BORON DYNAMICS IN VOLCANIC ASH-DERIVED SOILS FROM THE PACIFIC COASTAL PLAIN OF GUATEMALA

by

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(Under the Direction of Malcolm Sumner and Miguel L. Cabrera)

ABSTRACT

Boron (B) is an essential trace element for plants and animals, and its range between deficiency and toxicity is the narrowest among all the micronutrients in soils. Volcanic ash-derived soils naturally have low B contents, and crops growing in these regions suffer severe symptoms of B deficiency that compromise their yields and quality. B availability in soils is governed by adsorption and desorption reactions on mineral and organic functional groups, and a deep understanding of the surface chemistry of these components is essential to successfully managing this nutrient at the field scale. The purpose of this study was to understand the physicochemical reactions of B with soils from the Pacific coastal plain of Guatemala so that recommendations for economically important crops in the region could be improved. An organomineral characterization of a set of 23 soils belonging to five different soil orders revealed B is adsorption is controlled by amorphous aluminosilicates (allophane and imogolite), Fe oxy(hydroxydes), 1:1 clay minerals, and recalcitrant fractions of organic matter. The maximum B adsorption capacities for these soils — that are geographically close but differ greatly in their chemical properties — were obtained from Langmuir isotherms of the data and varied from 3 to 130 mg B kg^{-1}; with the degree of reversibility of the adsorption reactions depending on the andic character of the soil. Because the andic character of a soil can be estimated by a measurement of pH in a sodium fluoride (NaF) suspension, this test is tentatively proposed for predicting the potential of a soil to fix B. An estimation method to calculate appropriate field B rates for highly fixing soils based on adsorption equilibria is proposed. When these estimated B rates were applied in the field, deficient soil levels were improved and maintained in sufficiency ranges without causing toxicity during the elongation stage of sugarcane, which was the response crop model used to test the rates in two commercial farms in Guatemala. The increased plant absorption and improved yields demonstrate that the correct management of B has good potential to positively impact agricultural productions in Central America and other volcanic regions in the world.

INDEX WORDS: micronutrients, boron adsorption, boron desorption, hysteresis, andic character, allophane, imogolite, organic matter thermal stability, volcanic ash-derived soils, boron rates, boron fixation, boron availability, plant response

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DEDICATION

To God, by whose infinite love and through the inspiration of St. Francis of Assisi, makes me discover how to contribute with joy to the commitment of caring for creation. "*Through the greatness and the beauty of creatures one comes to know by analogy their maker*" (*Wis* 13: 5)

To my family, the pillars that supported me with love and accompaniment in the development and completion of this stage of life

To my mentor, friend, and role model: Malcolm Sumner; for allowing me to give continuity to the legacy of his career

To the memory of Ana María de Pira, RIP

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INTRODUCTION AND LITERATURE REVIEW

Boron (B) is an essential micronutrient or trace element because it is required in very small amounts relative to other plant nutrients to promote health and yield of numerous crops. According to Gupta (1993), B deficiency is the most widespread of all the known essential trace elements over a wide range of plant species throughout the world; consequently, crops on B-deficient soils cannot reach their full yield and quality potentials. Since its discovery as an essential trace element in the early twentieth century, the study of B chemistry in agriculture has grown rapidly (Shorrocks, 1997).

The range between toxic and adequate B concentrations in soil and plant systems is narrower than for any other nutrient element (Goldberg, 1993). For the majority of plant systems the only effective way B can be acquired is from the soil solution through the roots, as it is generally not mobile in phloem vascular tissue (with few exceptions) and it is not readily translocated from older to younger plant tissues. Consequently, foliar applications of B only meet the requirements of the tissue to which they are applied, frequently causing B starvation in other parts of the plant. For instance, when banana plants that were deficient in B were sprayed with B solutions of various concentrations, this resulted in leaf toxicity and no improvement in B deficiency symptoms, such as rosetting of the stem and “witches broom” in the roots (M. Avila, personal communication, 2013). Parent rock, its weathering products, and soil organic matter are the primary sources of B for plants, while chemical fertilizers (boric acid and borate salts) are the most common sources of B used to control deficiencies in crops (Gupta, 1993). High B concentrations in irrigation water can cause B toxicity, particularly, in arid and semi-arid regions (Goldberg et al., 2005).

Primary cell wall structure and membrane function are closely linked to adequate B nutrition; but its role in plant metabolic reactions is still a subject of considerable debate (Ganie et al., 2013). Many of the postulated metabolic roles of B in higher plant growth and development are considered secondary effects of the primary structural role of B as a component of the (RGII) fraction of cell wall pectin (Bonilla et al., 2009).

Evidence of rapid changes in membrane functions (e.g., phosphorus (P) uptake, proton release, and enzymatic reactions) induced by B deficiencies might support metabolic functions of B beyond its structural role as a cell wall stabilizer. Evidence exists to show that B is a critical component in the formation of the plasma membrane in pollen tubes (Jackson, 1989), and that organogenesis is affected by B deficiency as B complexes are implicated in cell-to-cell signaling (Bonilla et al., 2009). For instance, the symbiotic interaction between leguminous plants and rhizobia that triggers the development of root nodules is a specific organogenesis process regulated by molecular plant-bacterium interactions that are negatively impacted under B deficient conditions (Bolaños et al., 1996; Stougaard, 2000; Brewin, 2004).

Because the range between toxic and deficient B levels in soils and plants is very narrow, both excessive and deficient levels can be encountered in a crop during a single season (Reisenauer et al., 1973). M. Avila (personal communication, 2013) found that zones of deficiency and toxicity could occur on the same leaf after foliar applications of

B highlighting the immobility of B in plants. The levels of deficiency, sufficiency, and toxicity for different crops vary depending upon plant part and tissue age under consideration. For instance, the whole above-ground part of alfalfa is considered to be B deficient when B concentrations are less than 15 mg B kg^{-1} (dry matter basis) and toxic above 200 mg B kg^{-1} at the early bloom stage, whereas the top one third of the plant shortly before flowering is considered to be B deficient at less than 20 mg B kg^{-1} and toxic above 100 mg B kg^{-1} (Gupta, 1993). Regardless of the crop, symptoms of B deficiency generally appear first in younger tissues and toxicity in older tissue, because of the characteristic immobility of B in plants.

Mortvedt and Woodruff (1993) present details of US state recommendations for B applications to various crops. For crops with high B requirements, such as alfalfa and cabbage, recommended soil-application rates range up to 4.5 kg B ha^{-1}; while for those crops with medium B requirements, such as cotton and tomato, the range lies between 0.2 and 2.2 kg B ha^{-1}; and for crops with low B requirements, such as beans and grasses the rates are about 0.5 kg B ha^{-1}. Most recommended B rates and methods of application have not changed significantly during the past several decades in the United States (Mortvedt and Woodruff, 1993) because B leaching from the root zone and, to a lesser extent, crop removal are the main pathways responsible for compromising B availability to crops. Without any testing, these recommended rates have been adopted in other regions of the world where soil conditions are very dissimilar. In soils containing minerals with large surface areas, such as iron and aluminum oxides and hydroxides and amorphous aluminosilicates such as allophane and imogolite the main problem limiting B availability is not leaching but probably B fixation by surface complexation reactions; as a result in many cases these US based rates are too low and fail to solve deficiency problems. Hence, the physicochemical reactions between B and soil surfaces need to be studied to fully understand which factors govern the availability of this essential and frequently deficient element.

1.1 Boron chemistry in soils

In aqueous solution, B does not form B^{+3} cations because it has a high ionization potential resulting in the formation of covalent rather than ionic bonds with oxygen (Cotton and Wilkinson, 1980). Boric acid is a neutral planar molecule that behaves as a very weak Lewis acid by accepting a hydroxyl ion to form the tetrahedral borate anion (figure 1.1). The equilibrium constant for the hydrolysis reaction of boric acid is 5.75×10^{-10} (pK = 9.24) (Bassett, 1980). Under relatively low concentrations (≤ 0.025 mol B L^{-1}) only mononuclear B species are present while at higher concentrations stable polymeric ions exist with rapid depolymerization upon dilution of the solution (Cotton and Wilkinson, 1980).

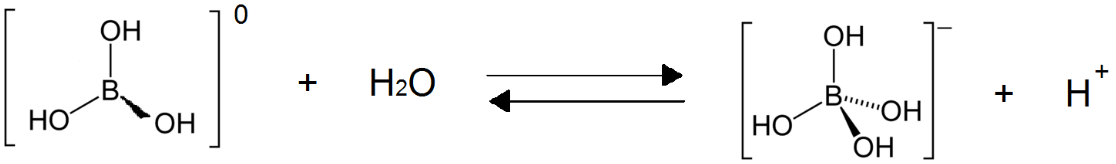

Figure 1.1: Dissociation of boric acid

Members of the tourmaline group are the most common B-containing minerals in soils (Whetstone et al., 1942). These minerals are borosilicates that contain about 3% B in their structure. Despite their presence in some soil environments, these minerals are highly resistant to weathering and virtually insoluble (Goldberg, 1993). On the other hand, hydrated B minerals are very soluble, and occur as deposits usually produced by chemical precipitation after evaporation of brine and/or seawater in arid regions (Goldberg, 1993). Boron can also be present in phyllosilicate clay minerals substituting in the tetrahedral layer for either Si or Al with contents varying from 10 to 500 mg kg^{-1} in muscovite, 10 to 30 mg kg^{-1} in kaolinite, and less than 50 mg kg^{-1} in chlorite (Harder, 1970).

Sorption reactions govern the amount of B available for plant uptake as plants respond only to B in the soil solution and not to the amount of B adsorbed on the solid phase (Ryan et al., 1977; Keren et al., 1985). Therefore, factors that affect B availability in soils are all related to the effects that they have on adsorption/desorption reactions. For instance, because B becomes less available to plants with increasing solution pH it is common to observe B deficiency after liming acid soils. This is due to the bell-shaped adsorption envelope (adsorption as a function of pH) of B with soil surfaces, where a maximum adsorption peak is observed at a pH value approximately equal to the log K for borate protonation (Sposito, 2008). Soil texture and clay mineralogy also play important roles in B availability. The amount of B adsorbed is dependent on soil texture and increases with increasing clay content (Mezuman and Keren, 1981; Elrashidi and O'connor, 1982), because clay minerals are one of the surfaces responsible for soil B adsorption.

The main B adsorbing surfaces in soils are iron and aluminum oxides, clay minerals, carbonates, organic matter, and amorphous aluminosilicates. Boron adsorption has been highly correlated with soil aluminum oxide content (Harada and Tamai, 1968; Bingham et al., 1971), while the iron oxide content was a significant variable in multiple regression equations explaining the variance in adsorbed B (Elrashidi and O'Connor, 1982). On a unit weight basis, B adsorption is greater for aluminum than iron oxides (Sims and Bingham, 1968; Goldberg and Glaubig, 1985), most likely due to the higher surface area of the former. In these studies, B adsorption on aluminum and iron oxide minerals is considered to be by ligand exchange with reactive surface hydroxyl groups (Goldberg et al., 1993; Su and Suarez, 1995).

Common 1:1 and 2:1 clay minerals also adsorb B on their edge hydroxyl sites. For 2:1 clays the reaction can be limited by the degree of isomorphous substitutions that generate permanent charge (Keren and O´Connor, 1982). For instance, pyrophyllite (an ideal 2:1 clay mineral with no permanent charge) has a greater B adsorption capacity than illite and montmorillonite (Keren and O´Connor, 1982) due to a lower repulsion of B in solution. Boron adsorption by clay minerals is a two-step process. First, B adsorbs onto the particle edges, to further migrate and become incorporated structurally into tetrahedral sites replacing structural Si and Al (Fleet, 1965; Couch and Grim, 1968). Because on a unit weight basis clay minerals adsorb significantly less B than do most oxide minerals, it is more appropriate to compare B adsorption capacities on a surface area basis. However, since B adsorbs on the edges of clay minerals — the surface areas of which are difficult to determine— this comparison is not always straightforward (Goldberg, 1997).

Calcium carbonate also acts as an important B adsorbing surface in calcareous soils (Goldberg and Forster, 1991) through exchange with carbonate groups (Goldberg, 1997).

The B adsorption maxima for soil samples after removal of calcium carbonate were statistically significantly lower than those for untreated soils, indicating that calcium carbonate is an important sink for B adsorption in calcareous soils (Goldberg and Forster, 1991).

The mechanisms by which B adsorbs on isolated natural and synthetic humic materials have been well studied, but the conclusions concerning the effect of organic matter in whole soil B reactions are not yet clear. Boron forms tetrahedrally coordinated surface complexes on dicarboxylic acid sites, alpha-hydroxy carboxylic acid sites, and diphenols on synthetic and natural humic substances (Lemarchand et al., 2005; Tossel, 2006; Goldberg, 2014), but within an organomineral assemblage organic materials have been reported to reduce the capacity of the pure mineral to adsorb B. For instance, Al hydroxide shows a decrease in adsorption capacity when coated with organic matter (Xu and Peak, 2007), and allophane showed a reduced capacity to sorb B even after it was reacted with an organic compound known to have high B affinity and adsorption capacity (Reinert et al., 2011).

For allophane, an X-ray amorphous clay-size mineral comprised of hollow nano-spherules, which is commonly associated with volcanic ash-derived soils (Parfitt, 2009), B can presumably substitute for Si in the inner tetrahedral layer of the nano-spherules (Su and Suarez, 1997) as well as being surface adsorbed in trigonal and tetrahedral coordination with aluminol groups of the gibbsite-like outer sheet. On a per mass basis allophane and iron and aluminum oxides adsorb B to the same extent which is higher than for clay minerals. According to Su and Suarez (1997), B can coprecipitate with allophane during synthesis in tetrahedrally coordinated positions, presumably by substituting for Si in that layer. The authors suggest that the structurally coprecipitated B is expected to be more resistant to release than the surface adsorbed B.

Boron containing minerals generally do not control B activity in soil solution because they are either too insoluble (tourmaline group minerals) or too soluble (hydrated B minerals). Thus, the amount of B in soil solution is usually controlled by B adsorption-desorption reactions (Goldberg, 1997). In most soils, B adsorption is readily reversible with the adsorption and desorption isotherms corresponding closely and exhibiting little or no hysteresis. The apparent irreversibility of B sorption has been attributed to conversion of readily desorbable B surface complexes into less readily desorbable complexes, incorporation of B into tetrahedral sites of clay minerals, and B diffusion into particle interiors.

1.2 Volcanic ash-derived soils

Volcanic ash-derived soils are distributed exclusively in regions where active and recently extinct volcanoes are located. These soils correspond to about 1% of the world’s land surface, though they represent a crucial land resource due to high populations living in these regions, and their inherent fertility stemming from an enhanced ability to accumulate organic carbon. They are generally classified as Andosols in the World Reference Base for Soil Resources (WRB classification) (IUSS Working Group WRB, 2015) and as Andisols in the U.S. Soil Taxonomy (Soil Survey Staff, 2014). These names are derived from “*Ando soils*” whose etymology corresponds to dark (*An*) and soils (*do*) in Japanese (Takahashi and Shoji, 2002).

The principal regions of the world where Andisols are distributed are summarized by Takahashi and Shoji (2002) as follows: in Europe, Italy, Sicily, Sardinia, and France (Massif – Central); in Africa and the Indian Ocean, Kenya, Rwanda, Tanzania, Ethiopia, Cameroon, Malagasy, Mauritius and Reunion, Canary Islands, Uganda, Sudan, and Zaire; in the Americas, Alaska, British Columbia, Washington, Oregon, California, Mexico, Costa Rica, Panama, Honduras, Guatemala, El Salvador, Nicaragua, West Indies, Ecuador, Colombia, Peru, Chile, Argentina, and Bolivia; in Asia and the Pacific, Hawaii, Aleutian Islands, Kamchatka Peninsula, Japan, Korea, Micronesia, Philippines, Indonesia, Papua New Guinea, Solomon Islands, Vanuatu, Fiji, Samoa, Tonga, and New Zealand. Approximately 60% of volcanic ash derived-soils occur in tropical regions.

The central concepts required for a soil to be classified as an Andisol are that it must be developing in volcanic ejecta and/or pyroclastic material, and that its colloidal fraction must be dominated by short-range-order minerals, and/or Al-humus complexes. Some soils narrowly fail to meet the criteria to be classified as Andisols, but their behavior is similar, and they might have sufficient andic character to make them behave essentially as Andisols.

Previous studies on Mexican and Hawaiian volcanic ash-derived soils have revealed high B adsorption capacities due to the presence of large amounts of amorphous minerals, Al-humus complexes, and organic matter. Bingham et al. (1971) reported maximum adsorption capacities ranging from 2.64 to 5.30 mmol B per 100 g of soil (285 - 572 mg B kg^{-1}) for volcanic ash-derived soils. Boron adsorption was positively correlated with amorphous aluminum minerals extracted with NaOH. For similar soils in southern Chile, Schalscha et al. (1973) reported adsorption capacities ranging from 2.98

to 18.87 mmol B per 100 g soil (322 – 2038 mg B kg^{-1}) which are about 20 to 40 times greater than those reported for non-allophanic soils. The adsorption capacities for the Chilean soils were positively correlated with allophane content estimated by Al and Si extracted with NaOH and with specific surface area.

Crops growing on these high B-fixing soils often suffer from severe deficiency symptoms with little to no response to fertilizer application at normal rates that are typically prescribed in other regions to manage B deficiency. Because B can become toxic at fairly low concentrations in soil solution, farmers in Andic regions are often unwilling to risk applying too much B to their crops despite the presence of deficiency symptoms. This is due to the lack of understanding of B dynamics in volcanic ash-derived soils and this can limit agricultural productivity in these regions.

1.3 Questions for study and objectives

The main question that this study poses is how does B interact with soils derived from volcanic-ash that renders it unavailable for plant uptake, and how should applications of this essential micronutrient in deficient crops be managed based on the physicochemical characteristics of andic soils. The overall goal is to quantify the extent of B adsorption on a set of volcanic ash-derived soils from the Pacific coastal plain of Guatemala, and to propose management recommendations for deficient crops. Central to this goal is the need for enhanced understanding of how soil mineral and organic components interact with this nutrient so that chemical reactions and transport can be modeled.

Objective 1: To identify the soils with the greatest importance for crop production on the Guatemalan Pacific Coastal Plain and to completely characterize their physicochemical properties and clay mineralogy.

Hypothesis 1: The clay fractions of soils from the Pacific coastal plain have high contents of amorphous minerals and organic matter both of which have high potentials for B adsorption.

Approach 1: To achieve the first objective the clay fraction was separated to identify the minerals present by X-ray diffraction, estimate the proportion of the active aluminum and iron phases by selective dissolution and Mössbauer spectroscopy, and identify the different fractions of organic matter in the soils by thermal analysis coupled with measurement of CO_2 and H_2O evolution by infrared gas analysis to identify the mineral and organic surface functional groups responsible for B adsorption.

Objective 2: To determine B adsorption isotherms for soils having a range of chemical characteristics, and to correlate the adsorption capacities with their andic character while comparing their reactivities with a set of non-andic soils.

Hypothesis 2: A quantified measurement of the andic character of the soils is directly proportional to the B adsorption capacity.

Approach 2: To achieve this objective, 25 agricultural soils were selected for the evaluation of B adsorption at constant temperature and natural soil pH. A variety of soil properties (organic matter and clay content, effective CEC, surface area, amorphous Al and Si, and pH in NaF as a measure of the andic character of the soils) were also determined to correlate with the adsorption capacities of the soils. An additional set of 5 non-andic soils were included to contrast the differences between soil mineralogical categories. The 5 reference soils were collected in the departments of Jinotega and Matagalpa in Nicaragua, and one from the Georgia Piedmont.

Objective 3: To evaluate B desorption from soils and the effect of andic properties on this process.

Hypothesis 3: The desorption process is not reversible but hysteretic, and the amount of B desorbed from the solid phase increases with decreasing andic character of the soils.

Approach 3: Boron desorption was investigated by replacing aliquots of B-free solution in tubes containing soil previously equilibrated with B solutions of different concentrations (from the B isotherm), and determine B desorption after re-equilibrating the suspension.

Objective 4: To evaluate crop responses to the B rates estimated from the adsorption equilibria at two sites on the Pacific coastal plain of Guatemala using a commercially important crop as a response model for availability of the applied B.

Hypothesis 4: The application of B fertilizer at a rate estimated from adsorption capacities provides adequate B for plant uptake and corrects the B deficiency in the crop.

Approach 4: Two field experiments were set up to evaluate soil available B (hot water soluble), sugarcane yields, and B uptake after application of rates estimated from adsorption capacities.

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CHAPTER 2

BORON ADSORPTION AND DESORPTION ON VOLCANIC ASH-DERIVED SOILS[1]

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[1] Terraza Pira, M.F., M.E. Sumner, M.L. Cabrera, and A. Thompson. Submitted to the Soil Science Society of America Journal.

2.1 Abstract

Many crops in volcanic regions exhibit symptoms of B deficiency but do not respond to B fertilizer rates that solve deficiency problems in non-volcanic-influenced soils. US recommended rates are routinely adopted in these regions without accounting for differences in soil B dynamics. Because of the paucity of investigations into and the resulting lack of understanding of B adsorption/desorption dynamics in volcanic ash-derived soils over the past 40 years, it would be incorrect to extrapolate the few data available to all volcanic ash-derived soils when they have not been analyzed as a function of andic character. This paper aims to create an understanding of what soil properties govern B availability in volcanic-influenced soils, and to establish if there are low-cost testing methods that can help estimate appropriate field B application rates in these soils. B adsorption/desorption isotherms were constructed for a group of volcanic ash- and non-volcanic ash-derived soils, and the derived parameters were compared with various standard soil tests. Our results show that soil B availability in volcanic-influenced soils is governed mainly by strong and stable B complexation with short-range-order (SRO) minerals. B adsorption maxima exhibit a wide variability not directly correlated with clay content, but rather with reactivity quantified by SRO mineral and organic matter contents. Organic matter is not a significant variable explaining specific surface area for the overall group of soils, but it becomes significant for soils containing less than 200 g clay kg^{-1}, suggesting that a new approach to analyzing whole-soil reactivity based on mineral surface abundance is needed. The maximum adsorption capacities of volcanic-influenced soils can be as much as 18-fold higher than for non-volcanic soils with the reversibility of adsorption reactions decreasing as andic character increases. These findings explain why

standard B fertilizer rates fail to solve deficiency problems in volcanic-influenced soils. Because pH in NaF is strongly related with acid-oxalate Al (SRO minerals) and B desorption index, this low-cost test can potentially be used as a measure of soil andic character to better reflect B availability and corresponding field application rates.

2.2 Introduction

Boron (B) is a trace element essential for plant growth, and its availability is influenced by adsorption and desorption reactions on soil surfaces (Keren et al., 1985). Plants respond only to B concentrations in the soil solution with the range between deficient and toxic levels being very narrow (Keren et al., 1985; Goldberg, 1997). Boron availability can be low in volcanic ash-influenced soils (Shorrocks, 1997), such as those along the Guatemalan south coast. Many crops in volcanic regions exhibit symptoms of B deficiency, but do not respond to the standard B fertilizer applications (ranging from 0.25 to 3.0 kg B ha^{-1} (Gupta, 2007)) that solve deficiency problems in non-volcanic-influenced soils (Sherrell and Toxopeus, 1978; Gupta, 1993; Shorrocks, 1997).

The recommended rates of B fertilization and methods of application have not changed significantly during the past several decades in the United States (Mortvedt and Woodruff, 1993). This is primarily because for most US soils, B loss (and decrease in crop availability) occurs by leaching below the root zone or, to a lesser extent, by crop removal. However, US recommended B application rates are routinely adopted in other regions of the world for soils that have very different B dynamics. For instance, in soils with high surface area minerals―such as allophane and ferrihydrite―, the main problem limiting B availability is likely to be B surface complexation and fixation. As a result, farmers in volcanic regions are getting incorrect B application rate recommendations. Resolving this issue requires regional specific research studies and a simple, low-cost testing method.

Boron adsorption on many soil types in various geographic regions has been positively correlated with pH, sesquioxides, organic matter, inorganic carbon and clay contents, specific surface area, soil salinity, and Al extracted with different solutions. Despite the well-known B reactions with these soil components, limited information on B dynamics in volcanic ash-derived soils is available in the literature, and even fewer efforts have been made to manage B deficiency in volcanic regions.

