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Chapter 3

Reactions of boron with soils

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Abstract

Boron is an essential micronutrient for plants, but the range between deficient and toxic B concentration is smaller than for any other nutrient element. Plants respond directly to the activity of B in soil solution and only indirectly to B adsorbed on soil constituents. Soil factors affecting availability of B to plants are: pH, texture, moisture, temperature, organic matter and clay mineralogy. Boron adsorbing surfaces in soils are: aluminium and iron oxides, magnesium hydroxide, clay minerals, calcium carbonate, and organic matter. Boron adsorption reactions can be described empirically using the Langmuir adsorption isotherm equation, the Freundlich adsorption isotherm equation, and the phenomenological Keren model. Chemical models such as the constant capacitance model, the triple layer model, and the Stern VSC-VSP model can describe B adsorption over changing conditions of solution pH and B concentration. Boron desorption reactions often exhibit hysteresis. The rate of B desorption can be described using the first order rate equation, the Elovich reaction rate equation, and the power function equation.

Introduction

Boron is an essential micronutrient element required for the normal growth of plants. Of all micronutrient deficiencies in plants, B deficiency is the most widespread in the USA (Sparr, 1970). Alfalfa (*Medicago sativa*) is most prone to B deficiency and receives more B fertiliser than any other economic crop (Murphy and Walsh, 1972). Boron deficiency is most likely in coarse textured soils in humid regions. Temporary B deficiency can be triggered by liming of acid soils because of increased B adsorption at higher soil pH (Reisenauer et al., 1973).

Plants vary in their B requirement, but the range between deficient and toxic soil solution concentrations of B is smaller than for any other nutrient element. Both deficient and toxic levels of B in the soil solution can occur during a single growing season (Reisenauer et al., 1973). In arid and semi-arid areas, B toxicity results from high levels of B in soils and from additions of B via the irrigation water (Nable et al., Chapter 12). In saline soils, lack of drainage leads to excessive concentrations of B in the soil solution. Land application of coal ash residues is often limited by their high B content (Adriano et al., 1980). Reclamation of high B soils requires about three times as much water as reclamation of saline soils (Keren and Bingham, 1985).

Compared with other nutrient elements, the chemistry of B in soils is very simple. Boron does not undergo oxidation-reduction reactions or volatilisation reactions in soils. Boric acid is a very weak, monobasic acid that acts as a Lewis acid by accepting a hydroxyl ion to form the borate anion (Figure 1). Boron containing minerals are either very insoluble (tourmaline) or very soluble (hydrated B minerals) and generally do not control the solubility of B in soil solution (Goldberg, 1993). The B concentration in the soil solution is generally controlled by B adsorption reactions, as is the amount of water soluble B available for plant uptake. Plants respond only to the B activity in soil solution; B adsorbed by the soil surfaces is not perceived as toxic by plants (Keren et al., 1985a, 1985b; Ryan et al., 1977). Factors affecting B availability and extent of B adsorption in soils are solution pH, soil texture, soil moisture, and temperature.

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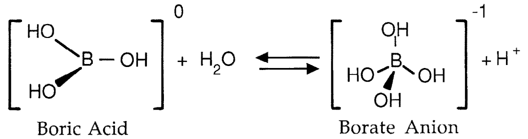

Figure 1. Dissociation of boric acid.

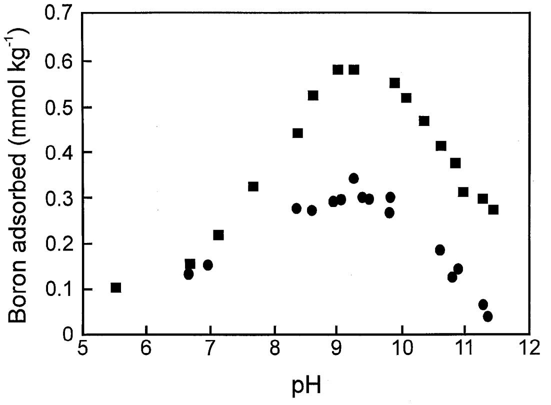

Figure 2. Boron adsorption on a surface (■) and a subsurface (●) sample of an arid zone soil as a function of pH.

Factors affecting boron availability in soils

pH

One of the most important factors affecting the availability of B in soils is pH. With increasing soil solution pH, B becomes less available to plants. Therefore, application of lime to acid soils can result in B deficiency symptoms in plants. Soluble B content in soils was highly significantly correlated with solution pH (Berger and Truog, 1945; Elrashidi and O’Connor, 1982). Boron uptake by plants at identical water soluble B content was greater at lower soil solution pH (Wear and Patterson, 1962).

Boron adsorption on soils is very dependent on solution pH (Figure 2). Boron adsorption by soils increased as a function of solution pH in the range of pH 3 to 9 (Barrow, 1989; Bingham et al., 1971; Keren et al., 1985a; Lehto, 1995; Mezuman and Keren, 1981; Schalscha et al., 1973) and decreased in the range of pH 10 to 11.5 (Goldberg and Glaubig, 1986a). Boron adsorption maxima were significantly positively correlated with solution pH (Evans, 1987; Okazaki and Chao, 1968).

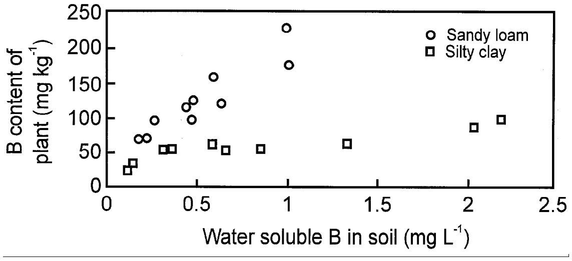

Figure 3. Boron uptake by alfalfa (*Medicago sativa*) as a function of water soluble B for two soil textures. Adapted from Wear and Patterson (1962).

