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Fallas-Corrales, R. A., Mendez, J. C., & Meeussen, J. C. L. (2025). Boron Adsorption and Interaction With Phosphate in a Volcanic Soil From the Humid Tropic. *Journal of Plant Nutrition and Soil Science*, 189 (2026)(3), 376-386. <https://doi.org/10.1002/jpln.70012>

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SPECIAL ISSUE Boron celebrates its 100th birthday as an essential element in plant nutrition

RESEARCH ARTICLE

Boron Adsorption and Interaction With Phosphate in a Volcanic Soil From the Humid Tropic

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Received: 29 December 2024 | **Revised:** 19 June 2025 | **Accepted:** 22 July 2025

Academic Editor: Monika Wimmer.

Funding: This research was supported by the Ministry of Science and Technology of Costa Rica (MICITT), contract number PINN-MICITT 2-1-4-17-1-014. and the University of Costa Rica, contract number: OAICE-53-2018.

Keywords: adsorption isotherms | andisol | charge distribution multisite ion complexation (CD-MUSIC) | ion adsorption modeling | nonideal competitive adsorption (NICA)–Donnan | ORCHESTRA

ABSTRACT

Background: Boron (B) deficiency is a major constraint for crop production in volcanic soils from humid tropical regions. Its availability can be influenced by adsorption to short-range order (SRO) minerals and soil organic matter (SOM) and by interactions with other nutrients.

Aims: To analyze the adsorption behavior and surface speciation of B in a volcanic soil from the humid tropics, including its interaction with phosphate (PO₄), and to test the applicability of a mechanistic multi-surface geochemical model for describing these interactions.

Methods: Boron adsorption isotherms were determined on a volcanic soil using two electrolyte solutions (NaNO₃ or CaCl₂) and two conditions of added PO₄ (0 and 1.6 mM). The results were interpreted using an advanced multi-surface ion adsorption model that combines the charge distribution multisite ion complexation (CD-MUSIC) model for describing ion adsorption to SRO minerals and the nonideal competitive adsorption (NICA)–Donnan model for adsorption to SOM.

Results: The model simulations, conducted in a fully predictive scheme, showed an excellent agreement with the experimental B adsorption data in both NaNO₃ and CaCl₂ solutions, even at micromolar B concentrations. Under natural soil pH conditions, SRO minerals were the dominant surfaces controlling B adsorption, whereas SOM played a minor role. The addition of PO₄ had a limited effect on B adsorption at low B concentrations; however, a moderate competitive effect was observed at higher B concentrations.

Conclusions: This study provides mechanistic insights into B adsorption and speciation in volcanic soils, emphasizing the importance of SRO minerals as binding surfaces and the limited role of phosphate competition. These findings can contribute to optimize B management in volcanic soils systems from the humid tropics.

1 | Introduction

Boron (B) is an essential plant micronutrient, and its importance has been extensively recognized since the seminal studies conducted by Warington and coworkers nearly a century ago (Warington 1923; Brenchley and Warington 1927). Boron deficiency can severely impair plant growth and reproduction, leading to reduced crop productivity and a decline in the quality of marketable products (Rerkasem et al. 2020). Globally, B deficiency is common in highly weathered soils, calcareous soils, and soils derived from volcanic ashes (Andisols) (Shorrocks 1997). Thus, a comprehensive understanding of the various chemical processes of B in soil–plant systems is essential to optimize its management and prevent its deficiency in crops.

The adsorption of ions to reactive soil surfaces is a key process influencing nutrient availability and mobility (Havlin 2013). Boron, however, has a relatively weak affinity for these surfaces, especially when compared to strongly bound nutrients like phosphate (PO_4). Previous studies have suggested that other processes, such as mineral weathering and organic matter mineralization, might significantly contribute to determining B solubility in soils (Su and Suarez 2004; Kot et al. 2016; Van Eynde, Weng, et al. 2020). Despite this, understanding the factors and mechanisms driving B adsorption remains crucial for predicting its environmental behavior and improving its use efficiency in agricultural systems. Boron adsorption is affected by intrinsic properties of the soil solution like pH and ionic strength, as well as by the content and type of reactive soil surfaces (e.g., mineral and organic matter), where the adsorption process occurs (Sarkar et al. 2014; Xu and Peak 2007).