The studies of agricultural volcanic ash-derived soils are limited to twelve Japanese soils (Hara and Tamai, 1968), twelve Hawaiian soils (Hue et al., 1968; Bingham et al., 1971), four Mexican soils (Bingham et al., 1971), and six Chilean soils (Schalscha et al., 1973); with contradictory conclusions concerning the effect of clay and organic matter contents on the capacity to adsorb B. Hara and Tamai (1968) did not model B adsorption equilibrium as a function of B concentration in solution, but reported a single data point for each soil with no quantification of the soils andic character. Similarly, Hue et al. (1968) did not present adsorption isotherm models to describe B adsorption, but only qualitative distinctions between mineralogy of soils affecting sorption behavior.

Bingham et al. (1971) and Schlscha et al. (1973) reported 20- to 40-fold greater adsorption capacities than for non-volcanic soils. Despite adsorption capacities being positively correlated with Al extracted with NaOH―used as a measure of short-range-order (SRO) minerals―, this Al might not arise only from allophane and imogolite but could come from other sources such as gibbsite. Because there has not been any attempt to understand B adsorption in volcanic ash-derived soils over the past 40 years, it would be incorrect to extrapolate the few data available to all volcanic ash-derived soils when they have not been analyzed as a function of andic character.

In pure laboratory synthesized allophane systems, B adsorption data (Su and Suarez, 1997; Son et al., 1998; Reinert et al., 2011) suggest that allophane forms strong and specific surface B complexes through ligand exchange reactions. However, these hypotheses have not been tested on whole soils with a continuum of allophane and other components. Previous studies on B adsorption in volcanic ash-derived soils have not taken this into account as a quantitative variable in describing B dynamics.

Understanding desorption hysteresis is crucial in managing B in agricultural systems especially in deficient soils that receive B fertilizers, because the concentration of B in the soil solution is determined by adsorption-desorption reactions. In volcanic ash-derived soils the degree of reversibility of these adsorption reactions has not been evaluated as a function of their andic character, and B supply for crops suffering deficiency symptoms depends to an important extent on the nature of these processes.

In some non-volcanic soils, B adsorption is readily reversible with the adsorption and desorption isotherms corresponding closely showing little or no hysteresis (Hatcher and Bower, 1958; Elrashidi and O'Connor, 1982). Other soils (Oxisols, Ultisols, and calcareous soils) exhibit hysteresis which means that the isotherm for desorption does not correspond with that for adsorption (Okazaki and Chao, 1968; Rhoades et al., 1970; Elrashidi and O'Connor, 1982; Chen et al., 2009; Majidi et al., 2010). The apparent irreversibility of B sorption has been attributed to conversion of readily desorbable into less readily desorbable B surface complexes, incorporation of B into tetrahedral sites of clay minerals, and B diffusion into particle interiors.

Because soil organic matter does not appear to affect desorption characteristics (Goldberg and Suarez, 2012), B desorption hysteresis is likely to be governed by other soil properties. The degree of hysteresis decreases with increasing pH induced by adding NaOH (Chen et al., 2009; Goldberg and Suarez, 2012) facilitating the desorption of adsorbed B probably due to a greater electrostatic repulsion of borate anions [$B(OH)_4^-$] by the increased negative surface charge at higher pH values. This is entirely different to the effect of alkalinity in calcareous soils where the B adsorption and hysteresis is caused by the presence of lime.

Andisols correspond to about 1% of the world’s land surface, although they represent a crucial land resource due to the high populations living in these regions, and their inherent fertility stemming from an enhanced ability to accumulate organic carbon. Many additional soils in volcanic regions narrowly miss classification criteria for an Andisol, but nevertheless their behavior is similar because they have sufficient andic character to make them behave essentially the same as Andisols.

Given that the B adsorption/desorption in volcanic ash-derived soils and soils with andic character is largely unstudied, several key questions must be answered to improve agricultural management of B in volcanic-influenced regions: (1) what soil properties govern B availability in volcanic-influenced soils? and (2) are there low cost testing methods that can help stakeholders estimate field B application rates for volcanic-influenced soils? To answer these questions, a group of volcanic ash-derived soils that suffer from B deficiency and a set of non-volcanic soils were (i) subjected to B adsorption/desorption isotherm experiments; (ii) the sorption/desorption behavior was compared with various standard soil tests including clay content, soil organic matter, and pH in NaF, among others; and (iii) correlations between the soil tests and sorption/desorption behavior were evaluated for applicability as a potential low-cost soil testing parameter that could be used to optimize B fertilization rates in the hopes of obtaining crop responses.

2.3 Materials and methods

For the study, 25 agricultural soils from the south coast region of Guatemala were selected for the evaluation of B adsorption at constant temperature and natural soil pH (Table 2.1). The soils were chosen from sugarcane and banana production areas in the departments of Retalhuleu, Suchitepéquez, Escuintla, and Santa Rosa. Boron adsorption was investigated using surface soil samples (0-15 cm) from different soil families belonging to six soil orders identified by Sánchez et al. (1996).

In the majority of cases, the soils that were not classified as Andisols still had sufficient volcanic ash influence to confer andic characteristics. An additional set of five non-volcanic soils were included to make comparisons between soil categories. The five reference soils were collected in the departments of Jinotega and Matagalpa in Nicaragua, and one from the Georgia Piedmont.

To construct the B adsorption isotherms 25 mL of seven solutions of different B concentrations (0, 2, 4, 8, 16, 32, and 64 mg L^{-1}) were added independently to 5 g soil and shaken for 20 h in a reciprocal shaker (~ 120 oscillations per minute) to reach equilibrium. After separation by centrifugation, final B concentrations were measured by the Azomethin-H method (Wolf, 1971). Because extracts were clear, the potential interference problem of dissolved organic matter with this method was not considered. B concentrations were chosen based on the fact that polymeric B species occur at concentrations in solution higher than 270 mg B L^{-1} (Cotton and Wilkinson, 1980), and this has been reported to produce a deviation from the Langmuir modeling equation (Elrashidi and O'Connor, 1982); since then, concentrations above 100 mg B L^{-1} have not been used in B adsorption studies. It is well documented that B reaches equilibrium with soils and soil constituents in batch experiments after 12 h (Griffin and Burau, 1974; Elrashidi and O'Connor, 1982; Arora and Chahal, 2007; Ranjbar and and Jalali, 2013).

The Langmuir empirical model was used as a mathematical description of a typical *L-curve* isotherm to expresses the amount of B adsorbed kg^{-1} dry soil as a function of the concentration of the free B in an equilibrium solution, as shown in the following equation:

$$n_i = \frac{bKc_i}{1 + Kc_i}$$

where *i* represents the adsorptive species, *b* represents the maximum adsorption capacity, which is the value of adsorbed species approached asymptotically when the concentration in solution becomes arbitrarily large, and *K* is an affinity parameter that determines the magnitude of the initial slope of the isotherm.

To fit the equation, an equivalent version of the Langmuir equation with rearranged terms was used plotting ${}^{c_i}/_{n_i}$ as a function of c_i and a linear equation was fitted where the slope corresponds to ${}^{1}/_{b}$ and the intercept to ${}^{1}/_{Kb}$ as follows:

$$\frac{c_i}{n_i} = \frac{1}{b}c_i + \frac{1}{Kb}$$

Desorption cycles were evaluated on six of the volcanic ash-derived and three of the non-volcanic soils. After separating the supernatant by centrifugation and pipetting, 25 mL of a B-free solution (0.01 mol L^{-1} $CaCl_2$) was added to each tube to re-equilibrate for desorption. Care was taken to ensure that no clumping took place during the re-equilibration. Experimental protocols to avoid clumping and loss of soil particles from the supernatant during the phase separation during the desorption steps were followed to avoid errors that could lead to mistakenly observing hysteretic behavior (Goldberg and Suarez, 2012). A total of two desorption steps were performed for each initial concentration. Final B concentrations in the supernatants from desorption cycles were measured by the Azomethin-H method (Wolf, 1971); all extracts were clear.

A desorption index (DI) was estimated as the ratio of adsorption and desorption linearized isotherms slopes as proposed by van Genuchten (1974) and Elrashidi and O'Connor (1982). When desorption is completely reversible DI equals to one, and it can be estimated by:

$$DI = \frac{n_{des}}{n_{ads}}$$

where n_{des} and n_{ads} are the slopes of the respective isotherms. The value of DI was calculated for all the initial B concentration points using the slope of the corresponding desorption isotherm. Also, an average DI was calculated for all B concentrations by using the average of the slopes for the two desorption isotherms.

A variety of soil properties were also determined to correlate with the adsorption capacities of the soils. Values for soil organic matter (SOM), clay content, effective cation exchange capacity (ECEC), specific surface area (SSA), acid-oxalate extractable Al and Si (Al_o and Si_o), and pH measured in NaF (pH_F) are presented in Table 2.1. Soil particle size distribution was measured by the Buoyoucos hydrometer method (Buoyoucos, 1962) and SOM was calculated from total C and N measured by combustion using a Leco C-N analyzer (Wang, 1998). ECEC was calculated as the sum of NH_4OAc (pH 7) extractable cations (Sumner and Miller, 1996). SSA was determined by the water vapor sorption method of Orchison (1953) which involves equilibration in desiccators over different concentrations of sulfuric acid to produce a range of vapor pressures and calculation based water vapor isotherms.

To quantify the andic character, amorphous Al and Si were extracted in 0.2 mol L^{-1} of ammonium oxalate in 0.2 mol L^{-1} oxalic acid (pH = 3 ± 0.05) (0.25 g soil to 25 mL) in a 50-mL centrifuge tube. The tubes were shaken for 4 h in the dark at room temperature (23^{o}C), and then analyzed by ICP-MS for Al and Si. A simple measure of the andic character that has been used for soil classification purposes (Soil Survey Staff, 2014) was also performed on all samples. It consists of a pH measurement in NaF (1 g soil to 50 mL of a 1 mol L^{-1} solution) after stirring for 2 min. A pH value higher than natural soil pH is obtained because fluoride (F^-) anions exchange for hydroxyl (OH^-) surface functional groups, causing an increase in the alkalinity of the aqueous phase. This pH value directly reflects the content of amorphous aluminosilicates (allophane and imogolite) and andic character because these minerals have a high proportion of surface hydroxyl groups due to their configuration and composition.

2.4 Results and discussion

Boron Adsorption

Boron adsorption isotherms show a typical *L-curve* shape to which the Langmuir isotherm equation was fitted with adsorption tending toward a maximum in the higher range of solution B concentrations evaluated (32 – 64 mg B L^{-1}) (Table 2.2). Boron maximum adsorption capacities, which correspond to the b parameter of the Langmuir equation (hereafter b_B), were estimated for all samples except the Cecil soil, for which no significant decrease in B solution concentration was observed in the last four points of the isotherm. A fit of the low concentration points (0 – 4 mg B L^{-1}) resulted in a b_B of 0.4 mg B kg^{-1}, which supports the claim that the main process limiting B availability in non-volcanic soils is leaching from the root zone. The Cecil soil has a negligible adsorption capacity probably due to its texture (64% sand) and low content of organic matter (Table 2.1).

B adsorption isotherms for volcanic ash-derived soils exhibited a wide range of maximum adsorption capacities (Figure 2.1) from 3 mg B kg^{-1} for the Santa Monica loamy sand to 130 mg B kg^{-1} soil for Puyumate sandy loam. Considering that the silt and sand fractions of the soil have negligible surface area, the adsorption capacities can be attributed almost entirely to the clay fraction; thus the adsorption capacities for the 25 volcanic ash-derived soils range from 20 to 922 mg B kg^{-1} clay versus a range of 0 to 53 mg B kg^{-1} clay for the non-volcanic control soils (Table 2.1).

Values of b_B for the clay fractions of the highly reactive soils in this study are comparable to those reported by Su and Suárez (1997) for synthetic freshly precipitated allophane ranging from 400 – 8000 mg B kg^{-1} clay; on the other hand, the less reactive soils have adsorption capacities that are comparable with those of the non-volcanic soils studied by Elrashidi and O´Connor (1982) ranging from 2.3 to 33.9 mg B kg^{-1} soil, corresponding to 22 to 112 mg B kg^{-1} clay.

Volcanic ash-derived soils have greater affinity for B adsorption than the non-volcanic soils. Boron adsorption is not directly related to clay content as was the case for the soils studied by Elrashidi and O´Connor (1982), but rather to clay fraction reactivity derived from the andic character of the minerals. This is illustrated well by comparing two samples (El Mirador and El Rama) with exactly the same clay content (401 g kg^{-1}) with b_B of 155, and 12 mg B kg^{-1} clay, respectively (Figure 2.2). The difference between clay content and clay reactivity as affected by andic properties can be explained based on the morphology and composition of the amorphous aluminosilicates that confer andic properties to the soils. The quantitative measurements of andic character for these two soils explain the difference in clay reactivity. Soil *El Mirador* has 11.2 and 6.5 mg kg^{-1} of acid-oxalate extractable Al and Si, respectively; and a fluoride pH of 9.79 (Table 2.1). Soil El Rama has 1.7 and 0 mg kg^{-1} of acid-oxalate extractable Al and Si, respectively; and a fluoride pH of 8.37.

Acid-oxalate extractable Al and Si, and pH_{NaF} are quantitative indicators of short-range-order minerals such as allophane and imogolite. These minerals have large SSA derived from their hollow nano-scale structures that expose surface hydroxyl groups with potential to adsorb B through ligand exchange reactions. Clay reactivity would refer then, to the allophane and imogolite content of the clay fraction, which seems to better describe the results found for these soils, for which the variability in observed b_B cannot be described merely by differences in clay content. Highly significant ($p = 0.01$) simple linear regression models were obtained between b_B and soil specific surface area (SSA), and the degree of significance was greatly increased (p = 0.001) when expressed on a unit clay basis (Table 2.3). This illustrates how clay fraction reactivity is a better explanatory variable for b_B than clay content.

Specific surface area for the entire set of soils was well explained by clay content, oxalate extractable Al, and ECEC using a multiple regression model where the only variable that was not significantly correlated was soil organic matter. Despite this negligible contribution of organic matter to the overall data, for the sub-set of soils containing less than 200 g of clay kg^{-1}, organic matter became important by significantly explaining the variability in SSA (Table 2.4). The differences between the multiple regression parameters for the overall set of samples and the sub-sets based on clay content suggest that B affinity for organic surfaces becomes significantly important only when mineral surfaces become less available, and that the contradictory results in the literature regarding the role of organic matter in adsorption reactions could be attributed to differences in the abundance of mineral surfaces.

This supports the findings of Bartolli et al. (2007) who demonstrated the antagonistic effects of organic matter and allophane on SSA for a set of Andisols. In their study, they concluded that the more the allophane is coated with organic matter, the more hydrophobic the soil surfaces become and the smaller the measured SSA is. Using this concept of allophane being coated by organic matter, the negative coefficients for organic matter in the regression model for SSA (Table 2.4) can be explained by a potential blocking mechanism of mineral hydroxyl functional groups and reduction in SSA, although the coefficients were not statistically significant. On the other hand, for soils with less than 200 g kg^{-1} clay, allophane is probably not the main component defining SSA and a positive contribution from organic matter is observed. It is worth noticing that the effects of organic matter on whole-soil B adsorption capacity for other soil types has been contradictory, with some authors showing positive (Olson and Berger, 1947; Elrashidi and O'Connor, 1982; Yermiyaho et al., 1995; Sharma et al., 2006) and others negative effects (Marzadori et al., 1991; Diana et al., 2010; Sarkar et al., 2014). Our findings showing different effects of organic matter depending on total clay size particles offer a new approach to analyzing whole-soil reactivity, but are not definitive for volcanic ash-derived soil behavior.

The large range in b_B values within the data set is probably due to heterogeneity stemming from wide variations in texture, clay mineralogy and organic matter. Regression analyses of the relationship between these three variables and b_B verified that adsorption capacities are not directly correlated with clay content, but rather with its reactivity quantified as allophane and organic matter contents (Table 2.5). For instance, the three Vertisols (Capullo, Colombita, and Buenos Aires) have low b_B (16, 21, and 47 mg B kg^{-1}, respectively) with large clay contents (300, 500, and 540 g kg^{-1}, respectively) whereas the three Andisols (La Cuchilla, Socorro, and Cadiz) have greater b_B (23, 49, and 90 mg B kg^{-1}, respectively) with smaller clay contents (101, 341, and 240 g kg^{-1}, respectively).

An independent investigation of the mineralogical and thermal properties of the soils used in this study revealed allophane contents in the clay fraction ranging from 20 to 740 mg g^{-1} clay in the Guatemalan soils, whereas the set of non-volcanic reference soils have less than 20 mg g^{-1} (Chapter 3). Other minerals identified by XRD and thermal analysis are phyllosilicates of the 1:1 layer type (most likely kaolinite) and 2:1 layer type (most likely montmorillonite and beidellite), and feldspar (most likely orthoclase). Soils with greater contents of allophane are more reactive due to the significantly greater surface area available for sorption reactions. The less reactive soils containing less than 100 mg allophane g^{-1} clay have an average b_B of 72 mg B kg^{-1} clay; whereas those with more than 100 mg allophane g^{-1} clay, had b_B averaging 316 mg B kg^{-1} clay. The variability in the contents of SRO minerals and other minerals with less affinity for B adsorption are responsible for the heterogeneity of the results in the study. For instance, the Buenos Aires soil with 540 g clay kg^{-1} soil, of which 23% is allophane, has a b_B of 87 mg B kg^{-1} clay; in contrast, the Puyumate soil with only 141 g clay kg^{-1} soil, of which 60% is allophane, has a b_B of 922 mg B kg^{-1} clay, almost 11-fold greater.

A multiple linear regression analysis between b_B and acid oxalate extractable Al, clay, OM and ECEC was performed on the 25 volcanic ash-derived soils in which only acid-oxalate Al content was statistically significant in explaining 60% of the variation in observed b_B. Furthermore, acid oxalate Al was highly exponentially correlated (R^2 = 0.85) with pH_{NaF} ($p = 0.01$) which is used as a measure of the andic character of the soils (Figure 2.3).

B desorption

The nine soils selected for desorption cycles exhibited widely different degrees of hysteresis—defined as irreversibility of adsorption reactions with lack of correspondence between the adsorption and the desorption isotherms— based on their volcanic influence. The volcanic-ash derived soils exhibit strong hysteresis, whereas the non-volcanic soils had near reversible sorption/desorption isotherms (Figure 2.4). Desorption indexes (DI) ranged from 0.6 for the Cecil soil (non-volcanic), to 6.1 for the Velasquez soil (volcanic) and it is strongly related with the andic character of the soils (Figure 2.5) represented as pH_{NaF}.

Experimental errors in adsorption-desorption studies can sometimes cause confusion as to whether hysteresis occurs or not (Goldberg and Suarez, 2012). In batch experiments, it is likely that clumping due to cohesion between particles occurs when re-shaking centrifuged soil suspensions, resulting in inaccessibility of some of the adsorbed B to the exchanging solution; as a result poor equilibrium between soil and solution occurs leading to apparent hysteresis. An additional experimental difficulty that might result in apparent B hysteresis is the loss of some soil particles from the supernatant during the phase separation in the desorption steps. Therefore, careful attention was paid to the adsorption-desorption protocols to avoid clumping and soil loss during our experiments, and the hysteretic behavior observed is assumed to arise only from differences in soil properties.

A multiple linear regression of the DI using the andic character (pH_{NaF}) and the SOM as explanatory variables demonstrated that the degree of hysteresis is dependent only on the SRO minerals present ($p = 0.01$), and not on organic matter content (ns). These results are in concordance with those found by Goldberg and Suarez (2012) who concluded that organic matter content does not have an effect on B desorption hysteresis.

The migration of B into particle interiors and possible substitution into soil minerals could explain the phenomena observed. Acid-oxalate dissolutions correspond to the content of amorphous aluminosilicates (allophane and imogolite), whose specific configuration of nano-balls and nano-tubules can lead to inaccessibility preventing B from being desorbed. As Su and Suarez (1997) suggested, B can presumably substitute for Si in the inner tetrahedral layer of the nano-spherules as well as being surface adsorbed on aluminol groups of the outer sheet.

pH_{NaF} as a predictor of B availability

For each soil, the amount of B adsorbed at equilibrium with 1.0 mg B L^{-1} in solution, which is considered to be adequate for most crops (Keren and Bingham, 1985), was related to the pH_{NaF} to provide a single easily-measured parameter to predict B availability. Two simple regression models were fitted to the data for this wide range of soils (Figure 2.6), one for soils with more volcanic ash influence in the central part of Escuintla (0 to 300 masl) with an $R^2 = 0.7681$ ($p = 0.001$), and another one for the less ash-influenced soils developed from basaltic lava flows in eastern and western Escuintla (0 to 300 masl), Santa Rosa (0 to 100 masl), Suchitepéquez and Retalhuleu (40 to 300 masl) with $R^2 = 0.9278$ ($p = 0.001$). In the absence of any other easily-measured parameter to assess the amount of B available to the crop, pH_{NaF} can be used for soil test purposes to predict likely response.

To actually evaluate the ability of this single test to predict B adsorption, an independent set of soil samples (seven from the central volcanic ash area and five from the western basaltic area) was collected to establish whether the prediction corresponded with the measured B adsorption data. The experimental adsorption for the central soils fell within the 95% prediction interval of the regression model, but only two of the five samples from the western area did (Figure 2.7a and 2.7b, respectively). Failure to predict

B adsorption within a range of confidence may be due to previous B fertilizer applications by farmers managing crops in the area. Thus the equations presented here are not intended to predict accurately the amount of B that would be adsorbed in equilibrium with an adequate concentration in solution, but rather to provide an estimate of mineral surfaces that could potentially limit B availability for plant growth in the region. Further modeling investigations are needed to provide better analytical tools that could make more precise predictions so that this trace element, which can reach both deficient and toxic levels in the soil solution very rapidly within a growing cycle, can be adequately managed.

2.5 Conclusions

Soil B availability in volcanic-influenced soils is governed mainly by formation of strong and stable surface B complexes with SRO minerals. B adsorption maxima exhibits a wide variability not directly correlated with clay fraction, but rather with clay reactivity quantified by the SRO mineral and organic matter contents. Organic matter is not a significant variable in explaining total SSA for the overall group of soils, but it becomes significant for soils containing less than 200 g of clay kg^{-1}, suggesting that a new approach to analyzing whole-soil reactivity based on mineral surface abundance is required that responds to previous contradictions about the role of organic matter in whole-soil surface reactions. The maximum adsorption capacities of volcanic-influenced soils can be as much as 18-fold higher than for non-volcanic soils, and the reversibility of adsorption reactions decreases as andic character increases. These findings explain why standard B fertilizer rates fail to solve deficiency problems in volcanic-influenced soils.

pH_{NaF} has a strong exponential relation with acid oxalate Al and a strong linear relationship with the desorption index. This low cost test can potentially be used as a measure of the andic character of the soils to help stakeholders estimate the content of mineral surfaces that could limit B availability for plant growth and better estimate field B application rates.