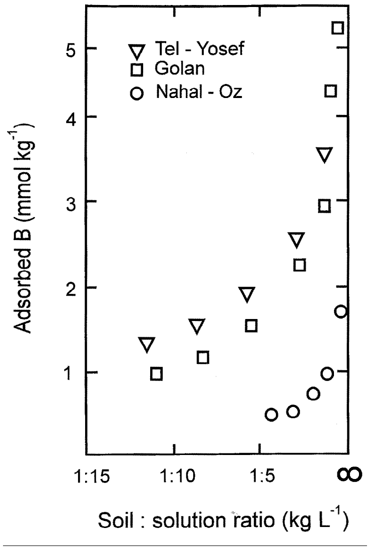

Figure 4. Boron adsorption as a function of soil to solution ratio for three soils. Adapted from Mezuman and Keren (1981).

Soil texture

Because coarse textured soils often contain less available B than fine textured soils, B deficiency often occurs in plants growing in sandy soils (Fleming, 1980; Gupta, 1968). Native B was significantly positively correlated with soil clay content (Elrashidi and O’Connor, 1982). At identical water soluble B content, plant B uptake was greatest for the most coarse textured soil (Wear and Patterson, 1962; Figure 3). Adsorbed B is dependent on soil texture, and increases with increasing clay content (Bhatnager et al., 1979; Elrashidi and O’Connor, 1982; Mezuman and Keren, 1981; Wild and Mazaheri, 1979). Boron adsorption maxima increased with increasing clay content (Biggar and Fireman, 1960; Goldberg and Glaubig, 1986a; Nicholaichuk et al., 1988; Singh, 1964). A highly sig-

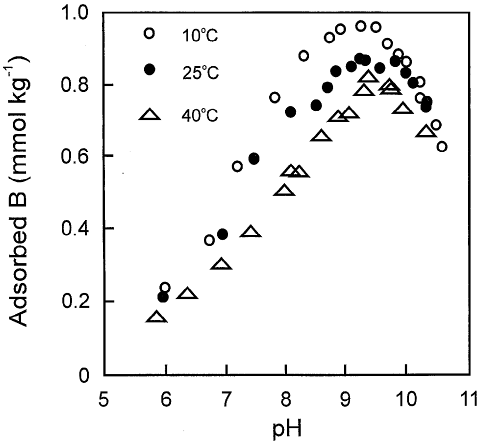

Figure 5. Boron adsorption on an arid zone soil as a function of temperature. From Goldberg et al. (1993a).

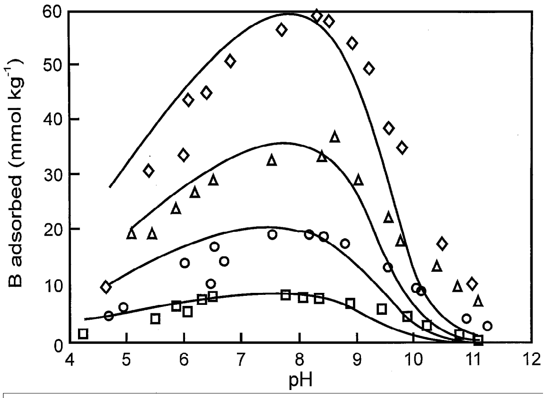

Figure 6. Boron adsorption on an aluminium oxide as a function of pH. Fit of the constant capacitance model to B adsorption from solutions containing 2 mg L^{-1} B (□), 5 mg L^{-1} B (○), 10 mg L^{-1} B (Δ), and 20 mg L^{-1} B (◊). Model results are represented by solid lines. From Goldberg and Glaubig (1988).

nificant correlation was found between soil content of the clay minerals kaolinite, montmorillonite, and chlorite and the B adsorption maximum.

Soil moisture

Boron availability generally decreases as soils dry, making B deficiency in plants more likely (Fleming, 1980). This may be because plants encounter reduced amounts of available B when extracting moisture from lower depths during dry conditions (Fleming, 1980). Diffusivity of B decreased with decreasing water content because drying reduces soil solution mobility and increases the diffusion path length (Scott et al., 1975). However, total diffusible B from repeated extractions was independent of water content (Sulaiman and Kay, 1972). Adsorbed B was independent of variations in soil moisture content from 50 to 100 percent of field capacity in one study (Gupta, 1968) and increased with decreasing soil water content in another (Mezuman and Keren, 1981; Figure 4). Wetting and drying cycles increased the amount of B fixation (Biggar and Fireman, 1960). The effect of drying became more pronounced with increasing additions of B (Biggar and Fireman, 1960).

Temperature

Boron adsorption increases with increasing soil temperature. However, this may be due to an interactive effect of soil temperature with soil moisture since B deficiency is associated with dry summer conditions (Fleming, 1980). Boron adsorption decreased as a function of temperature in the range of 10 – 40 °C on soils dominant in crystalline minerals (Biggar and Fireman, 1960; Goldberg et al., 1993a; Figure 5). In contrast, B adsorption increased slightly as the temperature of an amorphous soil was increased from 10 to 40 °C (Bingham et al., 1971).

Boron adsorbing surfaces in soils

Oxides

Aluminium and iron oxides play an important role in B adsorption behaviour on soils (Bingham, et al., 1971; Elrashidi and O'Connor, 1982; Harada and Tamai, 1968). Boron adsorption is highly significantly correlated with the aluminium oxide content of soils (Bingham et al., 1971; Harada and Tamai, 1968). Percent iron oxide was a significant variable in multiple regression equations explaining the variance in adsorbed B, soluble B, and total B for soils (Elrashidi and O'Connor, 1982).

Numerous studies have investigated B adsorption by various aluminium and iron oxides both crystalline and amorphous (Bloesch et al., 1987; Choi and Chen, 1979; de Bussetti et al., 1995; Goldberg and Glaubig, 1985, 1988; Goldberg et al., 1993a, 1993b, 1996; Hatcher et al., 1967; Keren and Gast, 1983; McPhail et al., 1972; Metwally et al., 1974; Scharrer et al., 1956; Sims and Bingham, 1968; Su and Suarez, 1995;

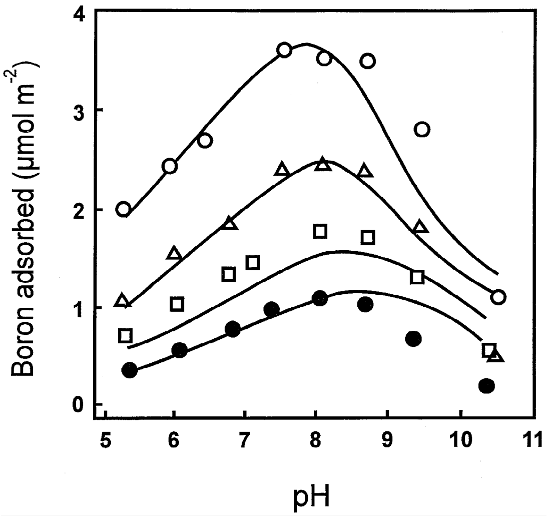

Figure 7. Boron adsorption on an iron oxide as a function of pH. Fit of the Stern VSC-VSP model to B adsorption from solutions containing 139 mg L^{-1} B (●), 270 mg L^{-1} B (☐), 525 mg L^{-1} B (Δ), and 921 mg L^{-1} B (○). Model results are represented by solid lines. From Bloesch et al. (1987).

