), which was cooled to 4 °C, and pressurized for 30 min. The most effective pressure to insure maximum cell disruption was 1800 psi. A magnetic stirrer was placed into the solution because stirring the pressurized solution accelerated the nitrogen absorption into the cells and kept the cells in uniform suspension. Cell disruption occurred when the mash/slurry was released to the atmosphere through the discharge tube. The discharge was collected in a side-arm suction flask. The rate of discharge did not affect the cell disruption. The liquid discharge was then filtered through a nylon filter using a slight

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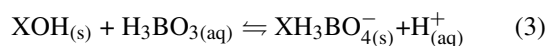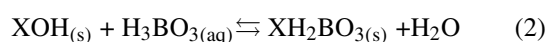
vacuum. The filtrate was resuspended in deionized water, sonified, refiltered, and resonified ten times. The solids were dried in a forced air oven for 72 h at 60 °C. Previous work by Allan and Jarrell (1989) had verified that the extraction method decreased lipid P to 12 ± 8% of that present in the intact root.

Boron adsorption experiments on the cell wall isolates were carried out in batch systems to determine adsorption envelopes, amount of B adsorbed as a function of solution pH per fixed total B concentration. Samples of cell wall solids were added to 50-mL polypropylene centrifuge tubes and equilibrated with aliquots of NaCl solutions by shaking for 2 h on a reciprocating shaker. Solid suspension densities were 2, 6, or 18 g·L^{-1}. Background electrolyte concentrations were 0.1, 0.01, or 0.001 M. The equilibrating solutions contained 0.463 mmol·L^{-1} B and had been adjusted to the desired pH range of 4–12 using 1 M HCl or 1 M NaOH. Additions of acid or base changed the total volumes by <2%. After reaction, the samples were centrifuged and the decantates analyzed for pH, filtered and analyzed for B concentration using the Azomethine-H method described by Bingham (1982).

The constant capacitance model (Stumm et al., 1980) was used to describe B adsorption behavior on the cell walls as a function of solution pH. The computer program FITEQL, Version 3.2 (Herbelin and Westall, 1996) was used to fit intrinsic B surface complexation constants to the experimental adsorption data. In the constant capacitance model, the dissociation reaction for the surface functional group, XOH (where XOH represents a reactive surface hydroxyl such as a carboxyl or phenol group on the cell wall surface) is defined as:

$$XOH_{(s)} \leftrightharpoons XO_{(s)}^- + H_{(aq)}^+ \tag{1}$$
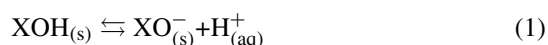
The constant capacitance model assumes that all surface complexes are inner-sphere. Therefore, the surface complexation reactions for B adsorption are defined as:

$$XOH_{(s)} + H_3BO_{3(aq)} \leftrightharpoons XH_2BO_{3(s)} + H_2O \tag{2}$$

$$XOH_{(s)} + H_3BO_{3(aq)} \leftrightharpoons XH_3BO_{4(s)}^- + H_{(aq)}^+ \tag{3}$$

The model application contains the speciation reaction for solution B:

$$H_3BO_{3(aq)} + H_2O \leftrightharpoons B(OH)_{4(aq)}^- + H_{(aq)}^+ \tag{4}$$

The intrinsic equilibrium constants for the dissociation reaction of the surface functional group is:

$$K_-(int) = \frac{[XO^-][H^+]}{[XOH]} \exp(-F\Psi/RT) \tag{5}$$

where F is the Faraday constant ($C \cdot mol_c^{-1}$), Ψ is the surface potential (v), R is the molar gas constant ($J \cdot mol^{-1} \cdot K^{-1}$), T is the absolute temperature (K), and square brackets represent concentrations ($mol \cdot L^{-1}$). The intrinsic equilibrium constants for the B surface complexation are:

$$K_B (int) = \frac{[XH_2BO_3]}{[XOH][H_3BO_3]} \qquad (6)$$

$$K_{B-}(int) = \frac{[XH_3BO_4^-][H^+]}{[XOH][H_3BO_3]} \exp(-F\Psi/RT) \qquad (7)$$

The mass balance expression for the surface functional group is:

$$[XOH]_T = [XOH] + [XOH_2^+] +$$
$$[XO^-]+[XH_2BO_3]+ [XH_3BO_4^-] \qquad (8)$$

where $[XOH]_T$ is the total number of surface sites.