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Tables and figures

Table 2.1: Selected properties of the 25 volcanic ash soils and 5 non-volcanic soils used for comparison

Soil name	**Family**	**Clay**	**SOM**	**Al†**	**Si†**	**ECEC**	**ECEC**	**SSA**	**SSA**	**pH**	$\boldsymbol{b}_{\mathbf{B}}$	$\boldsymbol{b}_{\mathbf{B}}$
		$g\ kg^{-1}$				$cmol_c\ kg^{-1}{}_{soil}$	$cmol_c\ kg^{-1}{}_{clay}$	$m^2\ g^{-1}{}_{soil}$	$m^2\ g^{-1}{}_{clay}$	*NaF*	$mg\ B\ kg^{-1}{}_{soil}$	$mg\ B\ kg^{-1}{}_{clay}$
----------------------- volcanic soils -----------------------												
Blanca Victoria	Coarse-loamy,Isohyperthermic,Typic Tropofluvents	300	28	4.2	2.1	13.71	45.71	49	162	9.25	6	20
Las Rosas	Clayey,Isohyperthermic,Vertic Natrustalfs	480	39	4.6	2.5	20.26	42.22	73	152	9.08	13	27
Maria Linda	Fine-loamy,Isohyperthermic,Fluventic Haplustolls	160	20	3.6	2.6	12.33	77.08	47	294	9.24	5	31
Colombita	Coarse-loamy,Isohyperthermic, Typic Pelluderts	500	31	6.5	3.4	14.58	29.16	78	156	9.34	16	32
San Francisco	Sandy,Isohyperthermic,Typic Ustifluvents	381	59	6.4	2.8	28.58	75.01	98	257	9.33	14	37
Chaparral	Sandy,Isohyperthermic,Pachic Haplustolls	340	36	4.2	1.9	29.72	87.40	109	321	9.17	13	38
La Felicidad	Coarse-loamy,Isohyperthermic,Typic Tropofluvents	301	32	4.8	2.6	25.50	84.78	62	206	9.42	14	47
Santa Monica	Sandy,Isohyperthermic,Typic Ustipsamments	61	15	5.4	3.7	5.00	82.18	16	262	9.32	3	49
San Jose A	Not classified	60	17	1.4	7.0	4.08	67.47	7	117	8.25	4	67
Capullo	Coarse-loamy,Isohyperthermic, Typic Pelluderts	300	23	2.0	1.0	9.11	30.36	26	87	8.93	21	70
San Antonio	Coarse-loamy,Isohyperthermic,Fluventic Hapludolls	321	61	5.7	2.8	33.86	105.48	73	227	9.67	27	84
Buenos Aires	Clayey,Isohyperthermic,Typic Pelluderts	540	30	6.4	2.4	10.35	19.17	59	109	9.42	47	87
Maria del Carmen	Clayey,Isohyperthermic,Typic Dystropepts	520	30	5.6	2.5	14.65	28.16	83	160	9.42	45	87
La Trinidad	Coarse-loamy,Isohyperthermic,Fluventic Haplustolls	181	16	1.6	1.5	14.97	82.73	49	271	8.80	19	105
Socorro	Medial-skeletal,Isohyperthermic,Typic Happludands	341	42	20.5	9.8	8.89	26.06	86	252	10.28	49	144
El Mirador	Clayey,Isohyperthermic,Typic Ustipsamments	401	42	11.2	6.5	29.84	74.44	101	252	9.79	62	155
San Patricio	Medial,Isohyperthermic,Typic Fulvudands	81	29	3.9	2.8	11.93	147.30	8	99	9.44	13	160
La Cuchilla	Medial,Isohyperthermic,Typic Hapludands	101	70	25.5	14.4	6.48	64.20	65	644	10.36	23	228
Malta	Sandy,Isohyperthermic,Fluventic Haplustolls	121	35	3.3	2.4	14.96	123.66	36	298	9.32	34	281

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San Jose B	Not classified	101	27	4.5	1.8	7.73	128.87	30	297	8.64	31	307
Buganvilia	Medial,Isohyperthermic,Typic Fulvudands	161	53	24.0	12.6	10.66	66.24	58	360	10.02	53	329
Cadiz	Medial,Isohyperthermic,Eutric Hapludands	240	57	25.2	13.2	17.52	73.02	98	408	9.94	90	375
Velasquez	Coarse-loamy,Isohyperthermic, Typic Fulvudands	181	79	32.0	17.4	10.02	55.41	104	575	10.25	83	459
Boton Blanco	Sandy,Isohyperthermic,Typic Ustifluvents	60	26	3.6	2.8	10.02	166.95	11	183	9.63	36	600
Puyumate	Fine-loamy,Isohyperthermic, Typic Fulvudands	141	68	25.6	13.5	10.53	74.66	73	518	10.29	130	922
-------------- non-volcanic soils -----------------------												
Cecil	Clayey, Kaolinitic,Thermic,Typic Kanhapludults	160	16	2.0	1.0	9.11	56.94	2	13	8.20	0	0
El Rama	Not classified (Probably an Oxisol)	401	57	1.7	0.0	5.77	14.39	24	60	8.37	5	12
La Valla	Not classified (Probably a Vertisol)	600	27	1.8	1.0	62.96	104.86	62	103	8.42	32	53
Tempake	Not classified (Probably a Vertisol)	341	69	4.2	2.0	24.22	71.00	29	85	8.15	11	32
Fertimar	Not classified (Probably a Vertisol)	682	24	1.5	0.0	41.79	61.28	55	81	8.16	18	26

†Extracted with acid oxalate solution

Table 2.2: Langmuir isotherm parameters for the soils studied

Order	**Soil name**	**K**	b_B †	R^2 ‡
Alfisols	Las Rosas	0.249	13	0.9868
Andisols	La Cuchilla	0.128	23	0.9879
	Socorro	0.119	49	0.9932
	Cadiz	0.050	90	0.9373
	Buganvilia	0.072	53	0.8888
	Puyumate	0.014	130	0.6941
	Velasquez	0.054	83	0.8920
Entisols	Santa Monica	0.217	3	0.9715
	San Jose A	1.483	4	0.6729
	La Felicidad	0.126	14	0.8378
	La Trinidad	0.101	19	0.9505
	San Jose FA	0.025	31	0.7988
	Boton Blanco	0.030	36	0.9120
	Maria del Carmen	0.086	45	0.9176
	Mirador	0.058	62	0.9899
Mollisols	Maria Linda	0.714	5	0.8777
	Blanca Victoria	0.104	6	0.9761
	San Patricio	0.103	13	0.9178
	Chaparral	0.099	13	0.8354
	San Francisco	0.070	14	0.7205
	San Antonio	0.131	27	0.9651
	Malta	0.062	34	0.7619
Vertisols	Colombita	0.456	16	0.7806
	Capullo	0.076	21	0.9319
	Buenos Aires	0.037	47	0.8977
Ultisol	Cecil	3.602	<1	0.9985
Oxisol §	El Rama	0.587	7	0.9261
Vertisol §	La Valla	0.074	32	0.8866
	Tempake	0.867	13	0.9968
	Fertimar	0.249	18	0.9583

† b_B: maximum adsorption capacity [mg B kg^{-1} soil]

‡: Goodness of fit for the Langmuir isotherm equation

§: Probable order

Table 2.3: Simple regression equations relating b_B and SSA for 25 volcanic ash-derived soils

Simple Regression Equation	$\mathbf{R^2}$
b_B soil = 0.4050 SSA soil + 8.5640	0.2165**
b_B clay = 0.6338 SSA clay - 4.43396	0.7364***

, and * Significant at $p = 0.01$ and 0.001, respectively. b_B soil: maximum adsorption capacity soil basis [mg B kg^{-1} soil]; SSA soil: specific surface area soil basis [m^2 g^{-1} soil]; b_B clay: maximum adsorption capacity clay basis [mg B kg^{-1} clay]; SSA clay: specific surface area clay basis [m^2 g^{-1} clay].

Table 2.4: Multiple linear regression models relating SSA with soil properties

	Overall	**< 200 g clay kg^{-1}**	**> 200 g clay kg^{-1}**
	$R^2 = 0.8837$	$R^2 = 0.9658$	$R^2 = 0.7008$
Variable		**Coefficients**	
(Intercept)	-9.4211	-21.7760*	-20.5769
Clay	0.8942***	4.8555**	1.0791*
SOM	-2.8268	9.4203*	-4.6487
Al	26.5814***	-5.8398	30.3201**
ECEC	2.1117***	-2.2525*	2.4847*

*,**, and *** Significant at p = 0.1, 0.01 and 0.001, respectively.

Table 2.5: Regression analysis between selected variables and b_B for 25 volcanic ash-derived soils

Simple Regression Equation	**R^2**
b_B soil = 0.077 allo + 19.838	0.2905**
b_B soil = 1.074 OM – 7.353	0.3938***
b_B soil = -0.001 clay + 34.376	4E-5 n.s.

, and * Significant at p = 0.01 and 0.001, respectively. b_B soil: maximum adsorption capacity soil basis [mg B kg^{-1} soil]; allo: allophane content [mg g^{-1} clay]; OM: organic matter [g kg^{-1} soil]; clay: clay content [g kg^{-1} soil].

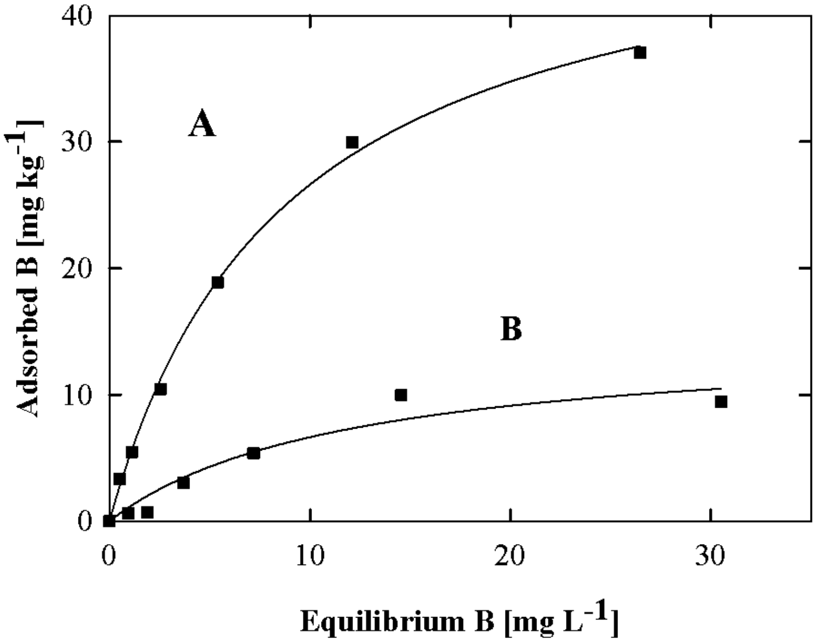

Figure 2.1: Boron adsorbed as a function of solution B concentration for surface soils: (A) *Socorro* and (B) *San Patricio*. Adsorption data are indicated by squares with the solid line representing the Langmuir adsorption isotherm.

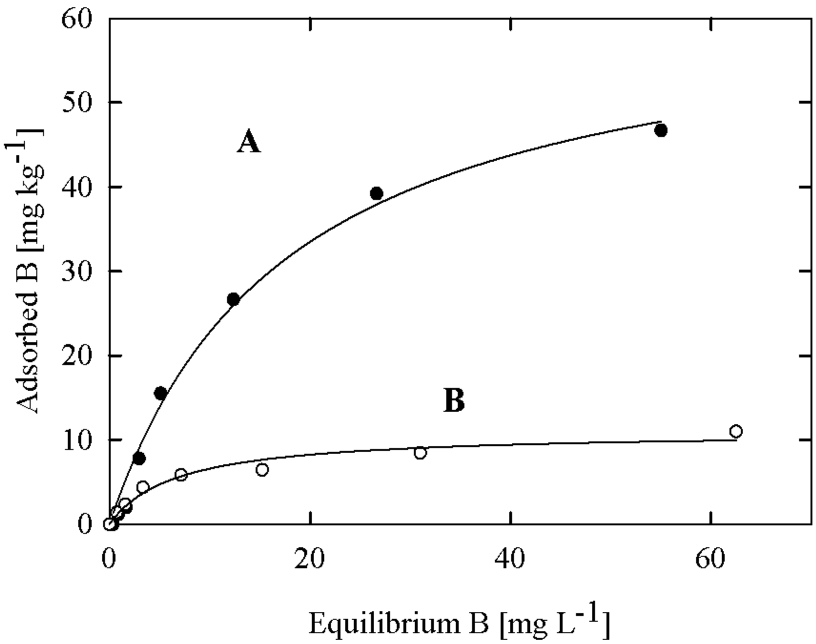

Figure 2.2: Comparison of B adsorption isotherms for the volcanic ash-derived surface soil *El Mirador* (A) and the non-volcanic surface soil *El Rama* (B). Solid lines represent Langmuir equation fit for the two soils, circles represent adsorption data. Both soils have clay contents of 401 g kg^{-1}.

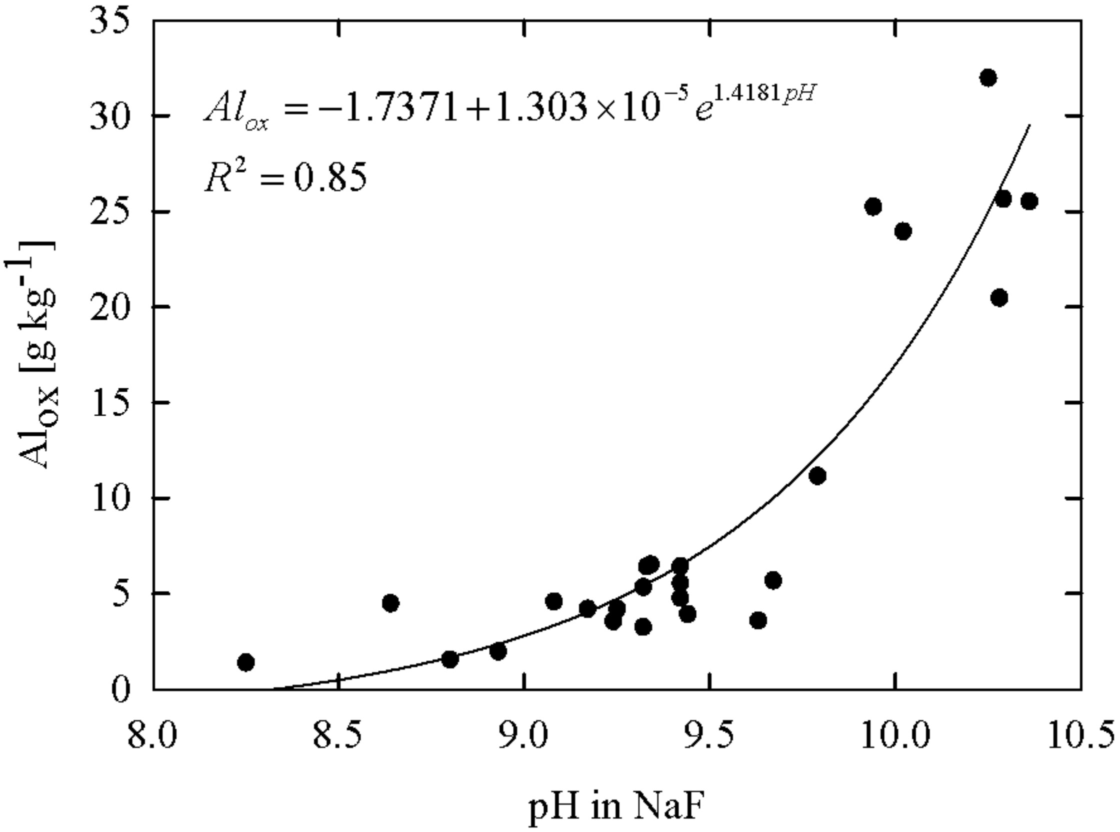

Figure 2.3: Relationship between pH in NaF and acid-oxalate extractable Al which approximates the abundance of allophane in the Guatemalan volcanic ash-derived soils.

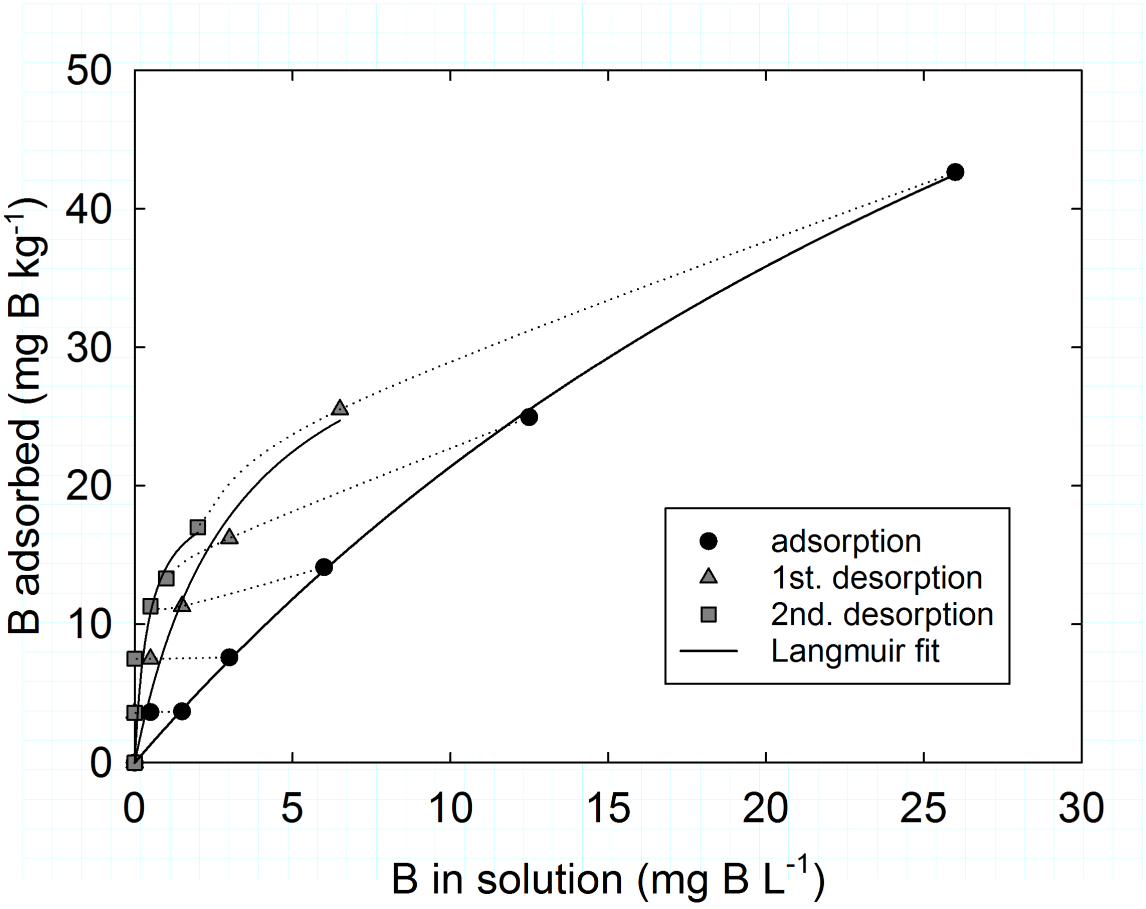

Figure 2.4: Adsorption-desorption isotherm for the volcanic ash-derived surface soil *El Mirador* showing strong hysteresis.

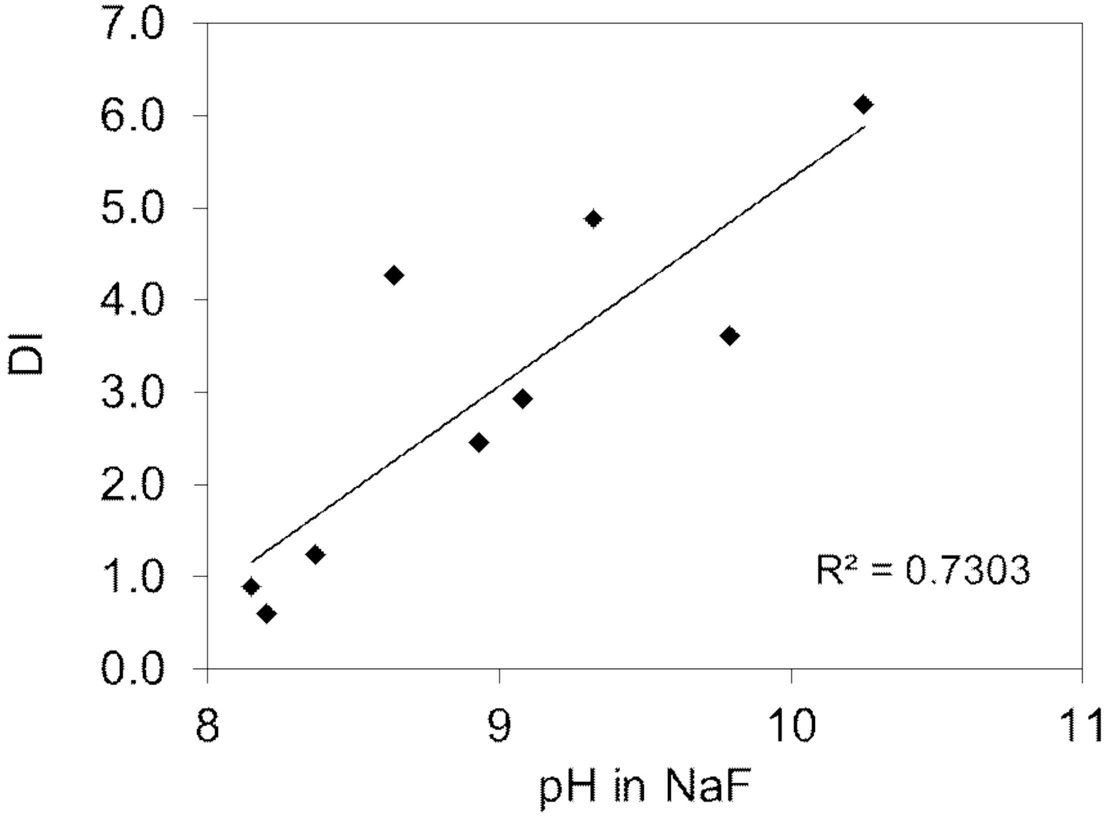

Figure 2.5: Relationship between pH in NaF and B desorption index (DI). DI = n_{des}/n_{ads}, where n_{des} and n_{ads} are the slopes of the linearized desorption and adsorption isotherms, respectively.

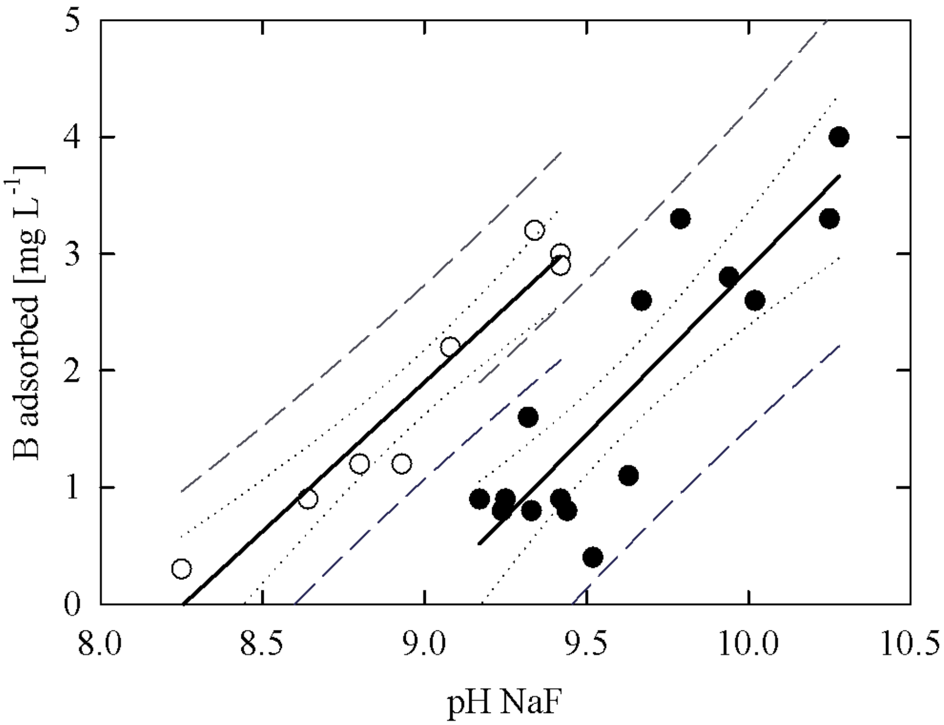

Figure 2.6: Relationship between pH in NaF and amount of B adsorbed at equilibrium with 1.0 mg B L^{-1} in solution. Black circles represent soils from central Escuintla; white circles represent soils from eastern and western Escuintla, Suchitepéquez, Retalhuleu and Santa Rosa. Dotted lines correspond to 95% confidence band (CB), dashed lines correspond to 95% prediction bands (PB). CB refers to the probability that the true best-fit line for the population lies within the interval. PB refers to the probability that the value of the dependent variable for a given value of the independent variable will be found within the interval range around the linear regression line.