Toner and Sparks, 1995). Boron adsorption on both crystalline and amorphous aluminium and iron oxides increased with increasing pH up to an adsorption maximum at pH 6 to 8 for aluminium oxides and pH 7 to 9 for iron oxide (Bloesch et al., 1987; Choi and Chen, 1979; Goldberg and Glaubig, 1985; McPhail et al., 1972; Metwally et al., 1974; Scharrer et al., 1956; Sims and Bingham, 1968; Su and Suarez, 1995). Above the maximum, B adsorption decreased with increasing pH (Figures 6 and 7). Boron adsorption was greatest on freshly precipitated solids and decreased with aging due to increasing crystallinity (Hatcher et al., 1967; Sims and Bingham, 1968). Boron adsorption per gram was greater for aluminium than iron oxides (Goldberg and Glaubig, 1985; Scharrer et al., 1956; Sims and Bingham, 1968). This is likely due to the higher surface area of aluminium oxides, since adsorption per square metre was similar in magnitude for aluminium and iron oxides (Goldberg and Glaubig, 1985). Boron adsorption on oxide minerals occurred rapidly, being virtually complete after one day of reaction time (Choi and Chen, 1979; Scharrer et al., 1956).

The mechanism of B adsorption on aluminium and iron oxide minerals is considered to be ligand exchange with reactive surface hydroxyl groups (Goldberg et al., 1993b; McPhail et al., 1972; Sims and Bingham, 1968; Su and Suarez, 1995). Ligand exchange with surface hydroxyl groups is a mechanism whereby anions become specifically adsorbed on mineral surfaces. This specific adsorption produces a shift in the point of zero charge (PZC) of the mineral to a more acid pH value. Boron adsorption occurs specifically since it produces a shift in PZC of aluminium and iron oxides (Alwitt, 1972; Beyrouty et al., 1984; Blesa et al., 1984; Fricke and Leonhardt, 1950; Goldberg et al., 1993b; Su and Suarez, 1995). Specifically adsorbed ions are held in inner-sphere surface complexes that contain no water between the adsorbing ion and the surface functional group. Kinetic experiments using pressure jump relaxation indicated that B adsorbs as an inner-sphere surface complex on aluminium oxide via ligand exchange of borate with surface hydroxyl groups (Toner and Sparks, 1995). Fourier transform infrared spectroscopic analyses have shown that B is adsorbed via ligand exchange as both $B(OH)_3^0$ and $B(OH)_4^-$ species on amorphous aluminium and iron oxide (Su and Suarez, 1995).

Boron adsorption on aluminium and iron oxides as a function of pH was exothermic, decreasing with increasing temperature from 5 – 40 °C (de Bussetti et al., 1995; Goldberg et al., 1993a; Su and Suarez, 1995). This effect was only significant near the adsorption maximum. Specific ion adsorption is expected to be exothermic (Helferrich, 1962). Boron adsorption on an iron oxide was independent of solution ionic strength; while B adsorption on an aluminium oxide decreased with increasing ionic strength (Goldberg et al., 1993b).

Competing ions such as silicate, sulfate, phosphate, and oxalate decreased the magnitude of B adsorption on oxides (Bloesch et al., 1987; Choi and Chen, 1979; de Bussetti et al., 1995; Goldberg and Glaubig, 1988; McPhail et al., 1972; Metwally et al., 1974). The effect of competing ions on B adsorption can be slight, in the case of sulfate, or substantial in the case of phosphate (Bloesch et al., 1987; Metwally et al., 1974). The ability of competing anions to leach adsorbed B from oxides increased in the order: chloride $<$ sulfate $<$ arsenate $<$ phosphate (Metwally et al., 1974). Significant silicate adsorption produced only a slight decrease in B adsorption by aluminium oxide suggesting that some B sorption sites show B preference (Goldberg and Glaubig, 1988).

Magnesium hydroxide can remove appreciable amounts of B from solution (Rhoades et al., 1970a). Due to magnesium hydroxide coatings, silicate minerals containing mainly magnesium in their chemical formulas adsorbed more B than a silicate without magnesium in its chemical formula (Rhoades et al., 1970a). The appreciable B sorption capacity of the sand and silt

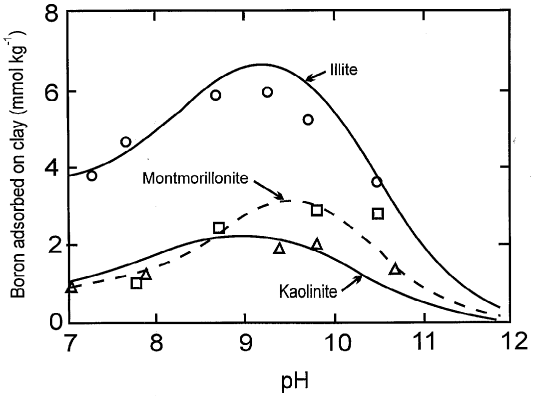

Figure 8. Boron adsorption on clay minerals as a function of pH. Fit of the phenomenological Keren model to B adsorption. Model results are represented by lines. From Keren and Mezuman (1981).

fractions of arid zone soils may result from clusters and coatings of magnesium hydroxide on silicate minerals (Rhoades et al., 1970a).