The charge balance expression is:

$$\sigma = [XOH_2^+] -[XO^-]-[XH_3BO_4^-], \qquad (9)$$

where s represents the surface charge ($mol_c \cdot L^{-1}$). The relationship between surface charge and surface potential, Ψ (V) is:

$$\sigma = \frac{CS_AC_p}{F}\Psi, \qquad (10)$$

where S_A is the surface area ($m^2 \cdot g^{-1}$), C_p is the solid suspension density ($g \cdot L^{-1}$), and C is the capacitance ($F \cdot m^{-2}$).

The total number of surface sites was set at a value of 0.17 $mol \cdot kg^{-1}$ as determined by Allan and Jarrell (1989) for maize root cell walls. The surface area was calculated using the equation provided by Allan (1987):

$$S_A = \pi (0.43 \text{ nm})^2 N_A(SOH_T)10^{-18}, \qquad (11)$$

where N_A is Avogadro's number. The capacitance was fixed at $C = 8.3$ $F \cdot m^{-2}$. This value is an average of the capacitance values for 4-d and 28-d root cell walls determined by Allan and Jarrell (1989). A similar value, 8.0 $F \cdot m^{-2}$, was found for surface charging of bacterial cell walls (Fein et al., 1997). High values of capacitance are found for porous materials. To obtain an acceptable model fit to the adsorption data, it was necessary to optimize the dissociation constant, $\log K_-(int)$, along with the B surface complexation constants, $\log K_B(int)$ and $\log K_{B-}(int)$.
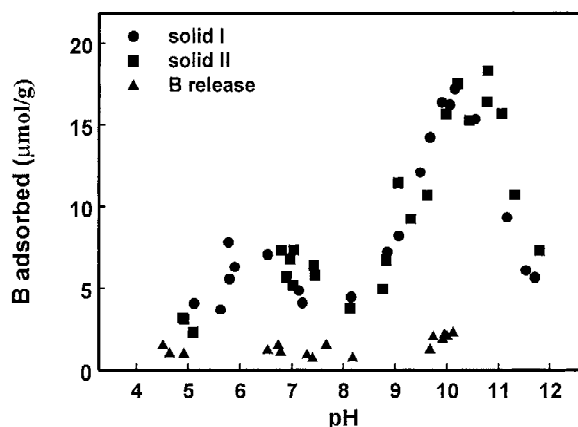

Figure 1. Boron adsorption on and B release from maize cell walls, $C_p = 2$ $g \cdot L^{-1}$, I = 0.1 M NaCl.

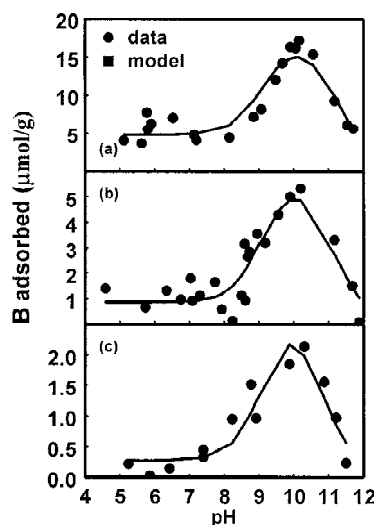*Figure 2.* Fit of the constant capacitance model to B adsorption on maize cell walls, I = 0.1 M NaCl: (a) $C_p = 2$ $g \cdot L^{-1}$, (b) $C_p = 6$ $g \cdot L^{-1}$, (c) $C_p = 18$ $g \cdot L^{-1}$. Circles represent experimental data. Model results are represented by solid lines.

Results and discussion

Boron adsorption on maize cell walls as a function of solution pH is indicated in Figures 1–3. Boron adsorption increased with increasing solution pH in the pH range 4.5–10, exhibited a peak in adsorption around pH 10–10.5, and decreased with further increases in solution pH above pH 10.5. This type of parabolic adsorption behavior is characteristic of B adsorption on oxide minerals (Goldberg and Glaubig, 1985), clay minerals (Goldberg and Glaubig, 1986), soils (Goldberg 1999), and organic materials (Gu and Lowe, 1990). Boron adsorption appeared to be un-
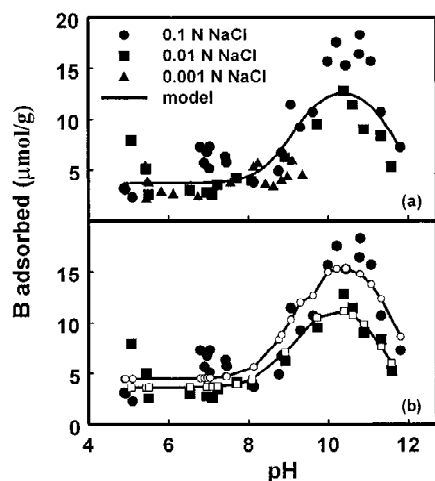
Figure 3. Fit of the constant capacitance model to B adsorption on maize cell walls as a function of ionic strength: (a) model was simultaneously optimized for all three ionic strengths and results are represented by a solid line; (b) model was optimized individually for each ionic strength and results are represented by solid lines.

affected by changes in solid suspension density (see Figure 2). The ionic strength dependence of the B adsorption reaction is indicated in Figure 3. Boron adsorption increased with increasing solution ionic strength. Such behavior is indicative of strong specific adsorption and formation of inner-sphere surface complexes (McBride, 1997).