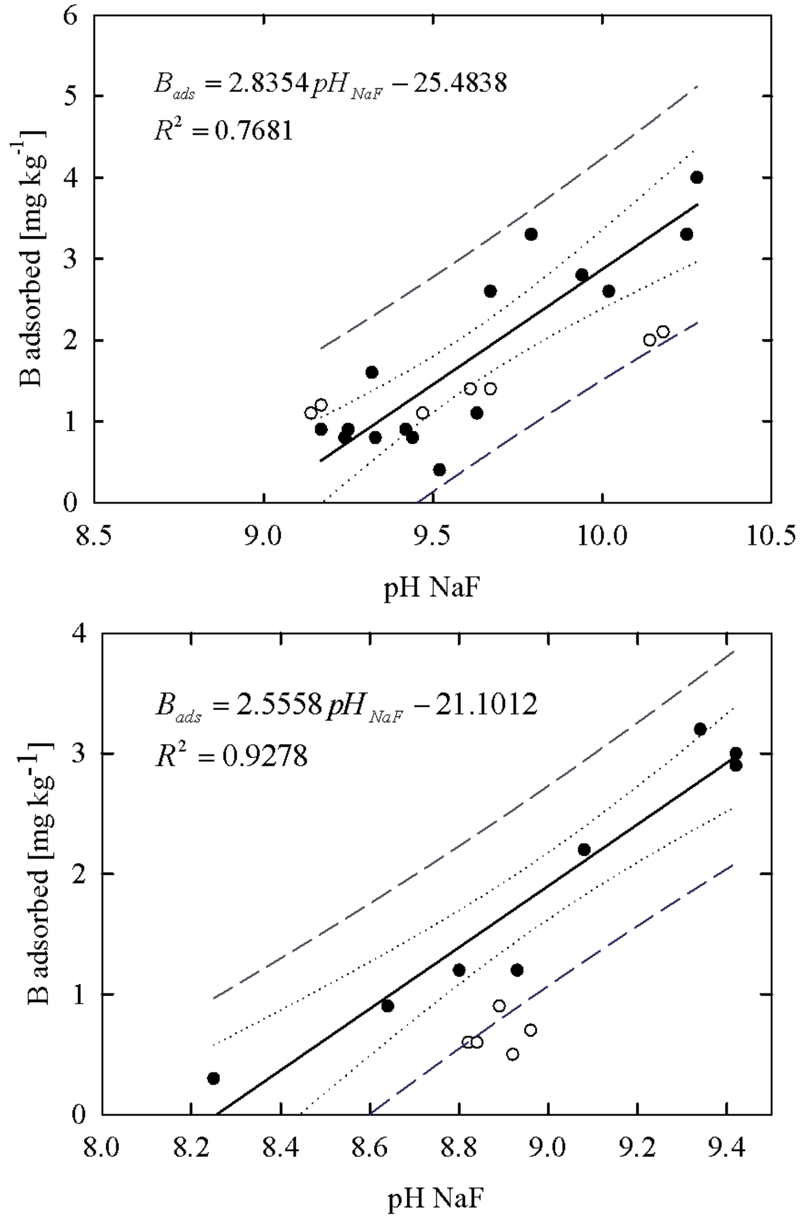

Figure 2.7: Ability of linear models to predict B adsorbed at equilibrium with 1.0 mg B L^{-1} in solution using pH in NaF as a single variable. Black circles represent initial set of soils; white circles represent independent samples to test prediction. Dotted lines correspond to 95% confidence band (CB), dashed lines correspond to 95% prediction bands (PB). CB refers to the probability that the true best-fit line for the population lies within the interval. PB refers to the probability that the value of the dependent variable

for a given value of the independent variable will be found within the interval range around the linear regression line. Top figure (2.7a) corresponds to soils from central Escuintla; bottom figure (2.7b) corresponds to soils from eastern and western Escuintla, Suchitepéquez, Retalhuleu and Santa Rosa.

CHAPTER 3

MINERAL CHARACTERISTICS OF VOLCANIC ASH-DERIVED SOILS AFFECTING BORON ADSORPTION[1]

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[1] Terraza Pira, M.F., M.E. Sumner, A.F. Plante, and A. Thompson. To be submitted to the Soil Science Society of America Journal.

3.1 Abstract

Boron (B) is an essential micronutrient whose availability in soils is governed by adsorption reactions. Volcanic ash-derived soils are naturally deficient in B, and maximum adsorption capacities (b_B) for this element can be as much as 40 times greater than for non-volcanic soils. Because the short-range-order (SRO) aluminosilicates (allophane and imogolite) and Fe (oxy)hydroxides are the mineral surfaces that dominate the surface reactivity of volcanic ash-derived soils, we hypothesized that these mineral surfaces are responsible for the wide variation in b_B observed, and that other minerals have negligible participation in B adsorption reactions at a whole-soil level. A set of 23 volcanic ash-derived soils from the Pacific coastal plain of Guatemala was subjected to mineral characterization to identify mineral surfaces that could explain the wide variability of b_B and soil specific surface area (SSA). Characterization using X-ray diffraction, selective dissolutions, Mössbauer spectroscopy, and thermal analysis demonstrated that soil's mineral reactivity is governed by short-range-order (SRO) aluminosilicates (allophane and imogolite), Fe (oxy)hydroxydes, and kaolinite with different degrees of crystallinity. The degree of crystallinity in kaolinite phases — measured as the temperature of the de-hydroxylation reaction— has an influence on both SSA and b_B. Ferrihydrite is probably the phase dominating SSA and providing affinity to B adsorption in volcanic ash-influenced soils that do not have allophane levels sufficiently high to be classified as Andisols. Smectites are present in some soils and, despite their contribution to SSA, they do not contribute in explaining the variability in b_B, probably because B does not react with planar sites. Cristobalite and orthoclase were also identified but considered inert in terms of B reactivity.

3.2 Introduction

The mechanisms by which boron (B) adsorbs to soil minerals have been well studied in pure mineral systems. The potential interactions between individual minerals and organic matter however, make it difficult to predict reactions in whole soils from pure mineral systems (Gustafsson, 2001). Boron adsorbing surfaces in soils are: aluminum and iron oxides, magnesium hydroxide, clay minerals, calcium carbonate, and organic matter (Goldberg, 1997). Isolated soil organic matter adsorbs more B than mineral soil constituents on a mass basis (Yermiyaho et al., 1988; Gu and Lowe, 1990), but it can also occlude B reactive adsorption sites on minerals (Harada and Tamai, 1968; Gu and Lowe, 1992; Marzadori et al., 1991).

The study of B adsorption on volcanic ash-derived soils is a specific concern because B is an essential trace element that limits the yields of economically important crops in volcanic regions (Chapter 2). To solve this nutritional problem, soil-B interactions must be fully understood, not only on isolated soil constituents, but most importantly within the native soil matrix. Considering that volcanic soils have an enhanced ability to accumulate organic carbon that exceeds the capacity other clay-rich soils (Zunino et al., 1982; Shoji et al., 1993), their inherent fertility make them disproportionately important in terms of food production relative to other soils, despite their small global abundance on the Earth’s land surface (Parfitt, 2009; Filimonova et al., 2016).

B forms inner-sphere surface complexes with trigonal and tetrahedral coordination (Su and Suarez, 1995) on minerals such as short-range-order (SRO) Fe and Al hydroxides, SRO aluminosilicates (allophane), 2:1 clay minerals, and kaolinite

(Beyrouty et al., 1984; Blesa et al., 1984; Goldberg et al., 1993; Su and Suarez, 1995); and outer-sphere complexes with Fe hydroxides (Peak et al., 2003). The mineral composition of volcanic ash-derived soils may include all of the above-mentioned minerals, but mineral surface area is often dominated by SRO aluminosilicates such as allophane and imogolite. Allophane and imogolite are X-ray amorphous clay-sized aluminosilicates comprised of hollow nano-spherules or nano-tubules, respectively. Both consist of an outer gibbsite-like sheet and an inner Si surface (Parfitt, 2009). Boron can substitute for Si in the inner tetrahedral layer of these nano-scale minerals (Su and Suarez, 1997) and it can be adsorbed at surface aluminol groups of the gibbsite-like outer sheet.

The B maximum adsorption capacities (b_B) for volcanic ash-derived soils are between 18 and 40 times greater than those of non-volcanic soils (Bingham et al., 1971; Schlscha et al., 1973; Chapter 2). We hypothesize that SRO aluminosilicates and Fe (oxy)hydroxides will be related to b_B, and that other clay minerals present will have negligible contribution to B sorption in volcanic ash-derived soils, despite their individual adsorption capacities in pure systems. To test this hypothesis, soils with a range of b_B were subjected to mineral composition analysis. The clay fractions of the soils were subject to X-ray diffraction (XRD), selective dissolutions, ^{57}Fe Mösbauer spectroscopy, and thermal analysis to identify mineral phases and relate them with specific surface area (SSA) and b_B.

3.3 Materials and methods

Soil description

Surface soils (0-15 cm) from 23 agricultural sites on the south coast of Guatemala were selected as representative of five soil orders that are present in that area (one Alfisol, six Andisols, five Entisols, seven Mollisols, and four Vertisols; identified by Sánchez et al. (1996)). The soils in this region are developed from igneous parent materials with intermittent and varying inputs of volcanic ash. Boron deficiency occurs widely on economically important crops growing in these soils. The empirical modeling of soil B adsorption on these soils is reported elsewhere (Chapter 2), but some selected characteristics including b_B are provided (Table 3.1).

Powder-XRD analysis

Clay fractions (< 2 μm) of the 23 soils were treated with 30% H_2O_2 to remove organic matter (Kunze and Dixon, 1986) prior to XRD. Analysis of oriented clay aggregates on glass slides was performed using a Bruker D8 Advanced Diffractometer (CoKα radiation) at a potential of 45 kV and a current of 45 mA, with a scanning rate of $0.01° \ 2\theta \ s^{-1}$ over a range of 2–70º 2θ. Identification of XRD crystalline phases was performed using the EVA software package (Bruker).

Selective dissolutions

Selective dissolutions with ammonium oxalate and sodium pyrophosphate reagents were used to estimate the percentages of allophane/imogolite and organically-associated Al, Fe, and Si in the clay fraction of the soils (Wada, 1989). For the acid-oxalate dissolution, a soil sample (0.25 g, fine-grind, air dried) was mixed with 25 mL of 0.2 mol L^{-1} acid oxalate reagent (0.2 mol L^{-1} of ammonium oxalate [$(NH4)_2C_2O_4$] and 0.2 mol L^{-1} of oxalic acid [$H_2C_2O_4$], with pH adjusted to 3±0.05) in a 50 mL centrifuge tube. The tubes were placed in a shaker and shaken for 4 hours in the dark at room temperature. For the sodium pyrophosphate dissolution a soil sample (0.5 g, fine-grind, air dried) was mixed with 30 mL of 0.1 mol L^{-1} sodium pyrophosphate ($Na_4P_2O_7$) (adjusted to pH 10±0.05) in a 50-mL centrifuge tube. The tubes were placed in a shaker and shaken for 16 hours at room temperature (23°C). After both extraction procedures samples were centrifuged and filtered, and the supernatant was analyzed to quantify Fe, Al, and Si using ICP-MS on a 1:1000 diluted extract. Five replicates of a single sample were made to assess the variability of the extraction protocol.

Allophane/imogolite abundance was calculated based on the Al:Si ratio for each sample from the oxalate-Al (Al_o), pyrophosphate-Al (Al_p), and oxalate-Si (Si_o) contents. The (Al_o– Al_p)/Si_o ratio multiplied by the molar ratio (28/27 for Al:Si) gives an estimate of the Al:Si ratio of allophane/imogolite content in the soil (Soil Survey Staff, 2014). The soil content of allophane/imogolite was calculated using its structural weight formula based on the estimated Al:Si ratio for each sample as follows: allophane has the general chemical formula $Si_yAl_4O_{6+2y} \cdot n\ H_2O$, where $1.6 \leq y \leq 4$, $n \geq 5$; and imogolite has the chemical formula $Si_2Al_4O_{10} \cdot 5\ H_2O$ (Sposito, 2008), thus the Al:Si ratio can vary from about 0.9 to 2.0, and the structural formula for each sample was estimated based on its measured Al:Si ratio.

Dithionite-citrate reagent was used to selectively dissolve all Fe (oxy)hydroxides (i.e., free Fe oxides) (Wada, 1989). For this extraction a soil sample (0.75 g, fine-grind, air dried) was mixed with 0.4 g of sodium dithionite ($Na_2S_2O_4$) and 25 mL of 0.5 M sodium citrate ($Na_3C_6H_5O_7.2H_2O$) solution in a 50 mL centrifuge tube. The tubes were placed in a shaker and shaken overnight (12 – 16 hours) at room temperature. After the extraction, samples were centrifuged and filtered, and the supernatant was analyzed to quantify Fe, Al, and Si using ICP-MS on a 1:1000 diluted extract. Five replicates of a single sample were made to assess the variability of the extraction protocol.

Thermal analysis of the mineral clay fraction

Thermal analysis was carried out on clay fractions (< 2 μm) of the 23 soils after the removal of organic matter with 30% H_2O_2 using a Netzsch simultaneous heat flux thermal analyzer (STA 409PC Luxx) equipped with a type-S (Pt/PtRh) TG–DSC sample carrier supporting a PtRh10-Pt thermocouple (Netzsch-Gerätebau GmbH, Selb, Germany). Samples were heated from ambient (25 °C) to 1000°C in a furnace atmosphere consisting of synthetic air (80% N_2 and 20% O_2) flowing at 30 mL/min. The evolved gas was analyzed (EGA) by infra-red gas analyzer (IRGA) coupled with the thermal analyzer to measure CO_2 and H_2O evolution from the heating reactions. Mineral phases were identified using thermogravimetry data (mass loss associated with thermal reactions) and water evolution from EGA, coupled with differential scanning calormetry (DSC) data. Peaks of H_2O were fitted using PeakFit software (SYSTAT) to estimate the fractions of water that were evolved from different dehydroxylation reactions depending on mineral thermal stability.

Although the samples were treated with H_2O_2 before the thermal analysis was performed, there is still a fraction of C that cannot be removed by oxidation with this chemical method (Plante et al., 2004). Therefore, carbon dioxide evolution was recorded showing that the total C remaining was negligible in terms of percent mass loss during the thermal analysis run, so the mass loss could be completely attributed to H_2O evolution.

^{57}Fe Mössbauer Spectroscopy

The Fe mineral composition of four representative sites (Velasquez, La Felicidad, Las Rosas, and Cadiz) was evaluated using transmission ^{57}Fe Mössbauer (MB) spectroscopy with a variable temperature He-cooled system with a 1024 channel detector at three collection temperatures (295K, 77K, and 4K) using a ^{57}Co source (~50 mCi) embedded in a Rh matrix kept at room temperature. Spectral fitting was performed using the Voigt-based fitting method of Rancourt and Ping (1991) with Recoil software, and the relative abundance of each Fe mineral phase was determined as a fraction of the total Fe spectral area.

3.4 Results and discussion

The main mineral phases identified in decreasing order of reactivity are: (i) SRO aluminosilicates (allophane and imogolite), (ii) Fe oxy(hydroxydes) with different degrees of crystallinity, (iii) 1:1 clay minerals (kaolinite and halloysite), (iv) 2:1 clay minerals (from the smectite group, most likely montmorillonite), and (v) primary minerals from the K-feldspar group (orthoclase) and silica polymorphs (cristobalite). For all these phases, the levels of reactivity that they confer to the soils in terms of SSA and b_B are discussed below.

SRO aluminosilicates

Selective dissolutions with acid oxalate and Na-pyrophosphate were used to quantify SRO aluminosilicates (e.g. allophane and imogolite) (Table 3.2). The SRO aluminosilicates content ranged from low values of 2.6 g kg^{-1} for the Capullo soil, to 102.6 g kg^{-1} for the Velasquez soil, which are comparable to the allophane content in surface horizons of Andisols from various climatic zones (Bartoli et al., 2007). The allophane and imogolite content has an exponential decay relationship with the ratio of Al pool extracted by Na-pyrophosphate and oxalate reagents (Al_p/Al_o) (Figure 3.1). Na-pyrophosphate selectively extracts Al associated with organic compounds. The higher points in the graph correspond to the soils classified as Andisols, whereas the right tail comprises the remaining soils with less andic character.

Because it is not possible to distinguish between allophane and imogolite using selective dissolutions, thermal analysis techniques can be used to differentiate between these SRO aluminosilicates (Dahlgren, 1994). Imogolite (nano-tubules) have a more rigid structure than allophane (nano-spheres). This makes imogolite's structural water (surface hydroxyl groups) more thermally stable (Russel et al., 1969). Both minerals show an endothermic peak between 50°C and 200°C as they lose physically adsorbed water, but imogolite undergoes a de-hydroxylation reaction that yields a characteristic endothermic peak between 390°C and 440°C (Yoshinaga and Aomine, 1962; Parfitt, 1990). DSC curves and H_2O evolution peaks from six soils (Buganvilia, Velasquez, Socorro, La Cuchilla, Puyumate, and Cadiz) showed an endotherm shoulder at 405 °C indicating presence of imogolite nano-tubules. For the other 17 soils imogolite was not identified, suggesting that only allophane was present.

The deconvoluted H_2O peaks were matched with the de-hydroxylation temperatures for each mineral, and the fraction of the total area for each peak was used to estimate how much water was evolved from each mineral phase (e.g. Figure 3.2). Water evolution was successfully modeled ($R^2 = 0.999$) as the sum of several hidden peaks with different temperature maxima, and phases' individual abundance was assigned by matching these temperatures with DSC reaction temperatures. For instance, for the Puyumate soil two water peaks (168 and 282 °C) correspond to 81.5% of evolved water from total SRO aluminosilicates, one peak (400 °C) corresponded to 5.1% of evolved water from imogolite, and one peak (474 °C) corresponded to 13.4% of evolved water from kaolinite (Figure 3.2). In general, water from imogolite de-hydroxylation was observed only in 5 samples ranging from 2.2 to 10.1% of the total water evolved (Table 3.3). The physically adsorbed water loss from total SRO aluminosilicates and the de-hydroxylation of 1:1 clays was observed in all soils. The percentage of water loss from SRO aluminosilicates ranged from 46.2 to 87.9%; and the 1:1 clay minerals de-hydroxylation ranged from 2.0 to 60.4% of the total water evolved.

Both halloysite and smectites can lose physically adsorbed water at the same temperature range as allophane and imogolite, but there is no experimental or analytical procedure available to differentiate between them. Despite this limitation, the correlation between extractable SRO aluminosilicates and mass loss (H_2O) improved substantially when water peaks were used to correct the thermogravimetric data. The amount of water evolved as a percentage of original clay mass is exponentially correlated ($R^2 = 0.82$) with the amount of extractable SRO aluminosilicates (Figure 3.3), indicating the validity of these two analytical techniques to quantify andic character in volcanic ash-derived soils.

Effect of SRO aluminosilicates on surface properties

Correlation coefficients between the amount of SRO aluminosilicates and clay properties were positive and highly significant. For clay B adsorption capacity the coefficient is 0.65 ($P < 0.001$) and for clay SSA it is 0.88 ($P < 0.001$). These strong statistical relations suggest that SRO aluminosilicates govern the B surface reactivity properties of these soils even when present in small amounts.

The gibbsite-like outer surface of SRO aluminosilicates have hydroxyl functional groups that readily react with B to form complexes. Both imogolite and allophane develop surface charge from unsatisfied oxygen ion bond valences, similar to the surfaces of kaolinite and halloysite, but the point of zero charge for this functional groups is higher for imogolite (at pH 8.4) and allophane (between 5.4 to 8.0) (Sposito, 2008). This suggests that allophane and imogolite have two characteristics that make them substantially more important in terms of B adsorption compared to other aluminosilicates: (i) they have a large surface area, and (ii) at circumneutral pH values they have higher abundance of hydroxyl surface functional groups to react with B via ligand exchange reactions.

Fe species

Contrary to what was expected, dithionite-citrate extractable Fe (Fe_d) was lower than oxalate extractable Fe (Fe_o) in our soils (Table 3.2). The oxalate solution usually solubilizes only the SRO Fe fraction (Birkeland et al., 1989), whereas dithionite-citrate solution dissolves the total free iron oxides. Our results agree with those reported by Vodyanitskii et al. (2007) and Meijer et al. (2007) who found Fe_o/Fe_d ratios higher than one for soils with andic properties. Some authors suggest that in soils derived from volcanic parent materials Fe_o value represents not only the SRO Fe-constituents, but also dissolves Fe in magnetite and maghemite lattices (Rhoton et al., 1981; Walker, 1983; van Oorschot and Dekkers, 2001; van Oorschot et al., 2002) and Fe–Ti oxide minerals such as titanomagnetite and ilmenite (Algoe et al., 2012). This is particularly true for volcanic ash soils where the presence of these minerals is a common feature in Si-undersaturated igneous rocks, especially basic tephra, basalts and andesites which frequently yield soils with andic properties (Algoe et al., 2002).

Our Mösbauer Spectroscopy (MBS) results show possible presence of maghemite in some soils (Table 3.4), and total TiO_2 contents ranging from 0.7 to 1.2% (data not shown), which can account for the Fe_o/Fe_d ratios observed. Another possible reason is that standard extraction procedures of the dithionite-citrate extraction fail to completely dissolve the total Fe oxides because some of them exist in association within allophane clouds (Filimonova et al., 2016) and this occluded Fe is not quantified unless previous allophane dissolution is performed.

The dithionite-citrate extracted Al pool (Al_d) in some of our soils is larger than the Fe_d pool. According to Schwertmann et al. (1977), Al_d represents the Al substituted in Fe oxides but in our case it must also dissolve a separate Al pool in those soils where Al_d is higher than Fe_d. Filimonova et al. (2014) reported that Al_d can also stem from feldspar dissolution. Our powder XRD results support the presence of feldspar minerals that could be dissolving in the dithonite-citrate extraction. Six of the seven soils with orthoclase identified in their clay fraction have Al_d higher than Fe_d. Al substituted in Fe oxides is significant in terms of B adsorption reactions in soils because of the substantial surface area and hydroxyl functional groups on its surface, but feldspars are not considered here to contribute in whole soil B reactions.

Using the specificity of ^{57}Fe MBS, four samples were selected to expand the understanding of Fe phases that are relevant in terms of B adsorption and that were difficult to detect by powder XRD and selective dissolutions. The crystal size and bonding environment (or solid-phase speciation) of Fe govern its influence on soil reactivity to a much larger extent than its total abundance. SRO and small particle sizes distinguish the most reactive, high surface area Fe components from larger bulk Fe-oxides (Bonneville et al., 2004; Roden, 2006).

The MBS spectra suggest that the Fe(III)-(oxy)hydroxide solid phases in these soils exhibit a continuum of crystallinities and they account for the majority of total Fe in the samples evaluated (Table 3.4). The Fe from silicates structures and organic matter associations was observed to have a lower contribution of the total Fe, accounting only for 4.6, 32.3, 17.2, and 4.3% of total Fe for soils Cadiz, La Felicidad, Velasquez, and Las Rosas, respectively.

Hematite was clearly identified in soils, La Felicidad and Velasquez, accounting for 12.6 and 22.1% of total Fe, respectively. On the other hand, the phase identified for soils, Cadiz and Las Rosas, could be either hematite or maghemite (Table 3.4). Ferrihydrite was clearly identified in the four samples, accounting for the majority of total Fe in the soil. The SRO Fe(oxy)hydroxides (ferrihydrite/nano-goethite) were divided depending on their degree of crystallinity (Table 3.5). Those at the more crystalline end were recognized as microcrystalline structures that order at room temperature (295 K). In the middle of the crystallinity continuum, were the sextets that order at 77 K and at liquid helium temperature (LHT = 4.2 K). At the most disordered end of the crystallinity continuum, were the collapsed sextets at 4.2 K which are assigned to nano-FeIII-oxyhydroxides that need even lower temperatures to order.

Effect of SRO Fe (oxy)hydroxides on surface properties

Ferrihydrite represents the most highly reactive Fe phase in this set of soils. It is characterized by a high surface-to-volume ratio in nanoparticles and an enhanced surface charge density, which expectedly facilitate the ligand exchange reactions (Filimonova et al., 2016) of B adsorption. Assuming a density of 4.0 g cm^{-3} for ferrihydrite (Childs, 1985), and 2.75 g cm^{-3} for allophane (Wada and Wada, 1977), we calculated the volumetric ratio ‘‘ferrihydrite:allophane” (Filimonova et al., 2016) which is lower than one for Andisols (0.3 for both Cadiz and Velasquez), and higher than one for non-Andisols volcanic-influenced soils (1.5 and 4.5 for La Felicidad and Las Rosas, respectively). These observed values can serve as an explanation of how ferrihydrite is an important mineral surface for B adsorption reactions in volcanic-influenced soils that do not have allophane levels sufficiently high to be classified as Andisols.

Another parameter evaluated was the “crystallinity index” (CI), which was calculated as the ratio between Fe(III)(oxy)hydroxides ordered at 77 K and 4 K (Table 3.4). Although the two Andisols evaluated have similar SSA and allophane contents, the one with lower CI has a higher b_B. The other two soils (non-Andisols) have similar b_B and allophane contents, and the one with lower CI has a higher SSA. This illustrates how SRO Fe phases may be actively contributing to both B adsorption reactions and total SSA for volcanic ash-derived soils.

1:1 Clay minerals

All soils were found to have 1:1 clay minerals in their clay-size fractions either by a broad and weak peak at ~ 7 Å in powder-XRD, or by an endotherm de-hydroxylation reaction in DSC between 450 – 700 °C accompanied by H_2O evolution and a further exothermic reaction of γ-allumina formation between 900 – 1000 °C (Table 3.3). This 7 Å phase could represent either kaolinite or halloysite (the sub-group associated with tubular morphology and lower crystallinity). To differentiate between these two, the oriented clay aggregates were subject to formamide solvation, and only two samples (Malta and Blanca Victoria soils) exhibited evidence of halloysite by a significant shift to a more expanded d-spacing after the treatment was applied; for the other 21 samples the 7 Å peak corresponds to kaolinite.