Clay minerals

Layer silicate clay minerals are important B adsorbing surfaces in soils (Brockamp, 1973; Couch and Grim, 1968; Fleet, 1965; Goldberg and Glaubig, 1986b; Goldberg et al., 1993a, 1993b, 1996; Harder, 1961; Hingston, 1964; Jasmund and Lindner, 1973; Keren and Gast, 1981; Keren and Mezuman, 1981; Keren and O'Connor, 1982; Keren and Sparks, 1994; Keren and Talpaz, 1984; Keren et al., 1981, 1994; Mattigod et al., 1985; Porrenga, 1967; Scharrer et al., 1956; Sims and Bingham, 1967; Singh, 1971). Clay minerals exhibit increasing B adsorption with increasing solution pH with adsorption maxima occurring at pH 8 to 10 (Hingston, 1964; Mattigod et al., 1985; Scharrer et al., 1956; Sims and Bingham, 1967); B adsorption decreases with increasing pH above the maximum (Figure 8). For clay minerals, the order of B adsorption per gram is: kaolinite < montmorillonite < illite (Harder, 1961; Hingston, 1964; Jasmund and Lindner, 1973; Keren and Mezuman, 1981; Scharrer et al., 1956; Sims and Bingham, 1967).

The rate of B adsorption on clay minerals consists of a fast adsorption reaction and a slow fixation reaction. Short term experiments have shown that B adsorption reaches equilibrium in less than one day (Hingston, 1964; Kerren et al., 1981; Scharrer et al., 1956). Long term experiments have shown that fixation of B increased even after six months of reaction time (Harder, 1961; Jasmund and Lindner, 1973). Boron adsorption by clay minerals is considered to be a two step process. Initially, B adsorbs onto the particle edges, subsequently migrates, and incorporates structurally into tetrahedral sites replacing structural silicon and aluminium (Couch and Grim, 1968; Fleet, 1965; Harder, 1961). The mechanism of the B adsorption step is considered to be ligand exchange with surface hydroxyl groups on the clay particle edges (Couch and Grim, 1968; Goldberg et al., 1993b; Keren and Sparks, 1994; Keren and Talpaz, 1984; Keren et al., 1994).

The effect of temperature on B adsorption by clays has been investigated (Couch and Grim, 1968; Goldberg et al., 1993a; Harder, 1961; Jasmund and Lindner, 1973; Singh, 1971). For a very short reaction time of two hours, B adsorption in the pH range of 5.5 – 9.5 decreased with increasing temperature (Goldberg et al., 1993a). Boron adsorption for longer reaction times of twelve hours to sixty days increased with increasing temperature (Couch and Grim, 1968; Jasmund and Lindner, 1973; Singh, 1971). These results suggest that initial adsorption of B is exothermic while the subsequent B fixation reaction is endothermic.

Boron adsorption on clays increased with increasing ionic strength of the solution (Couch and Grim, 1968; Fleet, 1965; Goldberg et al., 1993b; Keren and O'Connor, 1982; Keren and Sparks, 1994). The ionic strength effect was greater for sodium clay than for calcium clay (Keren and O'Connor, 1982) and was greatest around the B adsorption maximum (Goldberg et al., 1993b).

Decreases in water content decreased B adsorption on clays (Keren and Mezuman, 1981). Wetting and drying cycles increased B fixation with the greatest increase occurring during the first wetting and drying cycle (Keren and Mezuman, 1981).

Competing anions affect the magnitude of B adsorption on clays (Brockamp, 1973; Goldberg and Glaubig, 1986b; Goldberg et al., 1996; Jasmund and Lindner, 1973). The presence of chloride, nitrate, and sulfate had little effect on B adsorption on clays; the presence of phosphate, however, appreciably reduced B adsorption (Jasmund and Lindner, 1973). The magnitude of B adsorption on kaolinite was affected slightly while B adsorption on montmorillonite was completely unaffected by substantial silicate adsorption suggesting that the majority of B adsorbing sites are specific to B (Goldberg and Glaubig, 1986b).

The magnitude of B adsorption on clay minerals is affected by the exchangeable cation (Keren and Gast, 1981; Keren and Mezuman, 1981; Keren and

O’Connor, 1982; Mattigod et al., 1985). Calcium clays adsorbed more B than sodium and potassium clays (Keren and Gast, 1981; Keren and O’Connor, 1982; Mattigod et al., 1985). An explanation for this result is that calcium 2:1 clays occur as tactoids consisting of several clay particles while the sodium forms exist in solution as single particles (Keren and Gast, 1981). In tactoids, the diffuse double layer and negative electric field from the planar surfaces is less extensive, making the edge sites of calcium clays more accessible to adsorbing borate anions than those of sodium clays (Keren and Gast, 1981). An alternative explanation for increased B adsorption in the presence of calcium is the formation and adsorption of the calcium borate ion pair (Mattigod et al., 1985).

On a per gram basis clay minerals adsorb significantly less B than do most oxide minerals. It may be more appropriate to compare B adsorption capacity on a surface area basis. However, since B adsorbs on the edges of clay minerals and edge surface areas of clays are difficult to determine, this comparison is not readily available.

Calcium carbonate

Application of lime increases B fixation by soils because it raises the soil solution pH. In addition to its effect on soil pH, calcium carbonate also acts as an important B adsorbing surface in calcareous soils (Elseewi, 1974; Elseewi and Elmalky, 1979; Goldberg and Forster, 1991). Boron adsorption was greater on soils having higher calcium carbonate content (Elrashidi and O’Connor, 1982; Elseewi, 1974). Acid soluble B was highly significantly correlated with calcium carbonate content of soils (Elseewi and Elmalky, 1979). Retention of B on calcium carbonate occurs via an adsorption mechanism (Ichikuni and Kikuchi, 1972). The mechanism could be exchange with carbonate groups.

The magnitudes of the B adsorption maxima for soil samples treated to remove calcium carbonate were statistically significantly lower than those for untreated soil samples indicating that calcium carbonate acts as an important sink for B adsorption in calcareous soils (Goldberg and Forster, 1991). Boron adsorption on reference calcites increased with increasing solution pH from pH 6 to 9, exhibited a maximum at pH 9.5, and decreased with increasing solution pH from pH 10 to 11 (Goldberg and Forster, 1991; Figure 9).