Previous studies have shown that B adsorption in soils and minerals reaches a maximum under alkaline conditions (pH ~8–10) and decreases under acidic conditions (Goldberg and Glaubig 1985; Keren and Mezuman 1981; Suarez et al. 2012). Consequently, most reports on B adsorption have been developed in high-pH systems. In contrast, the underlying mechanisms that limit B availability in acidic volcanic soils from tropical regions (typically pH ~4.5–6.0) have been less explored. Despite the reported low B availability in these soils (Terraza-Pira et al. 2018), little research has been conducted on this subject.

Volcanic soils in the humid tropics present a set of conditions that might limit the availability of B. For example, the abundance of highly reactive short-range order (SRO) minerals, such as allophane and ferrihydrite, combined with high soil organic matter (SOM) content can promote B adsorption (Terraza-Pira et al. 2023). On the other hand, the acidic pH conditions combined with intense rainfall may promote significant B leaching from the root zone. Currently, it is not clear which of these contrasting processes limits the most B availability in these conditions.

Phosphate fertilization can add further complexity to B dynamics in volcanic soils. The PO_4 fertilizers are applied intensively to volcanic soils because of their high P-adsorption capacity (Parfitt, 1990, 2009; Kurokawa and Kamura 2018). Phosphate has a strong affinity for the variable charge surfaces of SRO minerals, and it is possible that PO_4 competes with B for adsorption sites, potentially

increasing B solubility. However, previous research on PO_4 –B adsorption interactions has shown inconsistent results. Although some studies reported competitive adsorption (Bloesch et al. 1987; Rashid 1971), others did not observe competition (Bingham and Page 1971; Goldberg et al. 1996).

Mechanistic studies show that the surface speciation of B is influenced by both pH and PO_4 concentration. For instance, in model ferrihydrite systems, B primarily adsorbs as tetrahedra, inner-sphere bidentate complexes, whereas at low-to-neutral pH, the trigonal B forms both inner- and outer-sphere complexes (Van Eynde, Mendez, et al. 2020). The coexistence of these species has been supported by spectroscopic evidence (Su and Suarez 1995, 1997; Xu and Peak 2007). Competition between PO_4 and B is likely to occur for inner-sphere adsorption sites, whereas outer-sphere species remain unaffected due to the neutral charge of boric acid (H_3BO_3) (Van Eynde, Mendez, et al. 2020). Analyzing these interactions in volcanic soils would lead to a better understanding of B solubility under acidic conditions with high PO_4 inputs.

Surface complexation models (SCMs) are valuable tools for describing changes in B adsorption related to variations in the chemical conditions of the system. For instance, the constant capacitance (CC) model has been widely applied to describe B adsorption in different soils (Goldberg 2004; Goldberg and Glaubig 1986). Although practical, this modeling approach has some limitations; for example, it only considers the formation of one inner-sphere B species, and the model parameters are specific for the experimental conditions, limiting a broader 'applicability.

Alternatively, the Charge Distribution (CD) model (Hiemstra and Van Riemsdijk 1996), combined with the Multisite Ion Complexation (MUSIC) model (Hiemstra et al. 1989), provides a description of ion adsorption processes to metal (hydr)oxide surfaces that is more closely related to the actual physicochemical adsorption mechanisms. This approach has been successfully applied to describe B adsorption in model Fe (hydr)oxides systems (Goli et al. 2011; Van Eynde, Mendez et al. 2020). Additionally, for SOM, the nonideal competitive adsorption (NICA)–Donnan model (Kinniburgh et al. 1996) has been used to describe accurately B adsorption, using both generic (Milne et al. 2003) and specific B parameters (Goli et al. 2019). The integration of these two approaches (the CD-MUSIC and NICA–Donnan models) allows the simulation of multi-surface adsorption processes under complex, variable, and more realistic soil conditions, accounting for the changes in surface speciation and multi-ion interactions.