Even though only two soils had positive XRD identification for halloysite, DSC measurements exhibited endotherm peaks corresponding to more rapid loss of hydroxyls consistent with weakly crystallized kaolinite. More weakly crystallized kaolinite loses hydroxyls more readily than the well-crystallized kaolinite (Carthew, 1955). Soils classified as Andisols, Entisols and Mollisols showed both a more amorphous background in XRD and a lower temperature of de-hydroxylation on DSC for the 1:1 clay phases (averaging 478°C) than the Vertisols and Alfisol (averaging 513°C) (Table 3.3).

Goldberg (1999) had previously reported that low crystallinity kaolinite (differentiated by larger SSA) had higher B adsorption capacity than bulk kaolinite. Assuming negligible adsorption from sand and silt fractions, the B adsorption capacity of the clay fraction is strongly negatively correlated (-0.57, P = 0.001) with kaolinite de-hydroxylation peak temperature. A correlation coefficient of -0.56 was observed for this temperature and the clay SSA (Table 3.2). Our results agree with those of Goldberg (1999). The negative correlation explains that a lower crystallinity represented here as a lower de-hydroxylation temperature, is associated with larger SSA and higher B adsorption capacity. Because B forms inner-sphere complexes via ligand exchange reactions with the edges hydroxyl groups (Goldberg, 1993) therefore less crystalline kaolinites have more exposed surface functional groups with higher potential for complexation reactions with B.

Despite the absence of halloysite in the majority of our soils, different degrees of crystallinity of kaolinite are responsible for differences in observed soil b_B. Despite the low SSA of kaolinites (5 to 40 m^2 g^{-1}; Sposito, 2008), these results suggest that these mineral phases have an important contribution in explaining b_B variability at a whole soil level.

2:1 Clay minerals

The clay fractions of 10 soils exhibit a broad ~ 10 Å reflection which expands upon ethylene glycol solvation to ~ 17 Å in powder XRD, confirming the presence of smectite (most probably montmorillonite) (Table 3.2). Only La Trinidad soil was confirmed to have a smectite phase by thermal analysis, showing a broad and weak endotherm de-hydroxylation peak at 660 °C (independent of the peak attributed to 1:1 clay minerals) that was attributed to a 2:1 clay phase. In addition, two more soils (Cadiz and Boton Blanco) also presented an endotherm at 660 and 630°C, respectively, that can be attributed to the presence of smectite.

Smectite phases are present in small amounts in the clay fractions of the soils in which they were identified based on the evidence provided by the broadness and weakness of the XRD peaks and the small proportion of water evolved in the thermal analysis. Only 10.4, 5.6, and 4.5% of the water loss was attributed to de-hydroxylation of smectites in soils from La Trinidad, Cadiz, and Boton Blanco, respectively (Table 3.6). The presence of smectites in soils confers substantial surface area (SSA for pure smectites ranges from about 40 to 800 m^2 g^{-1}) but this surface is not directly available for B complex formation because B will not react with the basal permanent charge.

To test the hypothesis that smectite SSA does not participate in B adsorption reactions, the soils were divided into two groups based on smectite phase identification (either by XRD or by thermal analysis), and correlation analysis between the clay SSA and the clay b_B was performed partitioning between smectitic and non-smectitic soils. For the group of smectitic soils the correlation was not statistically significant ($P = 0.47$), but it was significant ($P = 0.07$) for the group of non-smectitic soils. These statistical correlations suggest that volcanic ash-derived soils with smectite phases in their clay fraction have large SSA that is not directly available for complexation reactions with B.

Furthermore, the mechanisms of B adsorption by montmorillonite and montmorillonitic soils correspond to a non-specific, weaker, and less stable adsorption based on outer-sphere surface complexation reactions (Goldberg, 1993). Even when montmorillonite has B adsorption capacities of a magnitude comparable to those reported for other minerals, the complexes formed are less stable because of the nature of the chemical bonds involved in the reactions. Therefore, smectitic soils have large SSA, but maximum B adsorption is not as large as for the soils dominated by SRO aluminosilicates with comparable SSA. For instance, La Felicidad soil (smectitic) has a SSA of 62 $mg^2 g^{-1}$ and a b_B of 14 mg B kg^{-1}, whereas La Cuchilla soil (non-smectitic) has a SSA of 65 $mg^2 g^{-1}$ and a b_B of 23 mg B kg^{-1}. This illustrates the contribution of mineral phases (allophane, imogolite, and ferrihydrite) to SSA comparable to that of smectites, but with greater B affinity must explain the difference on B adsorption capacity of soils with almost identical SSA.

Primary minerals

Primary minerals identified in the soils are not considered to contribute to any significant extent to B adsorption reactions in volcanic ash-derived soils. From powder-XRD analysis, a broad and asymmetrical peak at 4.1 Å was the only identifying peak attributed to disordered cristobalite in three soils (San Patricio, Colombita, and Cadiz; Table 3.2). Powder-XRD was the only analytical technique that evidenced the presence of this silica polymorph as has a fairly flat DSC pattern (Jones and Segnit, 1971). Cristobalite has been reported to naturally occur in various size fractions (predominantly clay) of several soils derived from volcanic ash in South America and Costa Rica (Wright, 1964; Mejia et al., 1968; Besoain, 1969; Calhoun et al., 1972; Cortes and Franzmeier, 1972). It is probably a component of the parent erupted magma from which these soils developed. Despite its presence in the clay fraction of these three soils it has low relevance in terms of physicochemical reactivity. Cristobalite lacks significant isomorphic substitution for Si, and has very few broken Si-O bonds and Si-OH (silanol) groups around particle edges, resulting in almost no surface charge.

Orthoclase (K-feldspar) with one recorded peak at 3.18 Å was identified in the clay fraction of seven soils (Buganvilia, Mirador, San Patricio, Malta, La Cuchilla, Puyumate, and Cadiz; Table 3.2). As for cristobalite, orthoclase presence in soil clay fractions has no relevance in terms of physicochemical reactions responsible for B adsorption, as it likely only contributes to relevant dissolution reactions by continuously replenishing K via dissolution (Huang, 1979).

3.5 Conclusions

The mineral surfaces responsible for B adsorption reactions in volcanic ash-derived soils are SRO aluminosilicates, Fe (oxy)hydroxides, and kaolinite. Only the soils with greater andic character (those classified as Andisols) contain considerable amounts of imogolite, and the rest are dominated only by allophane. Contrary to what was hypothesized, kaolinite phases contribute to whole-soil SSA and b_B despite their lower reactivity as compared with that of the SRO minerals. The degree of crystallinity of the kaolinite phase has an influence on the extent of surface area available and it has a direct impact on B adsorption capacity. Surface area from smectite phases is not available for B complex formation, though to some extent these 2:1 clay minerals can contribute to the formation of weaker outer-sphere complexes. Primary minerals are considered non-reactive and they might lead to overestimation of active pools of Al and Fe by selective dissolutions.

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Tables and figures

Table 3.1: Selected soil characteristics of the agricultural sites sampled (from Chapter 2)

	Site†	Clay-size particles, g kg^{-1}	Specific surface area, m^2 g^{-1}	B Maximum adsorption, mg B kg^{-1}
1	Buganvilia (A)	161	58	53
2	Santa Monica (E)	61	16	3
3	Mirador (E)	401	101	62
4	Velasquez (A)	181	104	83
5	Socorro (A)	341	86	49
6	San Patricio (M)	81	8	13
7	La Felicidad (E)	301	62	14
8	San Francisco (M)	381	98	14
9	San Antonio (M)	321	73	27
10	Malta (M)	121	36	34
11	La Cuchilla (A)	101	65	23
12	Puyumate (A)	141	73	130
13	Blanca Victoria (M)	300	49	6
14	Las Rosas (Af)	480	73	13
15	Buenos Aires (V)	540	59	47
16	Colombita (V)	500	78	16
17	Maria del Carmen (V)	520	83	45
18	Chaparral (M)	340	109	13
19	Maria Linda (M)	160	47	5
20	La Trinidad (E)	180	49	19
21	Capullo (V)	300	26	21
22	Cadiz (A)	240	98	90
23	Boton Blanco (E)	60	11	36

†Site name followed by soil order identification in parenthesis: Andisols (A), Alfisols (Af), Entisols (E), Mollisols (M), Vertisols (V)

Table 3.2: Soil mineral characteristics

	Site	Acid-oxalate extraction, g kg^{-1}			Allophane†, g kg^{-1}	Dithionite-citrate extraction, g kg^{-1}			Pyrophosphate extraction, g kg^{-1}			Other minerals ‡
		Al	Fe	Si		Al	Fe	Si	Al	Fe	Si	
1	Buganvilia (A)	24.0	15.0	12.6	78.7	3.3	1.2	1.6	5.7	1.8	2.4	ORT
2	Santa Monica (E)	5.4	5.0	3.7	17.6	0.7	0.0	1.0	1.8	0.4	1.8	-
3	Mirador (E)	11.2	9.7	6.5	43.2	2.1	1.2	3.1	3.8	0.0	1.6	ORT
4	Velasquez (A)	32.0	18.1	17.4	102.6	7.1	2.5	2.4	9.0	3.3	2.7	-
5	Socorro (A)	20.5	25.1	9.8	51.4	4.8	2.0	1.5	9.6	4.1	4.0	KAO
6	San Patricio (M)	3.9	5.1	2.8	13.5	0.6	1.1	1.3	1.0	1.2	1.3	CRI, ORT
7	La Felicidad (E)	4.8	3.1	2.6	9.4	0.7	0.0	1.8	3.5	1.4	5.6	SMC, PYR
8	San Francisco (M)	6.4	6.7	2.8	18.9	0.9	0.7	1.9	1.8	0.8	3.0	SMC
9	San Antonio (M)	5.7	3.9	2.8	20.1	1.2	0.0	2.5	4.0	0.0	1.4	SMC
10	Malta (M)	3.3	6.2	2.4	10.4	0.5	0.5	1.2	1.4	0.8	2.2	HAL, ORT
11	La Cuchilla (A)	25.5	12.4	14.4	80.1	4.9	1.2	1.6	6.8	1.8	1.7	ORT
12	Puyumate (A)	25.6	12.3	13.5	84.4	4.6	0.9	1.8	6.4	1.5	1.7	ORT
13	Blanca Victoria (M)	4.2	5.7	2.1	14.2	0.4	0.5	1.4	7.1	0.4	1.6	SMC, HAL
14	Las Rosas (Af)	4.6	10.8	2.5	6.2	0.5	0.6	1.3	18.2	7.7	20.2	KAO
15	Buenos Aires (V)	6.4	12.9	2.4	12.6	1.0	2.0	1.6	3.7	1.4	3.1	SMC, KAO
16	Colombita (V)	6.5	14.9	3.4	9.9	0.6	0.6	1.4	5.5	1.8	4.7	SMC, CRI, KAO
17	Maria del Carmen (V)	5.6	11.2	2.5	9.1	0.6	1.0	1.5	4.3	1.4	4.1	SMC, KAO
18	Chaparral (M)	4.2	2.1	1.9	13.3	0.4	0.0	1.7	3.6	0.0	1.7	-
19	Maria Linda (M)	3.6	7.7	2.6	13.8	0.2	0.6	1.1	6.0	0.7	1.7	SMC, KAO
20	La Trinidad (E)	1.6	4.4	1.5	3.7	0.0	0.5	1.0	4.3	2.3	6.9	SMC, KAO
21	Capullo (V)	2.0	4.9	1.0	2.6	0.2	0.6	1.1	10.7	3.6	11.1	SMC, KAO
22	Cadiz (A)	25.2	16.9	13.2	82.7	3.0	2.2	2.1	5.7	2.5	2.9	CRI, ORT
23	Boton Blanco (E)	3.6	4.7	2.8	12.0	0.8	0.2	1.3	1.4	0.5	1.2	-

†Estimated from oxalate and pyrophosphate extractable Al and oxalate extractable Si; ‡other minerals identified by X-ray diffraction: SMC = Smectite, CRI = Cristobalite, HAL = Halloysite, KAO = Kaolinite, ORT = Orthoclase, PYR = Pyrollusite.

Table 3.3: Thermal analysis interpretation for mineral clay fractions

		Endothermic	Assignment		H_2O	Area	H_2O	Exothermic	Assignment	
	Soil	**peak, °C**	**Reaction**	**Component**	**peaks, °C**	**%**	**†**	**peak, °C**	**Reaction**	**Component**
1	Buganvilia	133	1	AL/IM/HAL	188 - 338	87.9	18.5	926	3	AL/IM
		406	2	IM	457	10.1	2.1	1010	3	KAO/HAL
		612	2	KAO/HAL	536	2.0	0.4			
2	Santa Monica	115	1	AL/HAL	188 - 305	82	14.8	940	3	AL
		450	2	KAO/HAL	482 - 491	18	3.2	1004		
3	Mirador	110	1	AL/HAL	174 - 285	79.3	13.9	944	3	AL
		460	2	KAO/HAL	438 - 551	20.6	3.6	1010	3	KAO/HAL
4	Velasquez	137	1	AL/IM/HAL	161 - 275	78.6	19.3	921	3	AL/IM
		405	2	IM	379	2.2	0.5	1005	3	KAO/HAL
		456	2	KAO/HAL	465	19.2	4.7			
5	Socorro	125	1	AL/IM/HAL	141 - 230	50.6	10.2	826	3	AL/IM
		300	2	GOE	345	11.8	2.4	938	3	KAO/HAL
		491	2	KAO/HAL	444 - 568	37.4	7.6			
6	San Patricio	120	1	AL/HAL	140 - 226	70.2	14.2	935	3	AL/IM/HAL
		447	2	KAO/HAL	354 - 564	29.8	6.0			
7	La Felicidad	122	1	AL/HAL	158 - 256	62.8	10.2	895	3	AL
		488	2	KAO/HAL	366 - 627	37.3	6.0	1015	3	KAO/HAL
8	San Francisco	127	1	AL/HAL	167 - 272	74.6	12.8	904	3	AL
		468	2	KAO/HAL	409 - 618	25.4	4.4	1010	3	KAO/HAL
9	San Antonio	132	1	AL/HAL	161 - 295	75.1	14.3	904	3	AL
		482	2	KAO/HAL	431 - 632	24.8	4.7	999	3	KAO/HAL
10	Malta	125	1	AL/HAL	149 - 252	63.3	11.3	900	3	AL
		468	2	KAO/HAL	391 - 579	33.7	6.0	1000	3	KAO/HAL
11	La Cuchilla	140	1	AL/IM/HAL	175 - 305	77.9	17.5	904	3	AL/IM
		405	2	IM	407	6.7	1.5	1011	3	KAO/HAL
		455	2	KAO/HAL	486	15.4	3.5			

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12	Puyumate	132	1	AL/IM/HAL	168 - 282	81.5	20.5	904	3	AL/IM
		405	2	IM	400	5.1	1.3	1009	3	KAO/HAL
		446	2	KAO/HAL	474	13.4	3.4			
14	Las Rosas	120	1	AL/HAL	136 - 225	50.6	9.5	918	3	AL/KAO/HAL
		510	2	KAO/HAL	359 - 629	49.4	9.2			
15	Buenos Aires	143	1	AL/HAL	151 - 232	39.4	7.6	936	3	AL/KAO/HAL
		529	2	KAO/HAL	342 - 587	60.4	11.7			
16	Colombita	114	1	AL/HAL	183 - 312	48.4	9.3	934	3	AL/KAO/HAL
		501	2	KAO/HAL	520 - 552	51.7	10.0			
17	Maria del Carmen	116	1	AL/HAL	135 - 212	49.0	8.6	935	3	AL/KAO/HAL
		514	2	KAO/HAL	535 - 550	51.0	9.0			
18	Chaparral	155	1	AL/HAL	169 - 275	60.7	8.3	900	3	AL
		490	2	KAO/HAL	402 - 568	39.4	5.4	1013	3	KAO/HAL
19	Maria Linda	125	1	AL/HAL	124 - 196	66.8	12.6	917	3	AL/KAO/HAL
		505	2	KAO/HAL	338 - 482	33.2	6.3			
20	La Trinidad	127	1	AL/HAL	165 - 306	62.4	11.4	915	3	AL
		504	2	KAO/HAL	446 - 513	27.2	5.0	1005	3/4	KAO/HAL/SMC
		660	2	SMC	559	10.4	1.9			
21	Capullo	120	1	AL/HAL	231 - 363	46.2	7.1	936	3	AL/KAO/HAL
		512	2	KAO/HAL	435 - 633	53.8	8.3			
22	Cadiz	132	1	AL/IM/HAL	156 - 282	76.8	18.4	820	4	SMC
		405	2	IM	420	4.7	1.1	920	3	AL/IMG
		455	2	KAO/HAL	505	12.7	3.0	1001	3	KAO/HAL
		660	2	SMC	589	5.6	1.3			
23	Boton Blanco	117	1	AL/HAL	132 - 221	79.5	14.5	944	3	AL
		462	2	KAO/HAL	496	16.0	2.9	998	3/4	KAO/HAL/SMC
		630	2	SMC	582	4.5	0.8			

Reactions:

1 Loss of adsorbed H_2O
2 De-hydroxilation
3 γ-alumina formation
4 Recrystalization

† Mineral phase assigned: SMC = Smectite, HAL = Halloysite, KAO = Kaolinite, AL = Allophane, IM = imogolite. ‡H2O evolved expressed as per cent of initial mass.

Table 3.4: Mösbauer spectroscopy Iron (Fe) phase identification and crystallinity index (CI)

Soil	**Total Fe (%)**	**Phase**	**Abundance (%)**	**CI**
Cadiz	5.71	Silicates/Organic matter	4.6	0.47
		Hematite/Maghemite	17.9	
		Ferrihydrite	65.1	
La Felicidad	5.20	Silicates/Organic matter	32.3	0.84
		Hematite	12.6	
		Ferrihydrite	39.4	
Velasquez	6.95	Silicates/Organic matter	17.2	0.79
		Hematite/Maghemite	22.1	
		Goethite/Ferrihydrite	64.0	
Las Rosas	5.67	Silicates/Organic matter	4.3	0.40
		Hematite	12.3	
		Ferrihydrite	71.0	

Table 3.5: Mösbauer spectroscopy temperature of ordination of short-range-order (SRO) Fe phases

	SRO Fe(III)(oxy)hydroxides				
Soil	**295 K**	**77 - 295 K**	**4 - 77 K**	**< 4 K**	**Total**
Cadiz	9.1	3.2	33.4	19.4	**65.1**
La Felicidad	13.0	0.0	3.3	23.1	**39.4**
Velasquez	9.1	34.0	3.1	17.8	**64.0**
Las Rosas	10.2	0.7	39.7	20.4	**71.0**

Table 3.6: Correlation coefficients between clay surface properties and kaolinite de-hydroxylation temperature

	Clay B adsorption	Clay SSA	T (°C)
Clay B adsorption	1.00		
Clay SSA	0.53**	1.00	
T (°C)	-0.57**	-0.56**	1.00

** significant at P = 0.01

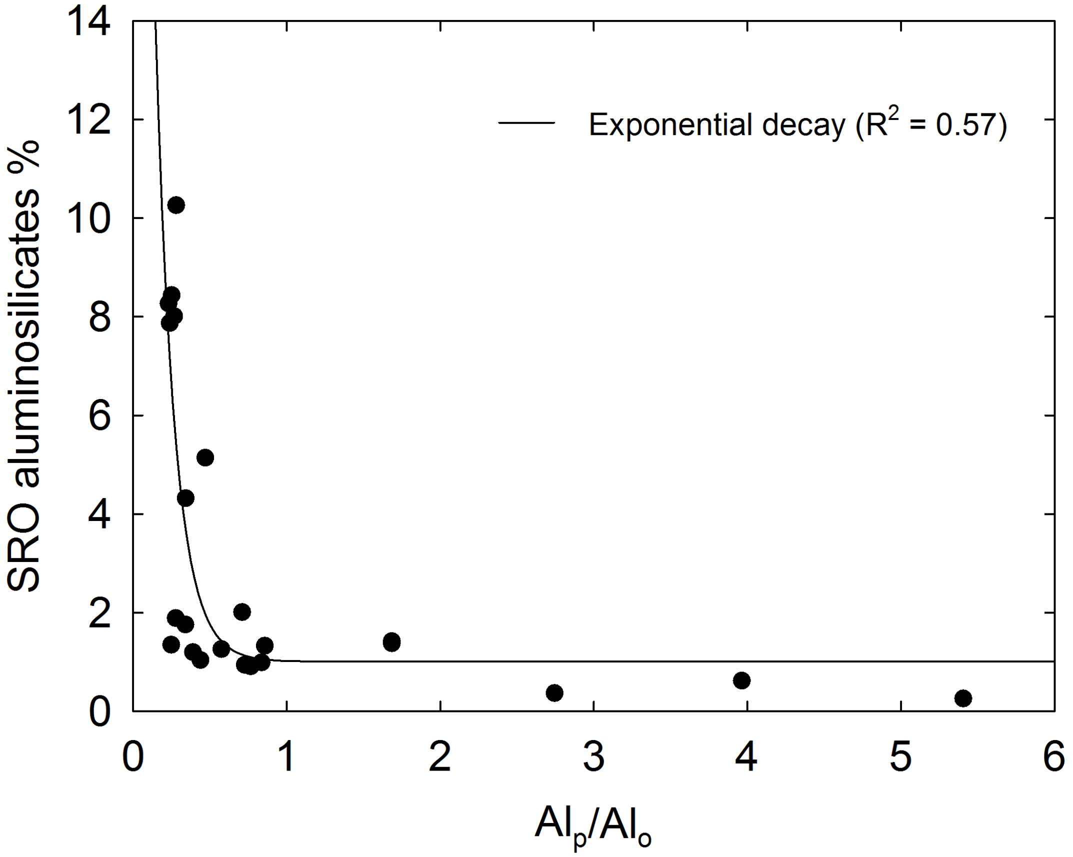

Figure 3.1: Allophane/imogolite content as a function of the pyrophosphate/oxalate extractable-Al ratio, Al_p/Al_o.

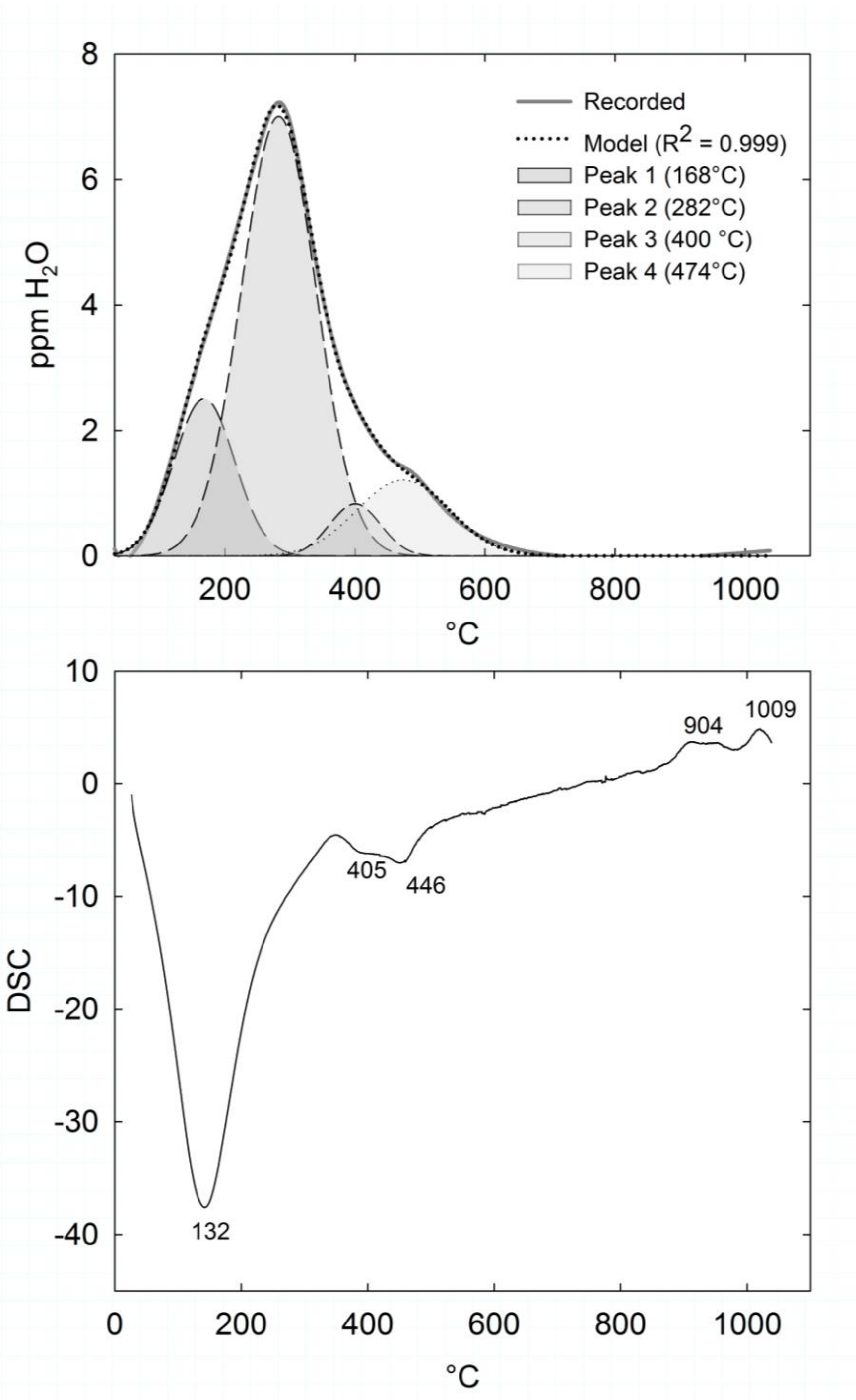

Figure 3.2: Water evolution (top) modeled as the sum of hidden peaks as a function of temperature and DSC curve (bottom) for andisol Puyumate.