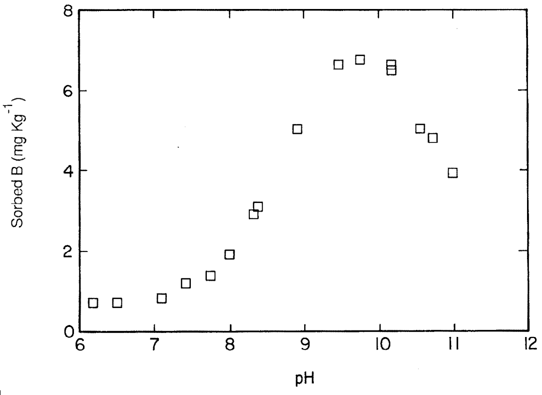

Figure 9. Boron adsorption on a reference calcite as a function of pH. From Goldberg and Forster (1991).

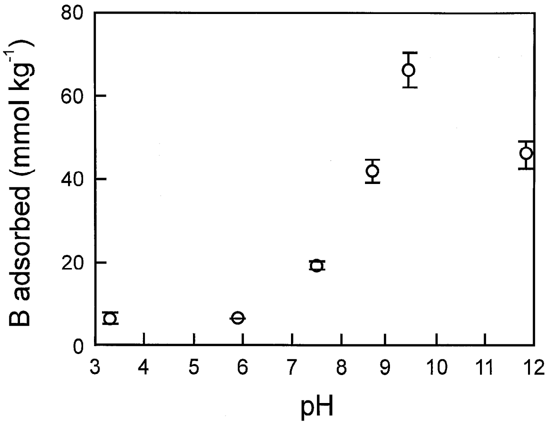

Figure 10. Boron adsorption on a humic acid extracted from soil. From Gu and Lowe (1990).

Organic matter

Organic matter is an important soil constituent affecting the availability of B. Native soil B and hot water soluble B were highly significantly correlated with organic carbon content (Berger and Truog, 1945; Elrashidi and O’Connor, 1982; Gupta, 1968; Miljkovic et al., 1966). Adsorbed B and B adsorption maxima were highly significantly correlated with organic carbon content (Elrashidi and O’Connor, 1982; Evans, 1987; Harada and Tamai, 1968).

Humus extracted from a soil retained significant amounts of B and was considered to play an important role in B adsorption (Parks and White, 1952). Soil organic matter adsorbs more B than mineral soil constituents on a weight basis (Gu and Lowe, 1990; Yermiyaho et al., 1988)). Boron adsorption on a min-

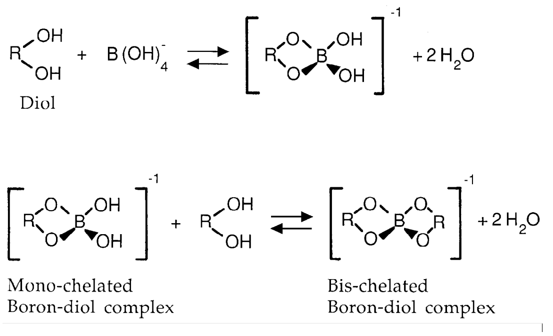

Figure 11. Formation of B-diol complexes.

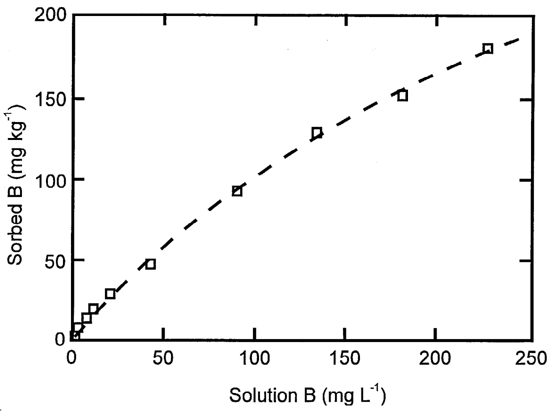

Figure 12. Fit of the Langmuir adsorption isotherm equation to B adsorption on a calcareous soil. Model results are represented by a dashed line. Adapted from Goldberg and Forster (1991).

eral soil increased with increasing additions of composted organic matter (Yermiyahu et al., 1995). The presence of organic material can also occlude B reactive adsorption sites on clays (Gu and Lowe, 1992) and soils (Harada and Tamai, 1968; Marzadori et al., 1991). Boron adsorption on an organic soil (Huettl, 1976; Lehto, 1995) and composted organic matter increased with increasing pH (Yermiyaho et al., 1988). Adsorption on a soil humic acid increased with increasing pH up to a maximum near pH 9, and decreased with increasing pH above 9 (Gu and Lowe, 1990, Figure 10). Boron adsorption on composted organic matter occurred rapidly, reaching equilibrium after three hours and increased with increasing solution ionic strength (Yermiyaho et al., 1988).

Ligand exchange is a possible mechanism for B sorption by organic matter (Yermiyaho et al., 1988). Boron–diol complexes may form with the breakdown products of soil organic matter (Parks and White, 1952); α-hydroxy carboxylic acid groups may act in B sorption on organic matter (Huettl, 1976). Figure 11 shows the formation reactions of mono-chelated and bis-chelated B-diol complexes. The formation of these complexes from reaction of borate with polyhydroxy compounds has been observed using nuclear magnetic resonance spectroscopy (Coddington and Taylor, 1989).

Modeling of boron adsorption

Empirical models

Adsorption isotherm equation

Empirical models provide descriptions of experimental adsorption data without a theoretical basis. Boron adsorption reactions on oxides, clay minerals, and soil materials have historically been described using adsorption isotherm equations (Choi and Chen, 1979; Elrashidi and O'Connor, 1982; Evans, 1987; Goldberg and Forster, 1991; Mondal et al., 1993; Nicholaichuk et al., 1988; Singh, 1971). The most popular are the Langmuir and Freundlich adsorption isotherm equations but Temkin and Brunauer–Emmett–Teller (BET) adsorption isotherm equations have also been used (Mondal et al., 1993).