Using this integrated multi-surface modeling approach, Van Eynde, Weng et al. (2020) effectively described the solid-solution partitioning of B and its surface speciation in temperate and highly weathered tropical soils under native nutrient conditions, that is, with no addition of B and PO_4 . However, to the best of our knowledge, the capability of this advanced multi-surface modeling approach has not been tested yet under two relevant conditions from a practical perspective. First, it has not been used to describe the PO_4 –B interaction following the addition of these nutrients at different rates. Second, it has not been applied

yet to describe this interaction in volcanic soils that are rich in both organic matter and SRO minerals. Thus, the novelty of our contribution lies in analyzing the B–PO₄ interaction in a volcanic soil with added nutrients and interpreting the results with this advanced SCM.

The objectives of this study are (1) to analyze the adsorption behavior and surface speciation of B interacting with PO₄ in a volcanic soil from the humid tropics and (2) to test the performance of a mechanistic SCM, previously calibrated for model systems, when it is applied to describe B adsorption in an agricultural volcanic soil. By addressing these objectives, this study will contribute to our understanding of B dynamics in tropical soil systems dominated by SRO minerals. This knowledge is important for optimizing B management and nutrient efficiency under agricultural production systems.

2 | Materials and Methods

2.1 | Soil Sampling and Characterization

The soil was sampled from the Ap horizon (0–20 cm) in a papaya plantation located in Pococi, Costa Rica (10.27929° N, 83.80252° W), located at an altitude of 110 MASL. The region has annual precipitations exceeding 4000 mm and mean annual temperature of 24°C. The soil developed from fluvio-volcanic parent materials and exhibits pronounced andic properties. The mineralogy is dominated by SRO materials, including aluminosilicates (e.g., allophane) and Al and Fe (hydr)oxides (Buurman et al. 1997; Nieuwenhuys et al. 1994, 2000; Stoorvogel and Eppink 1995).

The soil texture was determined by the hydrometer method (Kroetsch and Wang 2008), soil bulk density (Bd) by the core method, and soil porosity (Sp) was calculated ($Sp = 1 - \frac{Bd}{Pd}$) as described by Hao et al. (2008), where Pd is the soil particle density whose value was assumed as 2.65 g cm⁻³.

Before chemical analyses, the soil sample was dried at 50°C for 48 h and sieved through a 2 mm sieve. The chemical characterization included pH measurements in water (pH-H₂O) determined at soil-to-solution ratio (SSR) of 0.1 kg L⁻¹. The forms of Fe and Al were characterized by extracting the soil with the following solutions: dithionite-citrate (DC) to quantify the total content of pedogenic Fe and Al (hydr)oxides (Soil Survey Staff 2014); acid ammonium oxalate (AO) to estimate Fe and Al associated with SRO minerals and metal-humus complexes (van Reeuwijk 2002); and sodium pyrophosphate (Py) to estimate the Al content in Al-humus complexes (Soil Survey Staff 2014). Total C content was determined by dry combustion using a total C and N analyzer (Elementar vario Macro cube). Dissolved organic carbon (DOC) was measured in a 1:10 m/v soil water extraction using a TOC analyzer with the method 5310 B (Baird et al., 2017). Phosphate retention capacity was determined following the procedure described by Blakemore et al. (1987). Boron concentrations in soil extractions with 0.43 M HNO₃ (Groenberg et al. 2017) and 0.01 M CaCl₂ (Houba et al. 2000) were used as proxies for the total reactive and readily available fractions of B, respectively.