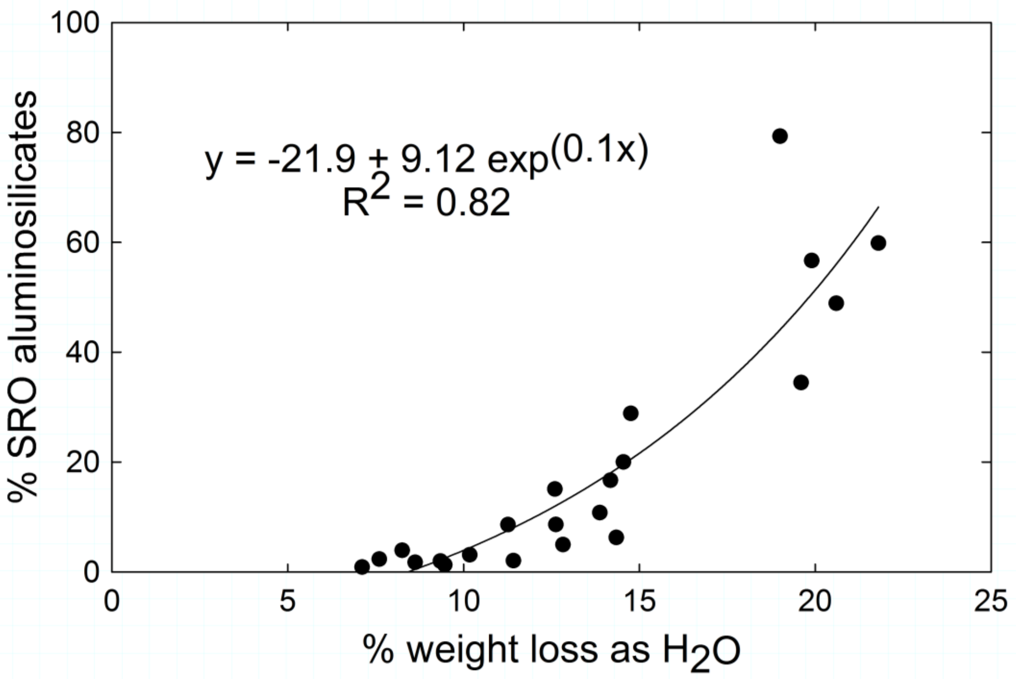

Figure 3.3: Exponential correlation between percent water loss as evolved water estimated from peak modeling and DSC and percent of SRO aluminosilicates in clay fraction calculated from selective dissolutions.

CHAPTER 4

EFFECTS OF ORGANO-MINERAL PROPERTIES OF VOLCANIC ASH-DERIVED SOILS ON BORON ADSORPTION[1]

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[1] Terraza Pira, M.F., M.E. Sumner, A.F. Plante, and A. Thompson. To be submitted to the Soil Science Society of America Journal.

4.1 Abstract

Boron (B) forms surface complexes with carboxylic and phenolic functional groups on natural and synthetic organic matter, with adsorption capacities even higher than for some minerals on a unit mass basis. However, the effects of organic matter on whole-soil B adsorption are contradictory, with some authors suggesting that it is positively correlated with adsorption capacities whereas others suggest that it decreases the mineral reactivity of B within the soil matrix. We hypothesize that the contradictory effects of organic matter on whole-soil B adsorption are due to different degrees of organic matter decomposability and association with mineral components, which are the two main factors affecting thermal stability. By using thermal analysis techniques, different pools of organic matter were identified for 23 soils derived from volcanic ash. The organic matter fractionation was used with other organo-mineral parameters such as allophane and imogolite content, total Fe oxides, and organically complexed Fe and Al to elucidate whether particular fractions of organic matter have different effects on surface properties, such as specific surface area (SSA) and B maximum adsorption capacity (b_B). To test our hypothesis, partial least squares regression (PLS-R) models of the data were fitted showing that different pools of SOM have different effects on surface properties. Labile organic matter (oxidized between 200–350 °C) is not a significant variable in explaining surface properties, recalcitrant organic matter (oxidized between 350–475 °C) is closely related to b_B, whereas refractory organic matter (oxidized between 475–650 °C) contributes significantly to SSA. We propose that using thermal analysis techniques to understanding the organic matter fractionation of soils can be a useful approach to elucidate surface properties at the whole-soil level.

4.2 Introduction

The mechanisms by which B adsorbs to isolated natural and synthetic humic materials have been well studied, though the conclusions concerning the effect of organic matter on whole-soil B reactions are not yet clear (Sarkar et al., 2014). Boron forms tetrahedrally coordinated surface complexes on di-carboxylic acid sites, alpha-hydroxy carboxylic acid sites, and di-phenols on both synthetic and natural humic substances (Lemarchand et al., 2005; Tossel, 2006; Goldberg, 2014). Within an organo-mineral assemblage, organic materials have been reported to reduce the pure mineral's capacity to adsorb B. For instance, a decrease in adsorption capacity occurred when Al hydroxide was coated with organic matter (Xu and Peak, 2007), and allophane showed a reduced capacity to sorb B when it was coated with an organic compound known to a have high B affinity (Reinert et al., 2011).

In whole soils, there are two contrasting behaviors concerning the role that organic matter plays in B retention. Some studies suggest that soil B adsorption increases with increasing organic matter content (Olson and Berger, 1947; Elrashidi and O'Connor, 1982; Yermiyaho et al., 1995; Sharma et al., 2006) whereas other authors report that organic matter causes a reduction in B sorption in soils (Marzadori et al., 1991; Diana et al., 2010; Sarkar et al., 2014). The use of pure minerals and isolated organic matter as models is not translatable to whole soil–B interactions.

Humic substances in soils have been traditionally classified based on solubility characteristics: humin, the insoluble fraction of humic substances; humic acid, the fraction soluble only under alkaline conditions; and fulvic acid, the fraction soluble under all pH conditions (Sposito, 2008). Regardless of differences in physicochemical properties such as solubility, these fractions are operationally defined and they do not directly imply the existence of three different molecular structures in soil humus (Sutton and Sposito, 2005). As of today, no single analytical method can fully characterize the structure and composition of SOM. However, thermal stability can serve as an indicator of the distribution of SOM between biogeochemically labile and stable fractions, with the advantage that the method is rapid and requires little sample preparation (Plante et al., 2009) so that relevant information regarding the reactivity of SOM in soils can be obtained; this is because thermal analysis does not provide information at the atomic or molecular level, but rather registers irreversible thermal reactions that occur at the whole-matrix level.

Because volcanic ash-derived soils have an enhanced ability to accumulate organic carbon (C) as compared with other clay-rich soils (Zunino et al., 1982; Shoji et al., 1993) the mechanisms by which organic matter is hosted and its effects on surface reactivity in these soil environments are questions of special concern. Because the literature reports significant B adsorption from independent mineral and organic soil constituents such as Fe and Al oxides, edges of aluminosilicates, organic matter, and allophane —all of which may be present in volcanic ash-derived soils— and because contradictory conclusions have been drawn concerning the role of organic matter interactions in whole soil B sorption, the question that drives this study is how can organo-mineral associations explain the widely variable soil b_B that had been observed for a set of volcanic ash-derived soils.

Chapter 3 presented a detailed characterization of the mineral surfaces for a set of volcanic ash-derived soils from the Pacific coastal plain of Guatemala in relation to their surface properties affecting B adsorption. The objective of this study is to use the same set of 23 agricultural top soils to evaluate the relationship between mineral properties and organic matter fractions based on their thermal stability, specific surface area (SSA), and B maximum adsorption capacity (b_B). To test the hypothesis that different fractions of organic matter have distinct effects on surface reactivity of volcanic ash-derived soils, a multivariate statistical analysis was used to assess these relationships so that a conceptual model of organomineral associations and their contribution to SSA and whole-soil b_B could be proposed.

4.3 Materials and methods

Soils description

Surface soils (0-15 cm) from 23 agricultural sites on the south coast of Guatemala where crop B deficiency is common were selected. The soils as represent five soil orders (one Alfisol, six Andisols, five Entisols, seven Mollisols, and four Vertisols, identified by Sánchez et al. (1996)) and are developed from igneous parent materials with intermittent and varying inputs of volcanic ash. The results of soil B adsorption on these soils and a detailed discussion on their mineralogy are reported elsewhere (Chapters 2 and 3). Briefly, clay fractions are composed of primary minerals (K-feldspar and crystobalite), 1:1 clay minerals (kaolinite and halloysite), 2:1 clay minerals (smectite, most probably montmorillonite), short-range-order (SRO) aluminosilicates (allophane and imogolite) and Fe (oxy)hydroxides. Imogolite was only identified in Andisols, whereas allophane and 1:1 clays (with different degrees of crystallinity) were identified in all samples. Smectites were identified only in 11 out of 23 samples.

Specific surface area (SSA) was measured by the water vapor adsorption method (Orchison, 1952), and b_B were determined in batch equilibrium experiments (Chapter 2). Active Al and Fe pools were extracted with selective dissolutions; briefly, acid-oxalate extractions were used to quantify SRO mineral pools, Na-pyrophosphite to quantify the organically associated Al and Fe, and dithionite-citrate for free Fe oxides (Chapter 3).

Organic matter fractionation

Total soil organic matter (SOM) was calculated from total C and N measured by combustion using a Leco C-N analyzer (Wang, 1998). To differentiate fractions of organic matter, thermal analysis coupled with CO_2/H_2O evolved gas analysis was carried out on bulk soils with experimental conditions according to Fernandez et al., 2012. Peaks of CO_2 were deconvoluted using PeakFit software (SYSTAT) and fractionation of organic matter was estimated according to thermal stability ranges available in the literature (Plante et al., 2005; De La Rosa et al., 2008).

Soil organic matter was divided in three groups according to resistance to thermal oxidation (Plante et al., 2005; De La Rosa et al., 2008): labile organic matter (200–350 °C), recalcitrant organic matter (350– 475 °C), and refractory organic matter (475–650 °C), the last group including black carbon and other thermally condensed organic compounds. Peak fitting analyses of the exothermic region of the thermal reactions (CO_2 evolution from organic matter oxidation) on bulk soils showed that local maxima consisted of several hidden peaks representing these three fractions of organic matter that decomposed in different temperature ranges.

The thermal fractionation of organic matter belonging to the different pools identified by distinctive peaks was estimated as the relative area of the curves within each temperature range. The total content of each pool was calculated as the fraction multiplied by total organic matter content (Table 4.1).

Statistical analysis

Cluster analysis was performed to assemble the soils into classes (clusters) in such a way that soils belonging to the same class are more similar to one another than to soils belonging to other classes. Proximity between soils was based on a set of organomineral variables measured on all samples. The variables used in the clustering process were: fractions of SOM based on thermal stability (labile, recalcitrant, and refractory), total free Fe oxides (dithionite-citrate extractable), organically complexed Al and Fe (Na-pyrophosphate extractable), SRO aluminosilicates (allophane and imogolite), and C:allophane ratio. The method used was Agglomerative Hierarchical Clustering (AHC). After clustering soils based on their organomineral properties, a multivariate regression technique was used to model soil b_B (based on the same variables) using partial least squares regression (PLS-R).

4.4 Results and discussion

Effect of total soil organic matter on surface properties

While simple linear regression of total soil organic matter (SOM_T) with SSA and b_B was statistically significant ($p < 0.05$), it explained only 35 and 37% of their variability, respectively (Figure 4.1). In a multiple linear regression using SOM_T and

SRO aluminosilicates (the main mineral surface explaining b_B for this set of soils (Chapter 3)) as independent variables for SSA and b_B, SOM_T is significant only for SSA ($p = 0.01$) but not for b_B (Figure 4.2).

An improvement in the goodness of fit for SSA was obtained when this variable was exponentially related with SOM normalized by the allophane content expressed as the C:allophane ratio ($R^2 = 0.486$) (Figure 4.3). This negative exponential relationship is consistent with that of Bartoli et al. (2007) for another set of volcanic soils. According to the mechanisms by which allophanic soils accumulate organic matter (Filimonova et al., 2016), the C:allophane ratio could be used as a good indicator of organic coatings on allophane surfaces. Our data shows that this mineral's association with organic matter has a negative exponential impact on specific surface area.

Soil organic matter thermal fractionation

Local maxima consisted of several hidden peaks representing these three fractions of organic matter that decomposed in different temperature ranges (Figure 4.4). Coefficients of correlation between the actual curve and the sum of the fitted curves were greater than 0.99 for all the samples. In general, recalcitrant organic matter was the most abundant pool in this set of soils. A possible explanation for these results is that the majority of soils have been under sugarcane cultivation for a long time (more than 20 years) with burning harvest methods that makes these soils devoid of labile organic matter. Allophane and nano-particulated Fe (oxy)hydroxides tend to accumulate more preferably labile organic matter and low-molecular-weight components such as aminoacids (Filimonova et al., 2016), so higher proportions of labile organic matter were expected for this set of allophane-rich soils.

Agglomerative Hierarchical Clustering (AHC)

Cluster analysis divided soils into three clusters based in their organomineral properties (Figure 4.5, Table 4.2). Cluster one grouped soils classified as Andisols (A); cluster two grouped Mollisols (M), Entisols (E), and some Vertisols (V); cluster three grouped one Vertisol and the only Alfisol (F). Briefly, the variables with the greatest distance between clusters centroids were allophane and imogolite content, organically complexed Al and Fe, recalcitrant SOM, and C:allophane ratio. Cluster one (Andisols) had the greatest allophane and imogolite content, and recalcitrant SOM fraction. Cluster three (Vertisol and Alfisol) has the greatest organically complexed Al and Fe, and C:allophane ratio. These values show that the andic character of the soils in each group decreases from cluster one to three.

Partial least squares regression (PLSR)

After clustering soils based on their organomineral properties, a regression technique was used to model the two surface properties of interest (SSA and b_B) to elucidate if different fractions of organic matter are related differently to mineral and surface properties. The first two components explained more than 50% of the variability in both the explanatory and the dependent variables. The correlation loading plot explains the relationship between the explanatory variables with the dependent variables based on the latent factors—t1 and t2— (Figure 4.6). b_B was positively correlated with the allophane and imogolite content, total Fe oxides concentration, and the recalcitrant fraction of organic matter, and negatively correlated with C:allophane ratio; whereas SSA was correlated with organically complexed Fe and Al, refractory fraction of organic matter, and (to a lesser extent) with the labile organic matter fraction.

Previously identified clusters were distinctively recognized in the loading plot (Figure 4.7). Cluster one, where the soils with the largest andic influence were grouped, was more related to allophane and imogolite content, total Fe oxides, and recalcitrant fraction of organic matter. Clusters two and three were distant from cluster one, with labile and recalcitrant fractions of organic matter, and organically complexed Al and Fe becoming more important variables to these clusters. From the loading plots, it is clear that B adsorption and SSA are closely related, but the way in which of the variables interact is different.

The standardized coefficients of the regression models were evaluated at the 95% confidence interval to test the significance of each variable in the regression equation explaining variability in b_{B} and SSA (Figure 4.8). The standardized coefficients for the significant variables explaining b_{B} are 0.293, 0.233, 0.213, and -0.166 for allophane and imogolite content, total Fe oxides, recalcitrant organic matter, and C:allophane ratio, respectively. The standardized coefficients for the significant variables explaining SSA are 0.130, and 0.472 for allophane and imogolite content, and refractory organic matter, respectively.

These two regression models confirm that fractions of organic matter with different thermal stabilities have different relationships with surface properties such as SSA and b_{B}. Recalcitrant organic matter is associated with higher reactivity towards B through ligand exchange reactions, whereas refractory organic matter contributes most to SSA despite its lower degree of reactivity. According to the modeling of our data, labile organic matter is not a significant variable in explaining either b_B or SSA for this set of volcanic ash-derived soils.

4.5 Conclusions

Total soil organic matter is poorly correlated with B adsorption capacity for this set of volcanic ash-derived soils. In a multiple linear regression only the most abundant mineral surface (allophane and imogolite) explains variations in B adsorption. After differentiating organic matter pools in each soil based on their thermal stability, a multivariate analysis demonstrated that different pools of organic matter influence surface properties of volcanic ash-derived soils differently. The partial least squares regression models for specific surface area (SSA) and B maximum adsorption capacity (b_B) revealed that the recalcitrant fraction of organic matter directly affects B adsorption capacities, and it has almost the same coefficient as the allophane and imogolite content, and total Fe oxides. On the other hand, the only thermal fraction explaining SSA is the refractory organic matter, even to a greater extent than the allophane and imogolite content. Labile organic matter was not a significant variable in any of the two surface properties evaluated for this set of soils. Based on our results, we propose that the contradictory effects of organic matter on B adsorption in soils are due to different degrees of organic matter decomposability and mineral association, which are the two main factors affecting thermal stability.

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Tables and figures

Table 4.1: Soil organic matter fractionation based on thermal resistance

	Site	Organic Matter, g kg^{-1}	% Fractions			Total pool content, g kg^{-1}		
			Labile	**Recalcitrant**	**Refractory**	**Labile**	**Recalcitrant**	**Refractory**
1	Buganvilia	53.4	37.7	62.3	0.0	20.2	33.3	0.0
2	Santa Monica	14.7	0.0	90.4	9.6	0.0	13.3	1.4
3	Mirador	42.4	0.0	78.9	21.1	0.0	33.4	8.9
4	Velasquez	78.8	25.1	64.7	10.2	19.7	51.0	8.0
5	Socorro	42.4	56.0	39.6	4.4	23.7	16.8	1.9
6	San Patricio	28.6	0.0	89.4	10.6	0.0	25.6	3.0
7	La Felicidad	31.9	0.0	84.5	15.5	0.0	26.9	4.9
8	San Francisco	58.6	0.0	80.9	19.1	0.0	47.4	11.2
9	San Antonio	60.6	0.0	79.0	21.0	0.0	47.9	12.7
10	Malta	35.1	0.0	85.7	14.3	0.0	30.0	5.0
11	La Cuchilla	70.4	0.0	91.9	8.1	0.0	64.7	5.7
12	Puyumate	67.6	0.0	93.2	6.8	0.0	63.0	4.6
13	Blanca Victoria	27.7	0.0	78.3	21.7	0.0	21.7	6.0
14	Las Rosas	39.2	58.7	18.2	23.1	23.0	7.1	9.0
15	Buenos Aires	29.6	59.7	28.3	12.0	17.6	8.4	3.6
16	Colombita	31.2	57.9	24.0	18.1	18.1	7.5	5.6
17	Maria del Carmen	29.9	49.3	38.5	12.3	14.7	11.5	3.7
18	Chaparral	35.9	0.0	78.7	21.3	0.0	28.3	7.6
19	Maria Linda	20.1	61.0	30.5	8.5	12.3	6.1	1.7
20	La Trinidad	16.4	43.1	40.1	16.8	7.1	6.6	2.8
21	Capullo	23.1	44.9	36.4	18.7	10.4	8.4	4.3
22	Cadiz	56.9	0.0	85.8	14.2	0.0	48.8	8.1
23	Boton Blanco	26.0	0.0	88.6	11.4	0.0	23.0	3.0

Table 4.2: Centroid parameter values for cluster analysis

	Cluster		
	1	**2**	**3**
Allophane+Imogolite	80.0	14.8	4.4
Total free Fe oxides	1.7	0.6	0.6
Organically complexed Al	7.2	3.5	14.5
Organically complexed Fe	2.5	0.9	5.7
Labile SOM	1.1	0.5	1.7
Recalcitrant SOM	4.6	2.3	0.8
Refractory SOM	0.5	0.5	0.7
C:Allophane ratio	0.8	2.6	7.6

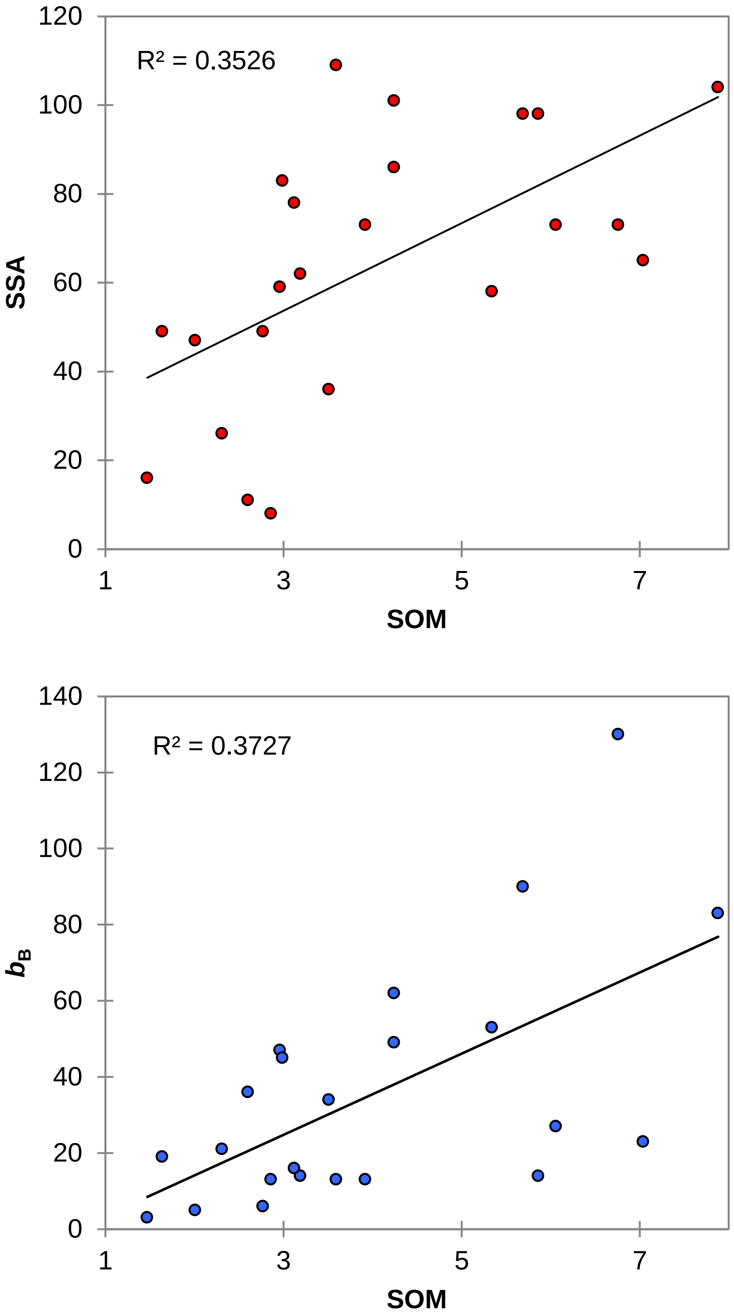

Figure 4.1: Linear correlation between soil organic matter (SOM) and (a) specific surface area (SSA), and (b) B maximum adsorption capacity (b_B). Both are statistically significant at $p = 0.05$.