The Langmuir adsorption isotherm equation was developed to describe gas adsorption onto clean solids, but has often been used to describe B adsorption by soil materials. The equation and its linear forms are provided elsewhere (e.g. Goldberg, 1993). Strictly, the Langmuir adsorption isotherm equation is obeyed only for a uniform adsorbent surface without lateral interactions, implying a constant free energy of adsorption (Brunauer et al., 1967). The Langmuir adsorption isotherm has been used to describe B adsorption on aluminium and iron oxide (McPhail et al., 1972), clay minerals (Gu and Lowe, 1992; Hingston, 1964; Singh, 1971) calcite (Goldberg and Forster, 1991), humic acids (Gu and Lowe, 1990), and soils (Bhatnagar et al., 1979; Biggar and Fireman, 1960; Bingham et al., 1971; Elrashidi and O'Connor, 1982; Evans, 1987; Hatcher and Bower, 1958; Marzadori et al., 1991; Mondal et al., 1993; Nicholaichuk et al., 1988; Okazaki and Chao, 1968; Schalscha et al., 1973; Singh, 1971). For many studies, the Langmuir adsorption isotherm equation was able to describe B adsorption only under conditions of low solution B concentration (Bhatnagar et al., 1979; Biggar and Fireman, 1960; Elrashidi and O'Connor, 1982; Goldberg and Forster, 1991;

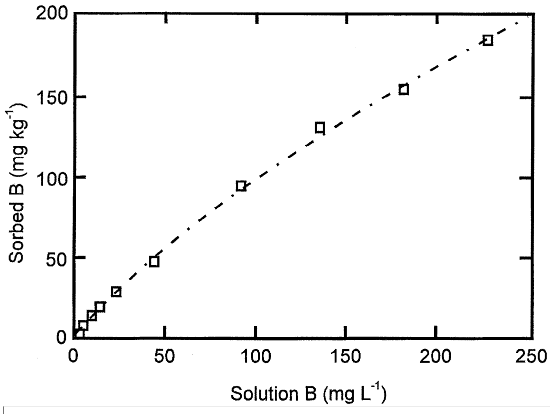

Figure 13. Fit of the Freundlich adsorption isotherm equation to B adsorption on a calcareous soil. Model results are represented by a dashed-dotted line. Adapted from Goldberg and Forster (1991).

Hingston, 1964; McPhail et al., 1972). The ability of the Langmuir adsorption isotherm equation to describe B adsorption on soil is indicated in Figure 12.

The Freundlich adsorption isotherm equation has often been used to describe B adsorption by soil materials. The equation and its linear form are provided elsewhere (e.g Goldberg, 1993). In the Freundlich adsorption isotherm equation, the affinity terms are distributed approximately log normally implying heterogeneity of B adsorbing sites (Sposito, 1984). The Freundlich adsorption isotherm equation is strictly valid only for adsorption data at low concentrations (Sposito, 1984), but has often been used to describe B adsorption by soils over the entire concentration range studied. The Freundlich adsorption isotherm has been used to describe B adsorption on aluminium oxide (Choi and Chen, 1979), clay minerals (Couch and Grim, 1968; Fleet, 1965; Jasmund and Lindner, 1973; Singh, 1971), calcite (Goldberg and Forster, 1991), and soils (Bhatnagar et al., 1979; Elrashidi and O'Connor, 1982; Evans, 1987; Goldberg and Forster, 1991; Lehto, 1995; Nikolaichuk et al., 1988). The ability of the Freundlich adsorption isotherm equation to describe B adsorption on soil is indicated in Figure 13.

Although the adsorption isotherm equations are often excellent at describing B adsorption, they are simply numerical relationships used to describe data (Harter and Smith, 1981). Independent experimental evidence for adsorption must be present before any chemical meaning can be assigned to adsorption isotherm equation parameters (Veith and Sposito, 1977). The adherence of experimental sorption data to the Langmuir or Freundlich equations provides no information about the chemical mechanism of reaction (Sposito, 1982).

In linearising adsorption isotherm equations, all data points are not given equal weighting and the variances of some of the values are disproportionately increased during the transformation (Barrow, 1978). Direct fitting of adsorption data using non-linear least squares methods avoids the difficulties of changes in error distributions and biased parameters associated with linear transformations (Kinniburgh, 1986). Non-linear least squares fits of B adsorption data were much improved over linear transformations as measured by the coefficient of determination, r^2 (Goldberg and Forster, 1991).

Since the use of adsorption isotherm equations is essentially a curve fitting procedure, the parameters obtained are only valid for the conditions under which the experiment was conducted. Prediction of B adsorption behaviour under changing conditions of soil solution B concentration, pH, and ionic strength is impossible.

Keren model

The Keren model is a phenomenological equation developed to describe B adsorption on clay mineral surfaces (Keren and Gast, 1981; Keren and Mezuman, 1981; Keren and O'Connor, 1982; Keren et al., 1981). In this model boric acid, $B(OH)_3^0$, borate ion, $B(OH)_4^-$, and hydroxyl ion, OH^-, all are assumed to compete for the same adsorption sites on the clay surface. Equations for the adsorption of these species and the total amount of B adsorbed are provided elsewhere (Keren et al., 1981).

One of the advantages of the Keren model is that it includes the pH variable and can therefore describe B adsorption behaviour over changing conditions of solution pH (Figure 8). The Keren model was able to fit B adsorption at several pH values and suspension densities using the same set of constants. The Keren model has been used to describe B adsorption by montmorillonite, kaolinite, illite, pyrophyllite, hydroxy aluminium, composted organic matter, and soils (Keren and Gast, 1983; Keren and Mezuman, 1981; Keren and Sparks, 1994; Keren et al., 1981, 1994; Mezuman and Keren, 1981; Yermiyaho et al., 1988, Yermiyahu et al., 1995). No physical significance can be attributed to the absolute values of the constants obtained with the Keren model (Keren et al., 1981; Yermiyaho et al., 1988).

Chemical surface complexation models

Introduction

Chemical models provide a molecular description of adsorption using an equilibrium approach. Chemical models of B adsorption have generally concentrated on the variable charge sites of oxide minerals. Chemical modeling of B adsorption at the oxide solution interface has been successful using various surface complexation models. In these models, B adsorption occurs via complex formation with surface hydroxyl groups on oxide minerals and edges of clay minerals.