2.2 | Boron Adsorption Isotherms

The adsorption of B and its interaction with added phosphate (PO₄) was assessed by B adsorption isotherms. Briefly, 3 g of dried soil was placed into 50 mL polypropylene tubes with 30 mL of a solution containing the background electrolytes and the corresponding B and PO₄ concentrations, keeping a fixed SSR of 0.1 kg L⁻¹. Each isotherm consisted of five points, with total added B concentrations ranging from 0 to 120 µg L⁻¹, added as H₃BO₃. To assess B–PO₄ interaction, two PO₄ conditions were assessed: 0 mM P (no added PO₄) and 1.6 mM P (with added PO₄), using KH₂PO₄ as the P source. Additionally, the effect of different electrolyte solutions on B adsorption was assessed using either 0.01 M NaNO₃ or 0.01 M CaCl₂ solutions as background electrolytes. The experimental adsorption vessels were shaken on a horizontal reciprocal shaker at 150 oscillations per minute and equilibrated for 5 days at a constant temperature (≈25°C). During equilibration, the solution pH was adjusted as needed using either 0.01 M NaOH or HCl to achieve the target pH values. The final equilibrium pH for isotherms conducted in NaNO₃ and CaCl₂ solutions was 5.48 ± 0.10 and 4.98 ± 0.10, respectively. After equilibration, the samples were centrifuged at 5000 rpm for 10 min, and the supernatants were filtered through 0.22 µm nylon membrane syringe filters. The equilibrium B concentrations were determined in the filtered supernatants by inductively coupled plasma mass spectrometry (ICP-MS; Thermo Scientific iCAP RQ).

All solutions were prepared in plastic laboratory ware to avoid contamination from borosilicate materials. Analytical-grade reagents and ultrapure water (18.2 MΩ, TOC 2 ppb) were used for all the prepared solutions.

2.3 | Native Boron Solubility Induced by PO₄

An additional experiment was conducted to determine the effect of increasing PO₄ additions on the solubility of native soil B. For this, soil was equilibrated with PO₄ added as KH₂PO₄ at rates of 0, 2, 4, 8, and 16 mmol P kg⁻¹ soil. The experiment was conducted using 0.01 M CaCl₂ as background electrolyte solution at a constant pH of 4.98 ± 0.10. The SSR, equilibration time, and methods for centrifugation, filtration, and B quantification were identical to those specified for the adsorption isotherms.

2.4 | Multi-Surface Ion Adsorption Model

A multi-surface ion adsorption model was implemented in the geochemical speciation software ORCHESTRA (Meeussen 2003) to describe the adsorption interaction of B and PO₄ on the reactive soil surfaces. This approach consists of two main components that consider (1) the CD model (Hiemstra and Van Riemsdijk 1996) for describing the adsorption of B and PO₄ to variable charge surfaces, including SRO minerals and clay edges, and (2) the NICA–Donnan model (Kinniburgh et al. 1996) for describing the adsorption of B to natural organic matter (NOM). Electrostatic Donnan model was not considered because B predominantly exists in solution as a neutral B(OH)₃⁰ species, rendering electrostatic interactions with planar faces of clays negligible. The

interaction between NOM and the surfaces of minerals with variable charge was considered by implementing the NOM-CD model (Hiemstra et al. 2013).

The modeling of the adsorption isotherms was first performed in a fully predictive scheme, that is, using generic adsorption parameters derived for ferrihydrite (Van Eynde, Mendez, et al. 2020) and humic acids (Goli et al. 2019) (Tables S2 and S3). Additionally, an alternative modeling scenario was tested by adjusting two parameters relative to the fully predictive approach for ferrihydrite: The affinity constant for outer-sphere B complexation was modified ($\Delta \log K = -0.20$), and the high-affinity B adsorption site density was increased ($\Delta N_s = 0.3 \text{ sites nm}^{-2}$). All the details about the model implementation are presented in the Supporting Information section.

3 | Results

3.1 | Characterization of the Soil

The volcanic soil used in this study is highly permeable with a sandy loam texture (Table 1), a low bulk density (0.90 g cm^{-3}), and high total porosity ($0.6 \text{ cm}^3 \text{ cm}^{-3}$). The soil is moderately acidic with a pH-H₂O of 5.85. The mineralogy is dominated by SRO minerals as indicated by the high content of AO extractable Al and Fe (Table 1). In contrast, the content of well-crystallized Fe (hydr)oxides is low, as inferred from the small difference between DC and AO extractable Fe. The higher Al content in the AO versus the DC extraction suggests that SRO aluminosilicates (e.g., allophane) are dominant over other pedogenic Al minerals, as the DC extraction is less effective than AO at dissolving these materials. The presence of Al-humus complexes in this soil can be inferred by the Py extractable Al data (Table 1). The reactive surface area (RSA) of variable charge minerals was optimized in ECOSAT software and resulted in $37.6 \pm 4.1 \text{ m}^2 \text{ g}^{-1}$ soil, and the amount reversibly adsorbed PO₄ (R-PO₄) to these minerals was $18.5 \pm 1.8 \text{ mmol kg}^{-1}$, both values estimated using native soil PO₄ as probe ion (Hiemstra et al. 2010; see details in the Supporting Information section).