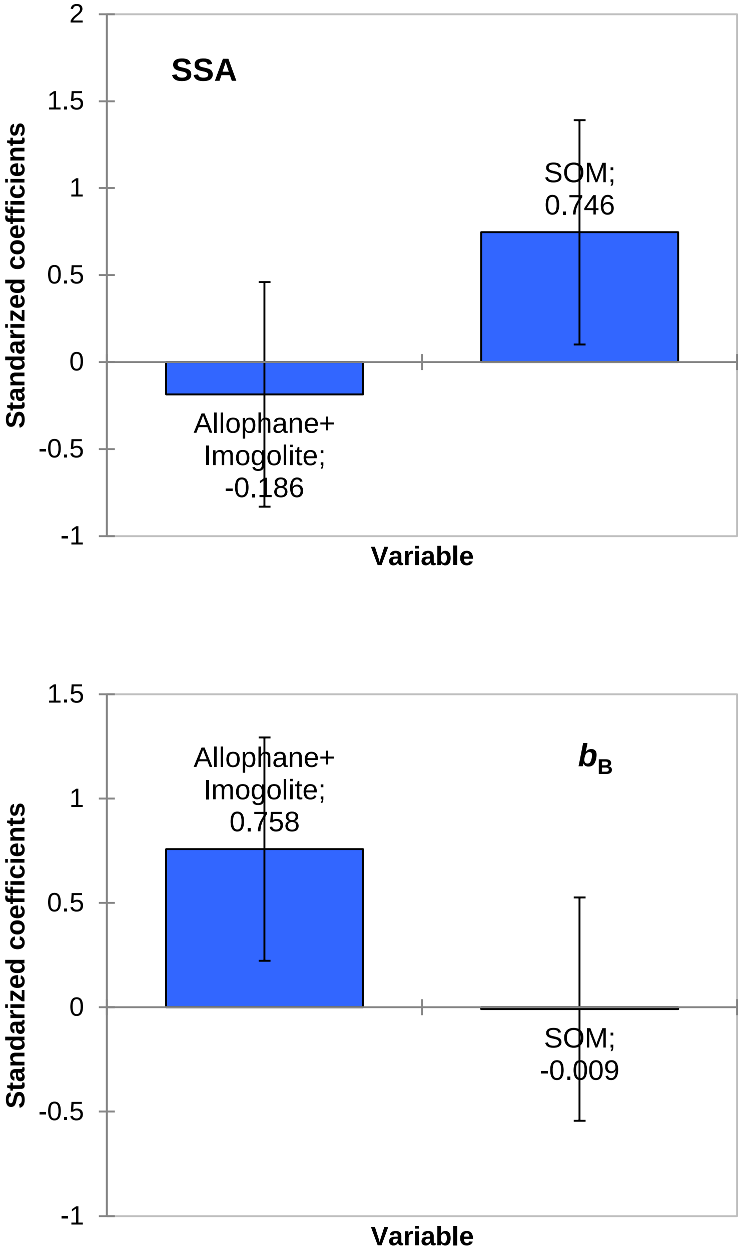

Figure 4.2: Standardized coefficients of multiple linear regressions for specific surface area (SSA) and B maximum adsorption capacity (b_B) as dependent variables, and soil organic matter (SOM) and allophane and imogolite content as explanatory variables. Bars represent 95% confidence intervals.

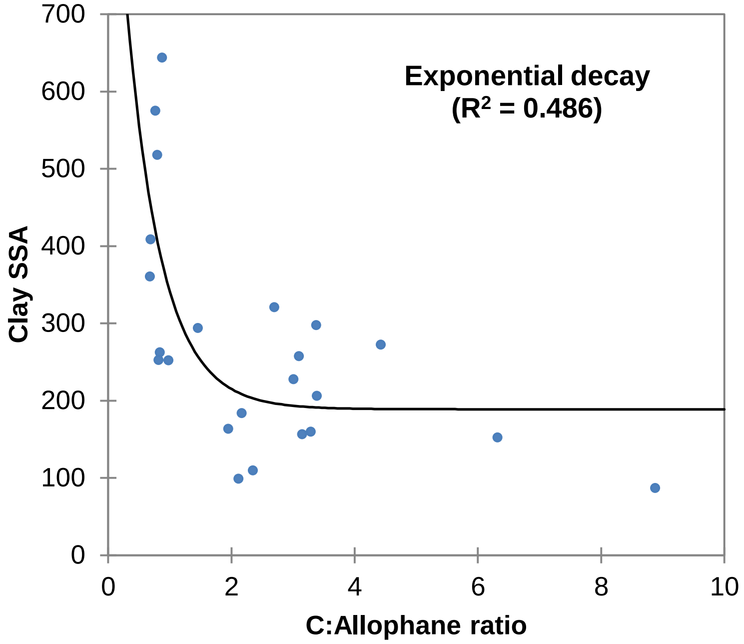

Figure 4.3: Exponential decay of clay specific surface area (SSA) as a function of soil organic matter corrected by the allophane content expressed as the C:allophane ratio.

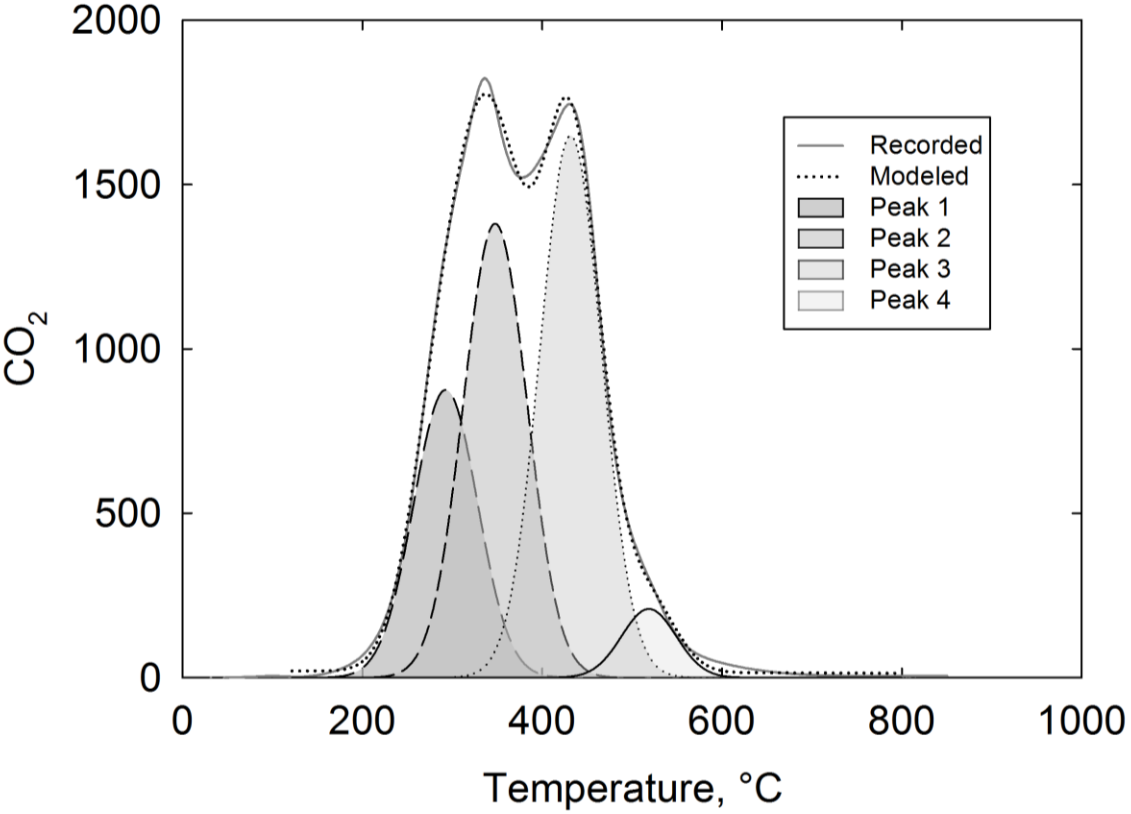

Figure 4.4: CO_2 evolution during organic matter thermal oxidation and peak modeling for soils from site, Socorro ($R^2 = 0.9992$).

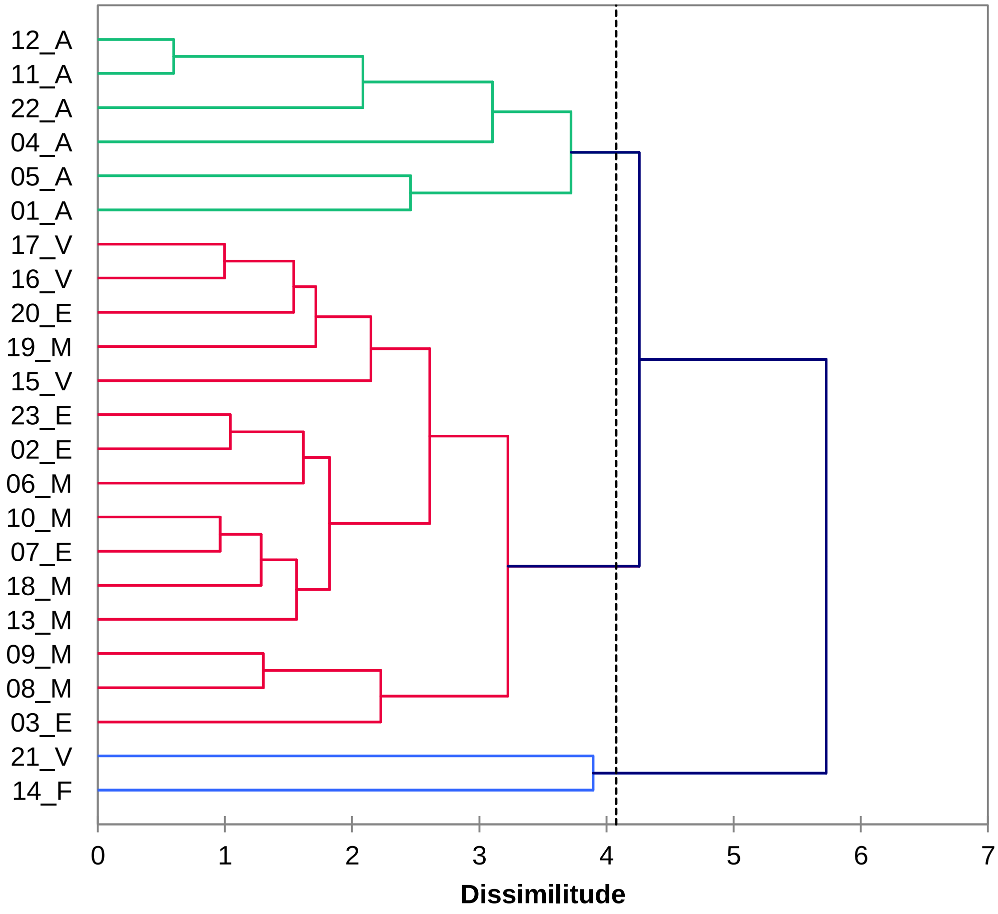

Figure 4.5: Agglomerative Hierarchical Clustering (AHC) dendrogram illustrating three clusters based on organomineral characteristics. Numbers on y axis correspond to the soil number in the tables, followed by a letter indicating soil order. Cluster one groups soils classified as Andisols (A); cluster two groups Mollisols (M), Entisols (E), and some Vertisols (V); cluster three groups one Vertisol and the only Alfisol (F).

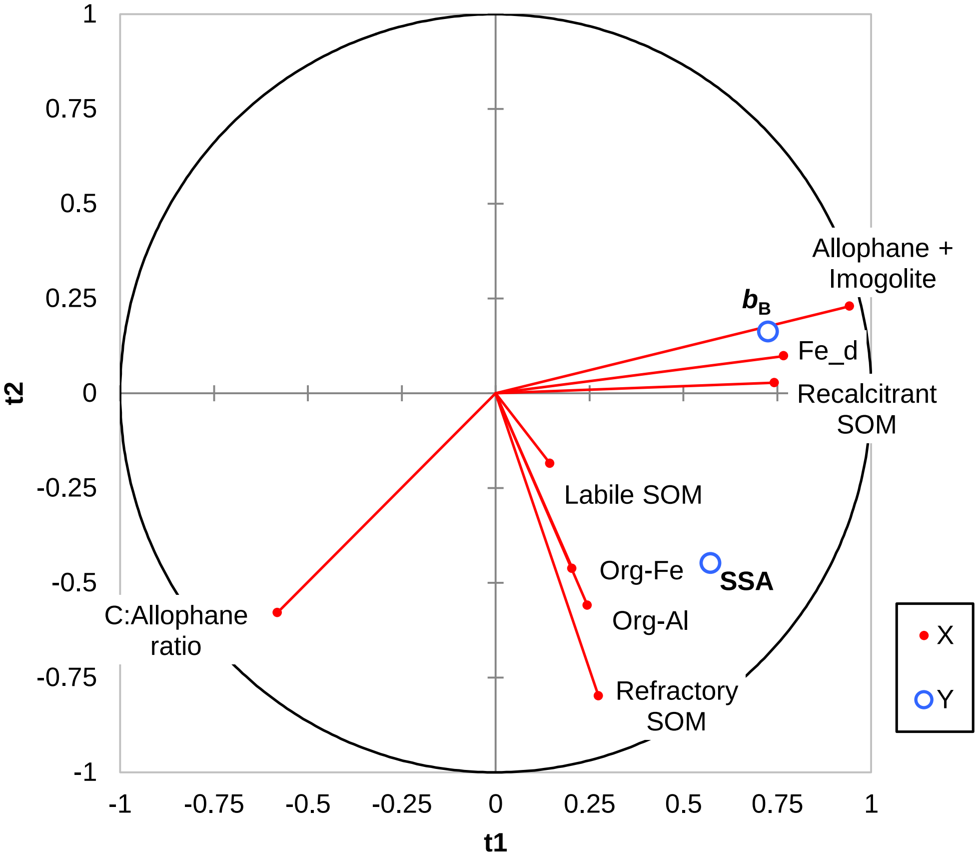

Figure 4.6: Correlation loading plot for factors one and two. Red lines correspond to explanatory variables (X) and blue empty circles correspond to dependent variables (Y).

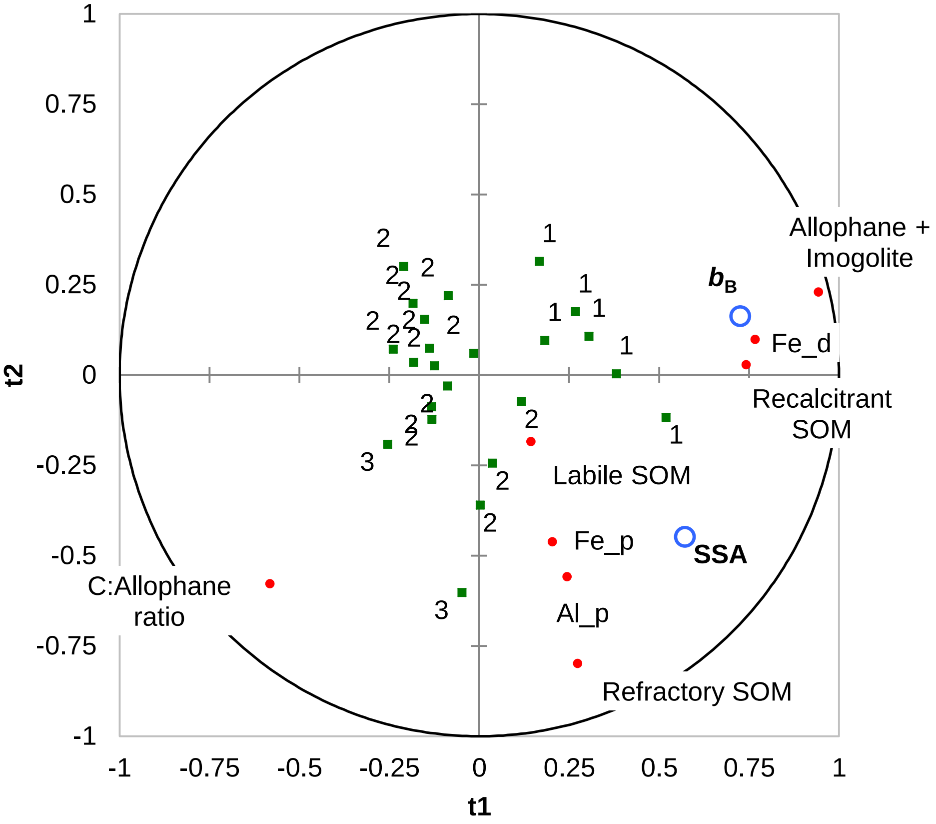

Figure 4.7: Correlation loading plot for factors one and two. Red dots correspond with explanatory variables (X), blue empty circles correspond to dependent variables (Y), and green squares correspond to soil samples belonging to clusters 1, 2, and 3.

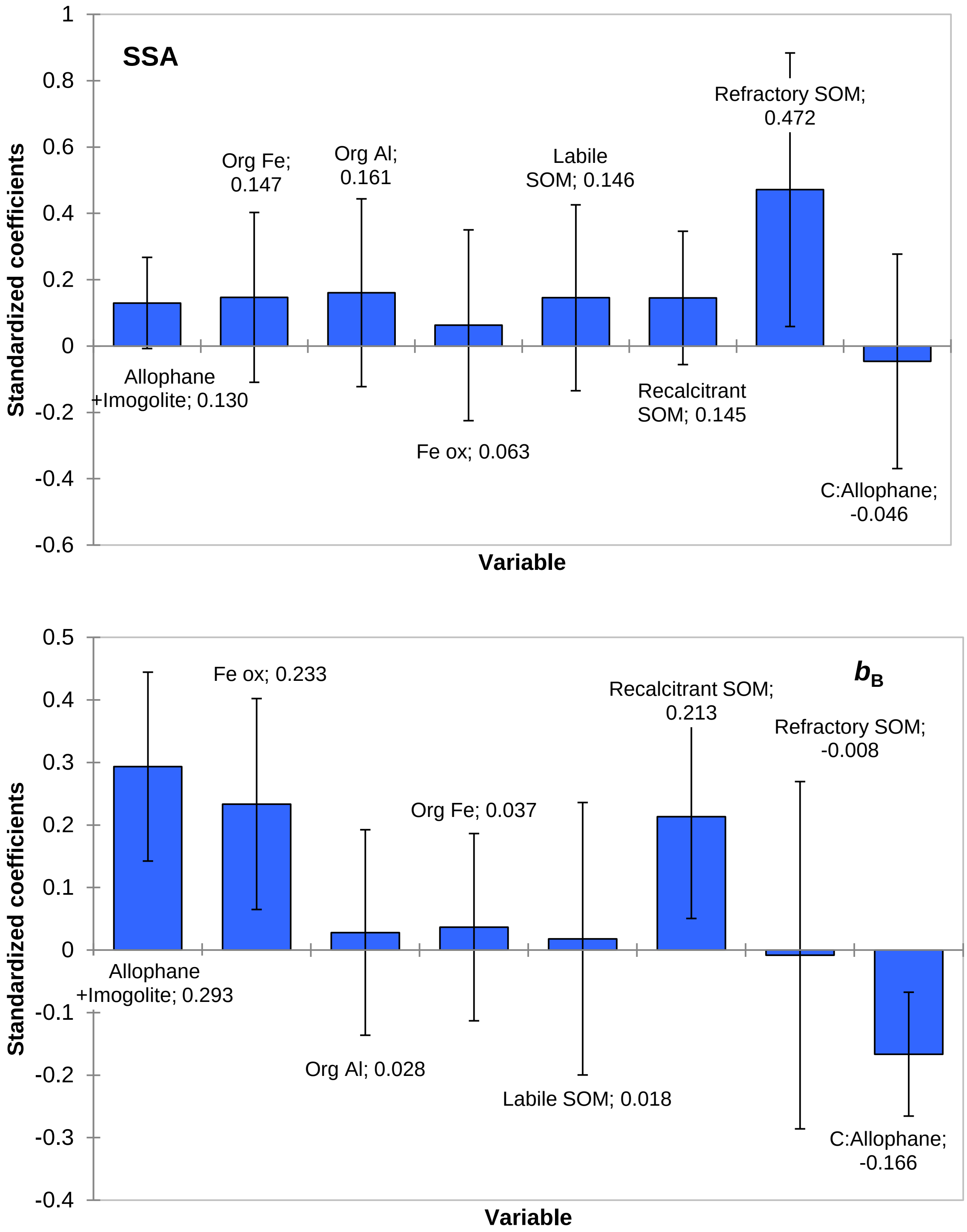

Figure 4.8: PLS standardized coefficients for specific surface area (SSA) and B maximum adsorption capacity (b_B). Bars correspond to 95% confidence intervals.

CHAPTER 5

ESTIMATION OF BORON RATES BASED ON ADSORPTION EQUILIBRIUM FOR HIGHLY FIXING SOILS[1]

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[1] Terraza Pira, M.F., and M.E. Sumner. To be submitted to Agricultural and Environmental Letters.

5.1 Abstract

Crops do not respond consistently to Boron (B) application rates when grown in soils with high potential for B adsorption, particularly on volcanic ash-derived soils and soils dominated by Al and Fe oxides. Because the concentration window between B deficiency and toxicity is very narrow, farmers seldom apply more than 4.0 kg B ha^{-1}. These rates have increased B availability for many crops in temperate regions where soils are dominated by crystalline clays with low potential to adsorb B, but they have failed to solve deficiency problems in volcanic ash-derived soils that have high surface area and strongly adsorb B. However, if B application rates are calculated based on the extent of B adsorbed by the soil, much more effective crop responses are likely to result. To test this hypothesis, two field experiments were conducted on the Guatemalan Pacific coastal plain using sugarcane as a crop response model. Boron was applied at rates up to 20.0 kg ha^{-1}, based on adsorption equilibrium experiments performed before the field trials. B application rates of 7.6 and 10.0 kg ha^{-1} increased soil B availability by 1.2 mg kg^{-1} soil, for the two sites evaluated which have maximum adsorption capacities of 53 and 70 mg B kg^{-1} soil. Sugarcane B absorption increased as soil available B increased, and no toxicity effect was found even after applications of 15.2 and 20.0 kg B ha^{-1}. One of the experimental sites had a positive increase of 5.7% in cane yield in response to increasing available B. These results suggest that deficiency problems in soils with large adsorption capacities can be effectively managed by choosing B application rates based on adsorption equilibria, since the formation of strong surface complexes is the main mechanism that limits B availability for plant uptake.

5.2 Introduction

There is an emerging interest in understanding the yield response to Boron (B) in various deficient crops growing in soils with high potential to fix B. B is the micronutrient most frequently found to be deficient in a variety of crops (Gupta, 1993), but current fertilizer recommendations are based on application rates for soils dominated by crystalline aluminosilicate clays that have significantly lower B sorption capacities (on a unit weight basis) than most oxide minerals and amorphous aluminosilicates like allophane (Goldberg, 1997; Su and Suarez, 1997). Soil application rates have ranged from about 0.5 to 4.0 kg B ha^{-1} depending on available soil B content and the crop of interest. For instance, B recommendations compiled from a survey of 50 state agricultural soil testing laboratories in the U.S. cited by Gupta (1993) show maximum rates of 3.0 to 4.5 kg B ha^{-1} for high B requirement crops such as alfalfa (*Medicago sativa L.*) and cabbage (*Brassica oleracea*), with the average B application rates ranging from 0.2 to 1.1 kg ha^{-1}.

Many authors have reported that B deficiencies are mainly found in humid regions on coarse-textured soils due to B leaching from the root zone (Goldberg and Su, 2007). Although leaching is the most important factor causing B deficiencies in permanently charged soils with low B adsorption capacities, adsorption reactions can severely limit B availability for plant uptake in soils with high surface areas containing aluminum and iron oxides, and allophane (Bingham et al., 1971; Elrashidi and O’Connor, 1982; Su and Suarez, 1995; Schalscha et al., 1973; Chapter 2). Because crops respond only to aqueous B and the window between deficiency and toxicity is very narrow (Keren et al., 1985), recommendations for B applications should be based on the B adsorption capacities of the soils so that the rates applied are sufficient to increase the soil solution concentration without reaching toxic levels. This is particularly important when dealing with highly weathered and volcanic ash-derived soils that fix B strongly.

Some authors have suggested that B toxicity can occur even when soil B levels are below sufficiency. Soil B applications as side-placed drenches of 200 L ha^{-}produced a reduction in sugarcane sucrose yield after application of 2 and 4 kg B ha^{-1}, even though the soil B levels after treatment remained below the 0.5 mg B dm^{-3}, considered to be deficient (Franco et al., 2011). There is little evidence in the literature of B toxicity occurring in crops grown on highly-weathered soils at rates higher than those used in temperate region soils. Widely different soil properties such as pH, clay and organic matter are responsible for the differences in the toxicity levels observed for corn (Lima et al., 2007). In Brazilian soils, the critical soil B concentration to ensure adequate corn production ranged from 0.9 to 2.3 mg B kg^{-1} soil (extracted by the hot water method) and for some soils the rates of application to reach those levels of available B were significantly greater than the usual soil rates applied (Lima et al., 2007).