Reproducibility of B adsorption was evaluated for two batches of cell wall material. As indicated in Figure 1, the magnitude of B adsorption on both materials was similar. Since B is a known constituent of cell walls, we measured the release of B into a background electrolyte solution containing no B. As seen in Figure 1, B release from the cell walls into solution is minimal.

The constant capacitance model was fit to the B adsorption envelopes on maize cell walls optimizing two B surface complexation constants. To obtain acceptable fit, it was necessary to optimize the dissociation constant for the surface functional group along with the B surface constants. Values for all surface complexation constants are presented in Table 1. The large absolute value of the dissociation constant, log K_-(int) suggests that the surface functional group dissociates at high pH, consistent with values for phenolic groups on the cell wall material. The pK_as for phenolic groups on humic acids fall in the range of 9–11 (Perdue, 1985). The fit of the constant capacitance model to B adsorption is indicated in Figures 1 and 2. In general, the model was well able to describe the adsorption envelopes for all conditions of solution pH, solid suspension density, solution ionic strength, and capacitance. The model was able to fit B adsorption for three different solid suspension densities equally well (see Figure 2) with very similar values of surface complexation constants (see Table 1).

The constant capacitance model was found to be insensitive to changes in capacitance in the range of $7.8 - 8.8$ F·m^{-2} as evidenced by invariance in the values of the surface complexation constants. Because of this result, further model fits were obtained with the capacitance fixed at a value of 8.3 F·m^{-2}.

The constant capacitance model assumes the constant ionic medium reference state and therefore cannot describe changes in adsorption occurring with changes in background electrolyte concentration. The modeling result indicated in Figure 3a is ionic strength invariant when B adsorption is optimized simultaneously for three different ionic strengths. When optimizing B adsorption individually at each ionic strength, the constant capacitance model was well able to describe the data (see Figure 3b). Values of the B surface complexation constants were very similar for all three ionic strengths. However, the absolute value of the dissociation constant, log K_-(int) was considerably smaller for the lowest ionic strength, indicating dissociation of the surface functional group at a lower pH value. This result suggests that changes in ionic strength influence the charging behavior of the cell wall functional groups.

Our application of the constant capacitance model contains the assumption that B adsorption takes place at one set of homogeneous reactive surface functional groups. Clearly, cell walls are complex multisite mixtures having a variety of functional groups. Thus, the intrinsic surface complexation constants determined in this study represent average composite values for all sets of reactive sites. The large absolute value of the dissociation constant is consistent with phenolic groups being the B reactive surface functional groups in the cell walls.

Our results indicated that B binding to maize cell walls can be described using a physico-chemical description of the B adsorption process. Experiments with diverse cultivars and plant species are needed to determine whether differences in B binding capacity of cell walls can explain differences in B tolerance in plants.

Table 1. Constant capacitance model surface complexation constants

Surface	Solid suspension density (g·L^{-1})	Background electrolyte (mol NaCl·L^{-1})	Capacitance (F·m^{-2})	log K$_B$(int)	log K$_{B-}$(int)	log K$_-$(int)
Solid I	2.0	0.1	7.8	1.83	−6.71	−11.41
Solid I	2.0	0.1	8.8	1.83	−6.72	−11.39
Solid I	2.0	0.1	8.3	1.83	−6.72	−11.40
Solid I	6.0	0.1	8.3	1.05	−7.21	−11.23
Solid I	18.0	0.1	8.3	0.56	−7.56	−10.94
Solids I &II	2.0	0.1	8.3	1.80	−6.74	−11.65
Solid II	2.0	0.1	8.3	1.77	−6.74	−11.91
Solid II	2.0	0.01	8.3	1.70	−6.90	−11.66
Solid II	2.0	0.001	8.3	1.67	−7.06	−9.80
Solid II	2.0	0.1, 0.01, 0.001	8.3	1.70	−6.86	−11.96

Acknowledgements

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