3.2 | Boron Adsorption Isotherms

Boron adsorption was similar for the two different background electrolytes (NaCl vs. CaCl₂), and the effect of pH differences between both background solutions had minor consequences on the overall adsorption (Figure 1). The experimental data are in line with the multi-surface model simulations, which predicted small changes in soluble B concentrations for the typical pH values of this soil between systems containing Ca²⁺ and Na⁺ as background solutions. Neither the ionic strength nor the valence of the background electrolyte cations (monovalent Na⁺ or divalent Ca²⁺) significantly affected the amount of adsorbed B and the shapes of the adsorption isotherms. Without added PO₄, B adsorption was linear across the evaluated B concentrations. However, with added PO₄, the linearity of B adsorption decreased, especially at the higher B concentration evaluated (Figure 1). Approximately only 32% of the total added B in the isotherm experiments was adsorbed to the soil surfaces (Table S4).

TABLE 1 | Characteristics of the alluvial volcanic soil from San Bosco, Pococi, Costa Rica.

Textural classification	pH H ₂ O	Fe DC	Al DC	Fe AO	Al AO	Fe Py	Al Py	P Ret	Total C	DOC
Sandy loam										
Clay (%)		174	248	152	1113	54	286	87	2.9	3.6
Silt (%)	5.85									
Sand (%)	80									

Abbreviations: AO, ammonium oxalate extract; DC, dithionite-citrate extract; DOC, dissolved organic carbon; P Ret, phosphate retention capacity (Blakemore et al. 1987); Py, sodium pyrophosphate extract; TOC, total organic carbon.

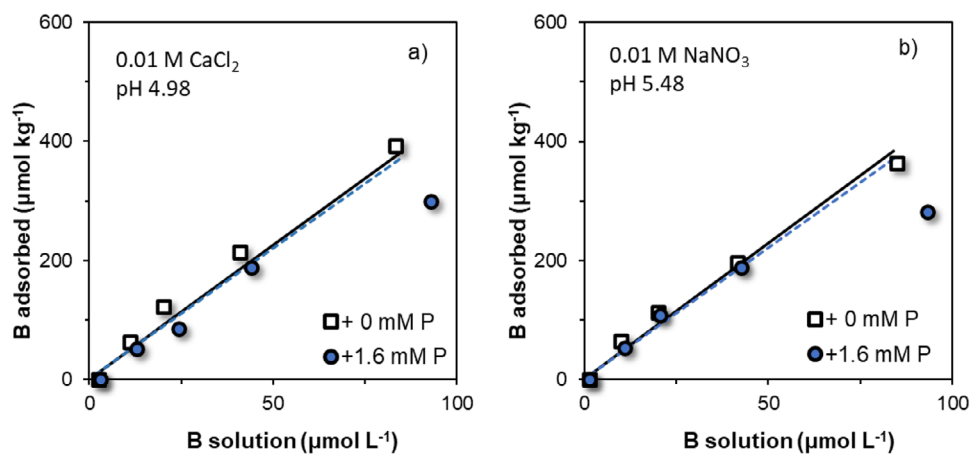


FIGURE 1 | Adsorption isotherms of boron (B) for conditions with no extra P and 1.6 mM P added to a volcanic soil from a humid tropical region in Costa Rica. The left (a) and right (b) panels are for systems in 0.01 M CaCl_2 and 0.01 M NaNO_3 as background solutions, respectively. The symbols are experimental data, and lines (solid = +0.0 mM P and dashed = +1.6 mM P) are the multi-surface complexation model predictions (CD-MUSIC-NICA-Donnan).