Boron application rates calculated based on the extent of B adsorbed should result in yield increases and B availability within the deficiency/toxicity window. To test this hypothesis, two field experiments were conducted using sugarcane grown on volcanic ash-derived soils on the Guatemalan Pacific coastal plain as a responding crop model. Boron was applied at rates up to 20 kg ha^{-1}, based on adsorption equilibria for the two sites (Buganvilia and Valesquez) reported previously (Chapter 2). Soil availability, sugarcane yield, and B uptake were recorded.

5.3 Materials and methods

The experiments were located on two commercial farms on the Pacific coastal plain of Guatemala that are currently under sugarcane cultivation. Soils on these farms are classified as Andisols and have developed from igneous parent materials with intermittent inputs of volcanic ash. Maximum B adsorption capacities are 53 and 83 mg B kg^{-1} soil, respectively (Chapter 2). Selected properties of soils are presented in Table 5.1.

The soil B application rates were calculated based on the adsorption equilibrium (partitioning of B between solid and aqueous phases) estimating the amount of B adsorbed at equilibrium with 1.0 mg B L^{-1} in solution from the adsorption isotherm (Chapter 2). For the final estimated B rate (EBR) the amount of B adsorbed on the solid phase at equilibrium with 1 mg B L^{-1} in the soil solution and the B required to raise the soil solution concentration to 1.0 mg B L^{-1} (at field capacity) in the first 0.2 m of the profile were used.

For instance, Buganvilia soil has a B adsorption equilibrium isotherm that can be modeled with the Langmuir equation

$$n_i = \frac{bKc_i}{1 + Kc_i}$$

with the following parameters: $b = 53$, and $K = 0.072$ (Table 5.2), which describes the partitioning between B adsorbed in the solid phase (n_i) —not available for plant uptake— and the B in soil solution (c_i) —available for plant uptake. Using this modeling function, one can estimate n_i at equilibrium with an adequate c_i that is within the sufficiency range. Using the soil's specific Langmuir parameters $n_i = 2.8$ mg B kg^{-1} soil when $c_i = 1.0$ mg B L^{-1}, this corresponds to 5.6 kg B ha^{-1} (using 2x10^6 kg of soil ha^{-1} at

0.2 m deep). This value was added to the dose of 2.0 kg B ha^{-1} that would be recommended in non-fixing soils to increase B availability in 1.0 mg kg^{-1}. The final estimated B rate (EBT) was calculated as the sum of these two parameters, for final application rates of 7.6 and 10 kg B ha^{-1} for Buganvilia and Velasquez soil, respectively. The treatments evaluated (Table 5.2) were half rate (0.5 EBR), full rate (1.0 EBR), and double rate (2.0 EBR), plus a control without applied B (0.0 EBR).

All treatments were evaluated in plots consisting of six 10 m long rows with a row spacing of 1.5 m, giving a total area of 90 m^2 per plot, with eight replications in a completely randomized design. Sugarcane variety CP-722086 was planted using current commercial planting protocols using 8.4 ton cane ha^{-1} as planting seed cane placed in a double chain at the bottom of the furrow (Melgar et al., 2014). The experiments were planted in July 2015 and harvested in January 2016. For harvesting, the total area of each plot was manually cut and packed stalks were weighted with a digital hanging scale.

Nitrogen (N) and phosphorus (P_2O_5) were applied to all treatments at 70 and 60 kg ha^{-1} respectively, as ammonium nitrate and triple super phosphate. Boron was applied at planting at the bottom of the furrow as solid sodium octaborate (powder) and incorporated with the soil before placing the planting canes. Soil samples were taken in the furrow (top 0.2 m) to measure available B by hot water extraction at 3 and 6 months after planting, and plant B absorption was measured by foliar analysis at 6 months (third visible dewlap [TVD] leaf blade).

Hot water extractable B was determined using the technique of Berger and Truog (1940) as simplified by Gupta (1967). Samples of 25.0 g of soil were boiled with 50.0 mL of deionized water for 5 min on a hot plate. After cooling, the slurries were stirred and filtered using two Whatman No. 42 filter papers, and B was determined by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES).

Plant tissue samples in paper bags were placed in an oven to dry for 24 h at 80°C. Dried samples were then ground in a Wiley mill and passed through a 20 mesh screen. The samples were digested following EPA Method 3052 (USEPA, 1995) as follows. Around 0.500g samples were weighed out and placed in fluorocarbon polymer microwave vessels. Then10 mL concentrated HNO_3 was added to each vessel and sealed. The sealed vessels were placed in a microwave digester (CEM Mars 6 Microwave, Matthews, NC, USA) and heated at 200°C for 30 minutes. The digests (solutions) were transferred quantitatively into volumetric flasks and brought to 100 mL volume with deionized water. Finally, the solutions were analyzed for various elements following EPA Method 200.8 (Creed et al., 1994) by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) (Spectro Arcos FHS16, Germany). All results were reported as parts per million (mg kg^{-1}). Calibration standards were from a certified source. Independent laboratory performance checks were also run with acceptable deviations for recoveries set at 100 ± 5%.

Because these experiments were in commercial fields, sugarcane was harvested as planting material at 6 months after planting. Results are presented as actual weight recorded per plot, and as tons of cane per hectare per month. Statistical analysis of yields, hot water extractable B at 3 and 6 months, foliar B, and biometry (height and stalk diameter) measurements were carried out using a one-way analysis of variance with the least significant different (LSD) at $p = 0.05$ probability level. The differences among the means were compared using Fisher’s LSD test for multiple comparisons.

5.4 Results and discussion

Increased availability of soil B

Hot water extractable B concentrations were below toxicity levels of 5 mg kg^{-1} (Nable et al., 1997) for all treatments at 3 and 6 months after planting (Table 5.3). The highest application rates evaluated (15.2 and 20.0 kg B ha^{-1} for sites 1 and 2, respectively) were as much as ten-fold greater than the ones used to alleviate deficiency in non-fixing soils. This supports the assertion that B rates should be estimated based on adsorption characteristics for soils that fix B strongly and that using the rates that are commonly used in non-fixing soils (0.5 – 2 kg B ha^{-1}) do not significantly increase B availability, which might explain the absence of responses in some crops showing deficiency symptoms (Franco et al., 2011).

The average increases in available B calculated as the difference between hot water extractable B in each treatment and the corresponding control plots for both sites were 0.62, 1.20, and 2.40 mg B kg^{-1} for the 0.5EBR, 1.0EBR, and 2.0EBR treatments, respectively all of which were statistically significant at $p = 0.05$ (Figure 5.1). Since the rates were based on the amount of B required to reach 1.0 mg B L^{-1} in the soil solution, these results show that the EBR responds in concordance with the expected increments of available B. This is the first time that B rates have been estimated based on soil physicochemical reactivity reflecting the importance that adsorption reactions play in the availability of this micronutrient in soils containing amorphous minerals. These results emphasize the importance of customizing B rates for different soils depending on their adsorptive capacities, so that the rates applied are adequate to meet B requirements without causing toxic effects.

Some authors have suggested that B toxicity can occur even when soil B levels are below sufficiency. Franco et al. (2011) cited various studies that reported both absence of crop response and toxicity effects to B applications in Brazilian soils. In their study on sugarcane responses to soil B applications as side-placed drenches of 200 L ha^{-1} 90 days after planting, they reported a reduction in sucrose yield after application of 2 and 4 kg B ha^{-1}, even though the soil B levels after treatment remained below the 0.5 mg B dm^{-3}, considered to be deficient. The toxicity observed was probably due to local high B concentrations that fostered increased uptake. Commercial experiments in Guatemala (data not published) also suggest that one application of sodium octaborate ($Na_2B_8O_{13}.4H_2O$) as a side-dressing reduced sugarcane yield in fields that had deficient levels of soil B also probably due to the toxicity of the locally-placed high concentration.

There is little evidence in the literature of B toxicity occurring in crops grown on highly-weathered soils at rates higher than those used in temperate region soils. Lima et al. (2007) evaluated critical and toxic B levels for 10 different soils treated with rates ranging from 0 to 12 mg B dm^{-3} soil in the state of Pernambuco, Brazil. Only five of the ten soils responded to the B rates applied, and from their correlations toxic rates ranged from 6.7 for an acidic yellow Oxisol, to 19.6 mg B dm^{-3} for a red Ultisol. Widely different soil properties such as pH, clay and organic matter were responsible for the differences in the toxicity levels observed. All these properties affect B adsorption reactions in soils, which emphasize the need for performing B adsorption studies to estimate the B rates to be applied for soils that have high B adsorption potential. Lima et al. (2007) suggest that the critical soil B concentration to ensure adequate corn production ranged from 0.9 to 2.3 mg B kg^{-1} soil (extracted by the hot water method) and for some soils the rates of application to reach those levels of available B were significantly greater than would be required for other soils.

Oliveira Neto et al. (2009) evaluated extractable (hot water) B in an acid red Oxisol with an initial soil B content of 0.23 mg dm^{-3} at all depths from surface to 0.4 m after application of increasing B rates. The highest rate (8 kg B ha^{-1}) increased hot water extractable B to 0.8 mg dm^{-3} in the first 0.1 m of the profile, to 0.6 mg dm^{-3} at a depth of 0.1 to 0.2 m, with a negligible increase below that. According to the hot water soil B values of Lima et al. (2007) even the 8 kg B ha^{-1} rate is insufficient to raise available B to an adequate level. These data emphasize the relative lack of B movement in soils with high B fixing capacities.

Impact on sugarcane B absorption

Foliar analyses taken at the Buganvilia site clearly show the responsiveness of sugarcane to soil B applications (Table 6.4), with the control and 0.5 EBR treatments recording deficient values and the 1.0EBR and 2.0EBR treatments recording sufficiency levels. According to Meyer et al. (1971), adequate foliar B levels for sugarcane range from 1.6 to 10 µg B g^{-1}. These values were derived from a survey of the South African sugar industry and merely represent the extant situation at the time of sampling. They cannot therefore be considered to be critical values in the true sense of the word. The Florida Sugarcane Handbook (McCray et al., 2010) reports an optimum foliar range of 15 to 20 mg B kg^{-1} in the top visible dewlap leaf blade sampled during the grand growth period which starts at about 120 days after planting lasting up to 270 days in a 12-month crop. This period is the most important phase of the crop when the actual cane forms and elongates. A critical value (concentration of B at which production losses due to nutrient deficiency reach 5-10%) of 4 mg B kg^{-1} is reported by McCray et al., (2010). Using the South African range, our control treatment is considered deficient, and the three treatments receiving B (0.5EBR, 1.0EBR, and 2.0EBR) are within the adequate range. On the other hand, according to Florida values, only the full and double rates (1.0EBR and 2.0EBR treatments) have B foliar levels above the critical value, and are yet far from the optimum range (McCray et al., 2010).

Impact on sugarcane yield

Sugarcane yield was statistically significantly different between treatments only at one site (Buganvilia) whereas at site 2 (Velasquez) the yield differences were not statistically significant. The two experiments behaved differently probably because of different initial available B contents in the soils which may reflect potentially different capacities to supply B through mineralization of organic matter. At Buganvilia where the initial soil B and organic matter content were lower, yield responses to increased B rates were recorded, where the 1.0 EBR and 2.0 EBR treatments were about 5.7% higher than the control and 0.5 EBR treatments. This yield increase was statistically significant at the $p = 0.05$ level (Table 5.5).

It was not possible to measure sucrose content in the sugarcane juice because the experiment did not run to maturity. The product of sucrose content and cane yield gives sucrose per unit area, which is the ultimate variable farmers are interested in maximizing. However, even without this information, results at Buganvilia support the hypothesis that has been proposed to assess B availability. Yields for Valesquez are not statistically significantly different (Table 5.6). The reasons for this are not clear but may be due to the differences in initial soil B content, higher content of organic matter that could supply more B by mineralization during the experiment, plant population variability within the plots, or some other uncontrolled factor in the experimental units.

Height and stalk diameter showed no significant differences at both sites 4 months after planting despite increases in B availability and absorption (data not shown). According to the literature (Fageria, 2009; Moore and Botha, 2014), B improves carbohydrate metabolism in sugarcane, which is probably not measurable in growth parameters such as height and diameter. B absorption recorded as a higher foliar B content increased with increasing B application rates, reflecting the responsiveness of this crop to increased soil B availability.

5.5 Conclusions

Soil B availability increased and was maintained for up to 6 months without causing toxicity after the application of B rates estimated based on B adsorption equilibria with highly fixing soils. Two soils from the Pacific coastal plain of Guatemala showed increases in available soil B content that follow the pattern predicted from the B adsorption capacity of each soil even after application of potentially toxic rates of up to 15.2 and 20.0 kg B ha^{-1}. Sugarcane B absorption increased as soil B availability increased, and did not reach levels consistent with potential B toxicity in the foliage. Sugarcane yield responded positively to increased levels of B availability at one of the two sites, and the increase in crop B absorption is an indication of potential responsiveness in sucrose concentration, though more work is needed to confirm the tentative conclusions specially when dealing with other crops that could be more sensitive to toxic B levels. Soil B rates to alleviate deficiency problems in soils with large adsorption capacities should be chosen based on adsorption equilibria, since the formation of surface complexes is the main mechanism that limits B availability for plant uptake.

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Tables and figures

Table 5.1: Selected physical and chemical properties of soils from the experimental sites

Parameter	Buganvilia (site 1)	Velasquez (site 2)
pH (H_2O)	7.3	6.1
pH (1 M KCl)	5.9	5.0
Conductivity, dS m^{-1}	0.1	0.1
Organic matter, g kg^{-1}	53.4	78.8
Cation exchange capacity, $cmol_c$ kg^{-1}	10.5	11.3
Exchangeable Ca, $cmol_c$ kg^{-1}	7.7	9.7
Exchangeable Mg, $cmol_c$ kg^{-1}	2.1	1.4
Exchangeable K, $cmol_c$ kg^{-1}	0.8	0.6
Extractable P, mg kg^{-1}†	54.1	13.7
NH_4^+ -N, mg kg^{-1}‡	2.4	7.3
NO_3^- -N, mg kg^{-1}‡	15.0	18.5
Extractable B, mg kg^{-1}§	0.5	0.6
Bulk density, kg dm^{-3}	1.1	0.9
Water content at field capacity, m^3 m^{-3}	0.2	0.2
Native B in solution, mg L^{-1}	<0.1	<0.1

† Olsen method

‡ KCl extraction

§ Hot water extraction

Table 5.2: Estimated boron rates (EBR) based on adsorption equilibrium

	Buganvilia (site 1)	**Velasquez (site 2)**
Maximum adsorption capacity, mg B kg^{-1} soil†	53	83
Affinity parameter (Langmuir equation)†	0.072	0.054
B adsorbed, mg kg^{-1}‡	2.8	4.0
B adsorbed, kg B ha^{-1}§	5.6	8.0
B solution, kg B ha^{-1}¶	2.0	2.0
Estimated Boron Rate (EBR), kg B ha^{-1}#	7.6	10.0

† From Chapter 2

‡ Amount of B adsorbed at equilibrium with 1.0 mg B L^{-1} in solution according to the Langmuir equation

§ Amount of B adsorbed in the volume of soil contained in 1 ha to 0.2 m deep

¶ Amount of B to maintain the soil solution at 1.0 mg B L^{-1}

B adsorbed plus B solution

Table 5.3: Soil B availability 3 and 6 months after application

			B, mg kg^{-1} †	
Site	**Treatment**	**B rate, kg ha^{-1}**	**3 months**	**6 months**
Buganvilia	0.0 EBR	0.0	0.57	0.70
	0.5 EBR	3.8	0.81	1.48
	1.0 EBR	7.6	1.07	2.13
	2.0 EBR	15.2	2.80	3.66
Velasquez	0.0 EBR	0.0	0.61	0.55
	0.5 EBR	5.0	1.56	1.05
	1.0 EBR	10.0	2.12	1.90
	2.0 EBR	20.0	2.85	2.70

† Hot water extraction

Table 5.4: Foliar B contents for sugarcane 6 months after planting

Site	**Treatment**	**B rate, kg ha^{-1}**	**Foliar B, µg g^{-1} †**
Buganvilia	0.0 EBR	0.0	1.46 c
	0.5 EBR	3.8	2.68 bc
	1.0 EBR	7.6	4.59 ab
	2.0 EBR	15.2	5.39 a

† Means in a column followed by the same letter are not significantly different at P = 0.05

Table 5.5: Sugarcane yields for different boron rates at site 1 (Buganvilia)

Treatment	**Yield†, kg plot^{-1}**	**Equivalent yield, Mg ha^{-1}mo^{-1}**
2.0 EBR	329.6 a	6.11a
1.0 EBR	327.7 a	6.07a
0.5 EBR	312.1 b	5.78b
0.0 EBR	309.4 b	5.73b

† Adjusted treatment means controlled by number of cane packs per plot, means in a column followed by the same letter are not significantly different at $p = 0.05$

Table 5.6: Sugarcane yields for different boron rates in site 2 (Velasquez)

Treatment	**Yield†, kg plot^{-1}**	**Equivalent yield, Mg ha^{-1}**
2.0 EBR	954.9 a	8.04a
1.0 EBR	951.6 a	8.01a
0.5 EBR	1055.0 a	8.88a
0.0 EBR	969.9 a	8.16a

† Adjusted treatment means controlled by number of cane packs per plot, means in a column followed by the same letter are not significantly different t p = 0.05

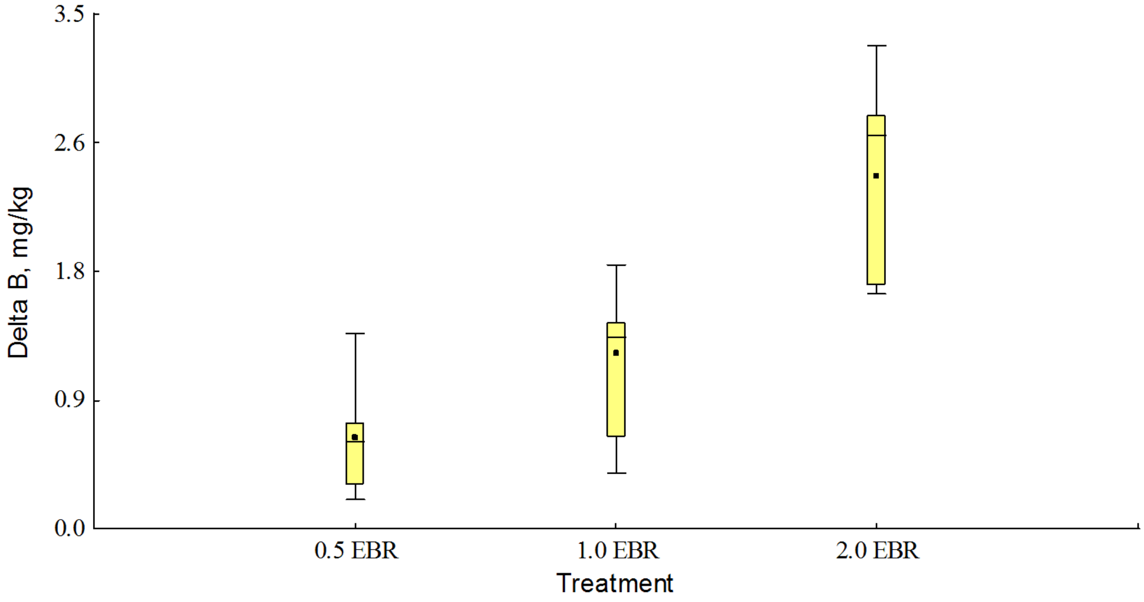

Figure 5.1: Increase in soil B availability (Delta B) after application of boron rates (EBR) estimated from B adsorption equilibria. Delta B calculated as the difference between each treatment and the control plot.

CONCLUSIONS

Boron (B) availability in soils is determined by adsorption and desorption reactions, and the study of the chemistry of mineral and organic surfaces that participate in these reactions allows developing management strategies to solve deficiency and toxicity problems for farmers in regions where this essential micronutrient compromises yields and quality of crops. Such is the case of the very fertile volcanic ash-derived soils in the Pacific coastal plain of Central America where the economically important crops suffer sever B deficiency, and current management practices have failed to correct this problem.

The organomineral characterization reveals the surface potential reactivity that governs B dynamics in soils. Mineralogy of volcanic ash-derived soils is dominated by SRO aluminosilicates and kaolinite. Only the soils with greater andic character (those classified as Andisols) contain considerable amounts of imogolite, and the rest is dominated by allophane. Small amounts of primary minerals (orthoclase and cristobalite) and 2:1 clay minerals (smectites, most probably montmorillonite) are also present but have less relevance in B adsorption reactions. The degree of crystallinity of the kaolinite phase has an influence on the extent of surface area available and it has a direct impact on B adsorption capacity. Surface area of smectite phases does not present sites available for B complex formation, though to some extent these 2:1 clay minerals can contribute to the formation of weaker outer-sphere complexes. Primary minerals are considered non-reactive and they might lead to overestimation of active pools of Al and Fe by selective dissolutions. The main mineral surface responsible for the observed differences of SSA and B adsorption capacities between volcanic ash-derived soils is the amount of SRO aluminosilicates, which govern the B surface reactivity even when they are present in smaller amounts than the threshold to classify a soil as an Andisol.

Total soil organic matter has a poor correlation with B adsorption capacity for this set of volcanic ash-derived soils. In a multiple linear regression only the most abundant mineral surface (allophane and imogolite) explains variations in B adsorption. After differentiating organic matter pools in each soil based on their thermal stability, a multivariate analysis approach demonstrated that discrete pools of organic matter influence surface properties of volcanic ash-derived soils differently. The partial least squares regression models for specific surface area (SSA) and B maximum adsorption capacity (b_B) revealed that the recalcitrant fraction of organic matter directly affects B adsorption capacities, and it has almost the same coefficient as the allophane and imogolite content, and total Fe oxides. On the other hand, the only thermal fraction explaining SSA is the refractory organic matter, even to a greater extent than the allophane and imogolite contents. Labile organic matter was not a significant variable in either of the two surface properties evaluated for this set of soils. Based in our results, we propose that the contradictory effects of organic matter on B adsorption in soils is due to different degrees of organic matter decomposability and mineral association, which are the two main factors affecting thermal stability.

Guatemalan south coast soils influenced by volcanic ash have very variable capacities to adsorb B, depending on the availability of mineral and organic surfaces, and the affinity of those surfaces for B. Soil texture does not predict the behavior of the adsorption maxima, since the andic character of the soils will determine the extent to which B will be adsorbed. The main surface responsible for adsorption is allophane, and organic matter becomes important only for those soils with clay contents smaller than 200 g kg^{-1}. The degree of hysteresis of desorption is a function of the andic character of the soils, with higher contents of extractable amorphous aluminosilicates causing irreversibility probably due to an interior migration and/or structural substitution. One single easily-measured parameter to predict potential B availability as a function of the andic character of the soils is the measurement of pH in NaF suspension, which has an exponential relationship with amorphous Al responsible for B adsorption, and a linear relationship with the amount of B adsorbed at equilibrium with 1.0 mg B L^{-1} in solution. The pH in 1 mol L^{-1} NaF can be used as an initial guide for soil test purposes to predict amorphous aluminum content, but should not be used directly as a predictor of likely responses.

Soil B rate recommendations to solve deficiency problems in highly fixing soils are based on historical recommendations formulated for soils with low potential to adsorb B. For volcanic ash-derived soils, the extent to which B adsorbs is a key concept in designing fertilization programs that are able of solving deficiencies, even when the rates of application proposed break the paradigm of toxicity effects above 4.0 kg B per hectare. Soil B availability increased and was maintained for up to 6 months without causing toxicity after the application of B rates estimated based on B adsorption equilibrium with highly fixing soils. Two soils from the Pacific coastal plain of Guatemala showed increases in available soil B content that follow the pattern predicted from the B adsorption capacity of each soil even after application of potentially toxic rates up to 15.2

and 20.0 kg B ha^{-1}. Sugarcane B absorption increased as soil B availability increased, and did not reach levels consistent with potential B toxicity in the foliage. Sugarcane yield responded positively to increased levels of B availability at one of the two sites, and the increase in crop B absorption is an indication of potential responsiveness in sucrose concentration, though more work is needed to confirm the tentative conclusions specially when dealing with other crops that could be more sensitive to toxic B levels. Soil B rates to alleviate deficiency problems in soils with large adsorption capacities should be chosen based on adsorption equilibrium, since the formation of surface complexes is the main mechanism that limits B availability for plant uptake.