Surface complexation models use an equilibrium approach with mass action and mass balance equations (Westall, 1980). Although these models are very successful at describing data over a wide range of experimental conditions, they cannot uniquely describe the physical nature of the interface (Westall and Hohl, 1980). Surface complexation models define surface species, chemical reactions, mass balances, and charge balance and calculate thermodynamic properties such as activity coefficients and equilibrium constants mathematically. The most significant advancement of surface complexation models is the consideration of the charge on both the adsorbate ion and the adsorbent surface. For this reason the models have wide applicability and predictive capability over changing conditions of solution B concentration, pH, and ionic strength.

Constant capacitance model

The constant capacitance model of the oxide aqueous solution interface (Stumm et al., 1980) has been applied to describe B adsorption on aluminium and iron oxides, clay minerals, and soils (Goldberg and Glaubig, 1985, 1986a, 1986b, 1988; Goldberg et al., 1993b; Toner and Sparks, 1995). Surface reactions, equilibrium constants, mass balance, and charge balance for the application of the constant capacitance model to B adsorption are provided elsewhere (Goldberg, 1993). In the constant capacitance model, anion adsorption is assumed to occur via a ligand exchange mechanism with the reactive surface functional group, SOH; no surface complexes are formed with ions in the background electrolyte. Specifically adsorbed ions reside in the surface plane of adsorption along with protons and hydroxyl ions. The constant capacitance model was able to describe B adsorption as a function of pH at four initial solution B concentrations using the same B surface complexation constant (Goldberg and Glaubig, 1988; Figure 6).

The ability of the constant capacitance model to predict B adsorption as a function of solution pH represents a major advantage over the Langmuir and Freundlich adsorption isotherm equations. In the case of oxide minerals, the constant capacitance model has this predictive capability using one less adjustable parameter than the Langmuir and Freundlich isotherm equations. In modeling B adsorption on clay minerals and soils, constants for the protonation and dissociation reactions of the surface functional group were also adjusted (Goldberg and Glaubig, 1986a, 1986b). In some cases, chemically unrealistic values of the protonation-dissociation constants were obtained potentially reducing the chemical significance of the model application to a curve fitting procedure (Goldberg and Glaubig, 1986a, 1986b).

Triple layer model

The triple layer model (Davis and Leckie, 1978, 1980; Davis et al., 1978) has been applied to describe B adsorption on aluminium and iron oxide and kaolinite (Blesa et al., 1984; Singh and Mattigod, 1992; Toner and Sparks, 1995). In contrast to the constant capacitance model, in the triple layer model anion adsorption can occur specifically via ligand exchange or nonspecifically through the formation of outer-sphere surface complexes with the reactive surface functional group, SOH. Outer-sphere surface complexes contain at least one water molecule between the adsorbing ion and the surface functional group. The triple layer model always includes outer-sphere surface complexation reactions for ions of the background electrolyte. Surface reactions, equilibrium constants, mass balance, and charge balances for the application of the triple layer model to B adsorption are provided elsewhere (Goldberg, 1993).

The triple layer model was able to describe B adsorption on aluminium and iron oxide and kaolinite using a ligand exchange mechanism (Blesa et al., 1984; Singh and Mattigod, 1992; Toner and Sparks, 1995; Figure 14). In describing B adsorption on iron oxide (Blesa et al., 1984) and kaolinite (Singh and Mattigod, 1992), additional surface complexes formed between the background electrolyte cations and inner-sphere B surface complexes were included. The model was less successful in describing B adsorption on iron oxide using an outer-sphere adsorption mechanism (Blesa et al., 1984). The triple layer model could describe B adsorption on an aluminium oxide using an outer-sphere adsorption mechanism. Howev-

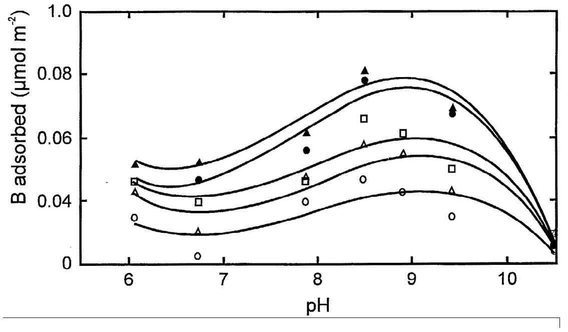

Figure 14. Fit of the triple layer model to B adsorption on a clay mineral from solutions containing 2 mg L^{-1} B (○), 4 mg L^{-1} B (Δ), 6 mg L^{-1} B (□), 8 mg L^{-1} B (●), and 10 mg L^{-1} B (▲). Model results are represented by solid lines. From Singh and Mattigod (1992).

er, only the inner-sphere adsorption mechanism could successfully describe both equilibrium and pressure jump kinetic data (Toner and Sparks, 1995). Experimental surface charge density data on iron oxide as a function of pH could be described using the triple layer model (Blesa et al., 1984). Unlike the constant capacitance model, the triple layer model can describe adsorption as a function of changing solution ionic strength since it considers surface complexation of the background electrolyte.

Stern variable surface charge variable surface potential model

The Stern variable surface charge variable surface potential (VSC-VSP) model (Barrow et al., 1980; Bowden et al., 1977, 1980). has been applied to describe B adsorption on aluminium oxide, iron oxide, and soil (Barrow, 1989; Bloesch et al., 1987). Equations for the application of the Stern VSC-VSP model to B adsorption are provided elsewhere (Goldberg, 1993). In contrast to the previous two models, the surface functional group is defined as OH–S–OH_2, allowing only one protonation or dissociation to occur for every two surface hydroxyl groups (Barrow et al., 1980). Although strongly adsorbed oxyanions form inner-sphere surface complexes, they reside in a separate plane located between the surface plane of protons and hydroxyls and the plane of outer-sphere surface complexation. The Stern VSC-VSP model emphasises parameter optimisation and neglects mass balance and the definition of surface species, surface reactions, and equilibrium constant expressions. The total number of surface sites and the maximum B adsorption are adjustable parameters in the Stern VSC-VSP model.