3.3 | Multi-Surface Modeling Description

The implemented multi-surface ion adsorption model effectively described, in a fully predictive approach, most experimental data of the B adsorption isotherms. Our modeling results (Table S4) suggest that, at the experimental pH values, B adsorption primarily occurs on the surfaces of the SRO minerals, forming predominantly outer-sphere complexes. On the other hand, adsorption on NOM is less relevant under the analyzed conditions. The model performed well for the +1.6 mM P system up to B solution concentrations close to $45 \mu\text{mol L}^{-1}$ (Figure 1). However, at the higher B concentration evaluated in this study, the model tended to overestimate the experimental B adsorption.

3.4 | P–B Adsorption Interaction

Increasing amounts of added PO_4 (up to 16 mmol kg^{-1}) did not affect the concentration of native B in the 0.01 M CaCl_2 extracts (Figure 2). The red point in Figure 2 represents the natural soil condition at sampling, that is, no extra P added. These results show that under the natural B concentrations for this soil system, the PO_4 addition does not promote additional B desorption. However, when B is added to the system at relatively high concentrations, the simultaneous addition of PO_4 affects B adsorption, as shown in the adsorption isotherms (Figure 1). For our soil without added B, the expected competitive effect of added PO_4 on B adsorption is modulated by the interfacial NOM adsorbed to reactive mineral surfaces. This modulatory effect of NOM is illustrated in Figure 2b through model calculations.

3.5 | Modeling the pH Dependence of Boron Sorption

Figure 3 presents model simulations for the distribution of the reactive B fractions at different pH values. The modeling used

intrinsic adsorption parameters at CaCl_2 and NaNO_3 background electrolytes (Figure 3a,b, respectively), and by implementing the same model parameters, but varying the RSA and the R-PO_4 to lower values (Figure 3c,d). The modeling speciation suggests that most of the B remains as soluble fraction at the typical pH values found in volcanic soils of the studied region (i.e., 4.5–6.0). For this pH range, about 31% of boron is adsorbed to soil particles for both background electrolytes (Figure 3a,b and Table S4).

The modeling results (Figure 3) indicate that a reduction of the oxide fraction of the soil (e.g., a volcanic soil with lower oxide contents) is not fully compensated by the increased B adsorption to the organic fractions. The increase in B adsorption with the increase of pH was more significant for the Ca-dominated background solution. The modeling suggests that for a condition with a lower RSA and lower R-PO_4 , while keeping the same P-loading and HNOM, more B will be present in the solution.

3.6 | Boron Adsorption in Ca vs. Na Systems

Model simulations of B adsorption on pure reactive surfaces of our soil (i.e., either oxides or humic acids modeled by separate) showed differences regarding the effect of the charge of the electrolyte cation (monovalent or divalent cations). The model results (Figure 4) suggest that electrolyte cation affects B adsorption to organic matter (humic acids) but not to the reactive minerals in soils. Specifically, more B is adsorbed to organic surfaces in CaCl_2 0.01 M than in NaCl 0.01 M systems (Figure 4a). On the other hand, B adsorption to (hydr)oxides was unaffected by ionic strength and cation valence of the electrolyte solution (Figure 4b). For our volcanic soil, there were no considerable differences in B adsorption for different background solutions (NaCl 0.01 M and CaCl_2 0.01 M), suggesting that adsorption is primarily dominated by the oxide fraction (Table S4) and, as modeling suggests, predominantly as an outer-sphere process.