In describing B adsorption on iron oxide, four adsorbed B species were considered: $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4$-(Bloesch et al., 1987). The fit of the Stern VSC-VSP model to B adsorption as a function of solution pH was good for four initial solution B concentrations optimising binding constants for four adsorbed B species (Bloesch et al., 1987; Figure 7). A comparably good fit was obtained for B adsorption on aluminium oxide using the constant capacitance model by optimising only one binding constant (Figure 6). The Stern VSC-VSP model was applied to B adsorption on a soil by postulating a continuous distribution of binding sites divided into thirty discrete elements (Barrow, 1989). With this very large increase in the number of adjustable parameters, this application of the Stern VSC-VSP model reduces to a curve fitting procedure.

Evaluation of chemical surface complexation models

The major advantage of the chemical models presented is that they consider surface charge resulting from the surface complexation reactions. Chemical surface complexation models provide molecular descriptions of adsorption phenomena. The molecular features of surface complexation models can be given thermodynamic significance (Sposito, 1983). However, as for empirical models, goodness of fit to experimental adsorption data cannot be used as evidence for the actual presence of any of the surface complexes postulated in the models.

The constant capacitance model is the simplest of the surface complexation models. As the complexity of a model increases, the number of adjustable parameters increases; the curve fitting ability of a model improves as the number of adjustable parameters increases. Chemical significance of a model application suffers when parameters whose values are available from independent experiments are adjusted, as is the case in the Stern VSC-VSP model for the maximum surface charge and the maximum B adsorption. In the Stern VSC-VSP model the accuracy of the chemical speciation is also compromised by the lack of mass balance for the surface functional group.

Boron desorption

Boron desorption reactions in soils have been investigated less extensively than B adsorption reactions (Biggar and Fireman, 1960; Elrashidi and O'Connor, 1982; Griffin and Burau, 1974; Hadas and Hagin, 1972; Hatcher and Bower, 1958; Okazaki and Chao, 1968; Rhoades et al., 1970b; Wild and Mazaheri, 1979). Results on the reversibility of B adsorption reactions in soils are contradictory. For some soils, the B desorption isotherm corresponded closely to the B adsorption isotherm (Elrashidi and O'Connor, 1982; Hatcher and Bower, 1958; Wild and Mazaheri, 1979). Other soils exhibited hysteresis, that is the B adsorption isotherm did not correspond to the B adsorption isotherm (Elrashidi and O'Connor, 1982; Okazaki and Chao, 1968; Rhoades et al., 1970b). Hysteresis was not significantly correlated with any of the following soil properties: clay, organic carbon, pH, electrical conductivity, cation exchange capacity, surface area, aluminium oxide content, and iron oxide content (Elrashidi and O'Connor, 1982). Adsorbed soil B was completely desorbed after five sequential extractions (Okazaki and Chao, 1968).

Boron desorption reactions on soil minerals have been found to be reversible in some studies (Bloesch et al., 1987; Harder, 1961; Hingston, 1964; Keren and Gast, 1981) and hysteretic in others (Harder, 1961; Jasmund and Lindner, 1973). The pronounced hysteresis of B desorption from composted organic matter is attributed to the formation of dihydroxy and hydroxy–carboxy bonds with B (Yermiyaho et al., 1988).

Various mechanisms of anion sorption may explain apparent irreversibility of B sorption including: ligand exchange, formation of bidentate surface complexes, and incorporation into clay mineral lattices. Ligand exchange is pH dependent and reversible with respect to pH changes; however, anion desorption at constant pH exhibits varying degrees of irreversibility (Hingston, 1981). “Kinetic irreversibility” of anion adsorption has been attributed to the conversion of reversibly adsorbed, monodentate forms to bidentate forms which are "irreversibly" adsorbed (Kafkafi et al., 1967). The formation of bidentate anion surface complexes thus account for the slowness of the desorption reaction. Adsorbed B may undergo a monodentate to bidentate conversion at the mineral surface (Keren and Gast, 1981). Incorporation of B into the tetrahedral sites of clay lattices may also explain irreversibility of B adsorption (Harder, 1961). Boron diffusion into the particle interior may be responsible for the decrease in B desorption rate from soils after long term reaction (Griffin and Burau, 1974).

Modeling of boron desorption

For non-hysteretic systems, B desorption reactions can be described using the empirical and chemical B adsorption models discussed above. The Langmuir equation was able to describe B adsorption–desorption on soils (Hatcher and Bower, 1958), but due to hysteresis, was unable to describe B leaching from soils (Rhoades et al., 1970b). Boron adsorption and B desorption could be fit with the same Freundlich parameters for non-hysteretic soils, but different sets of Freundlich parameters were necessary to describe B adsorption and B desorption for hysteretic soils (Elrashidi and O'Connor, 1982).

Boron desorption from soils as a function of time can be described by the first order rate equation, the Elovich rate equation, and the power function equation (Griffin and Burau, 1974; Peryea et al., 1985; Sharma et al., 1989). The power function equation provided the best fit to B desorption based on coefficient of determination, r^2 values (Sharma et al., 1989).

Future research activities

In the future, increased use of spectroscopic techniques will provide direct experimental evidence for B adsorption mechanisms. Fourier transform infrared spectroscopy can be used to evaluate B adsorption mechanisms in aqueous systems. The approach of Su and Suarez (1995) may be extended to evaluate B adsorption mechanisms on clay minerals, calcium carbonate, and perhaps organic matter. Nuclear magnetic resonance can be used to distinguish between protonated and unprotonated surface complexes and between inner- and outer-sphere surface complexes. The approach used by Bleam et al. (1991) for phosphate adsorption can be modified to evaluate the configuration of adsorbed B on aluminium oxides. Indirect experimental procedures of establishing B adsorption mechanisms, such as the pressure jump relaxation procedure of Toner and Sparks (1995), may also be applied to B adsorption on clay minerals and calcium carbonate.

It is anticipated that additional advances will be made in surface complexation modeling of B adsorption by incorporating experimental results of B surface configuration obtained with the techniques described above. Surface complexation modeling studies of B adsorption must be expanded to consider the effect of competing ions. Competitive surface complexation modeling approaches such as those of Manning and Goldberg (1996a, 1996b) should be applicable to B adsorption reactions on soil minerals. Incorporation of surface complexation models into transport models is necessary to allow prediction of B adsorption–desorption reactions in natural systems and during reclamation processes.

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