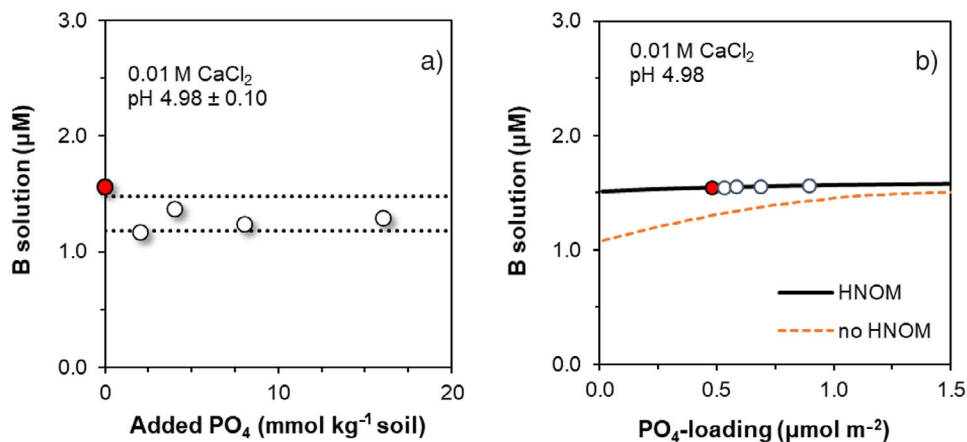


FIGURE 2 | Measured boron (B) concentrations as a function of added phosphate concentrations obtained in s CaCl_2 0.01 M systems (a). The red symbol represents the B concentration with no P added to the soil. The dotted lines represent $\pm 10\%$ of the mean value of all the data points. The right panel (b) presents model lines for the relationship between P-loading and B concentration in solution. The solid model line was obtained by considering in the Charge Distribution model the effect of interfacial SOM (HNOM) interacting with the mineral surfaces, whereas the dashed model line represents the model prediction when this interaction is not considered (no HNOM).

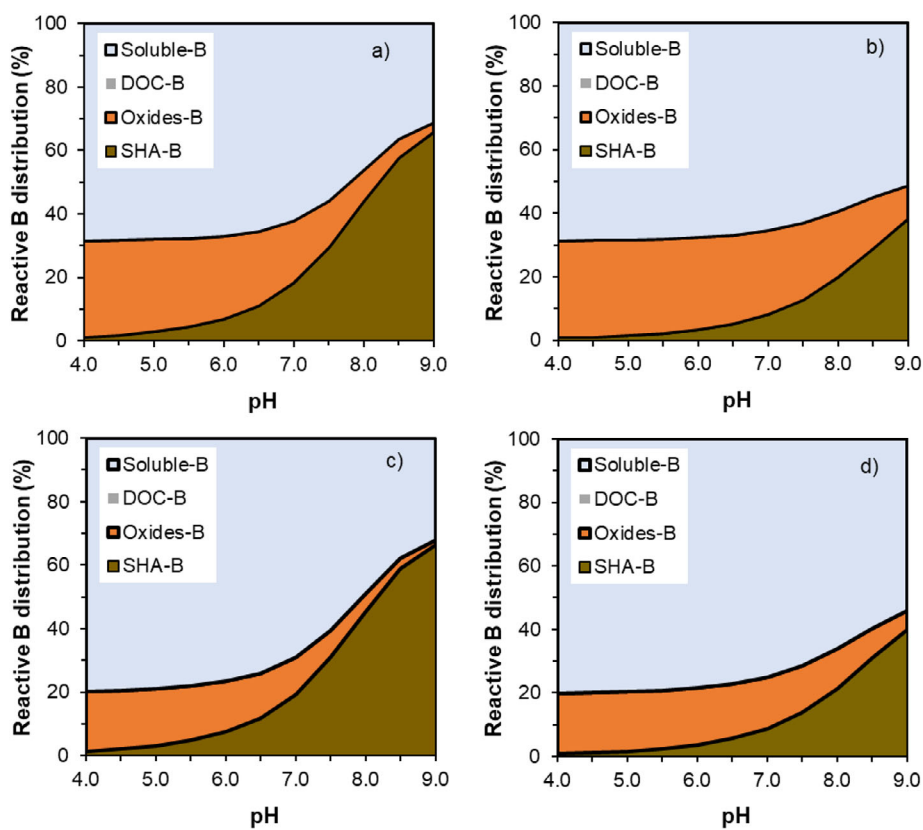


FIGURE 3 | Multi-surface ion adsorption modeling for the distribution of reactive boron (B) in the soil. Left panels (a and c) are for 0.01 M CaCl_2 systems, and right panels are for 0.01 M NaNO_3 systems (b and d). The upper panels (a and b) are for the RSA and R- PO_4 loading conditions determined by our soils using the probe-ion method with NaHCO_3 , fitted HNOM of 1.19 nm^{-2} . The lower panels (c and d) are for conditions where both RSA and R- PO_4 are lower (RSA = $20 \text{ m}^2 \text{ g}^{-1}$, R- PO_4 = 9.8 mmol kg^{-1}), while keeping the same P-loading and HNOM.

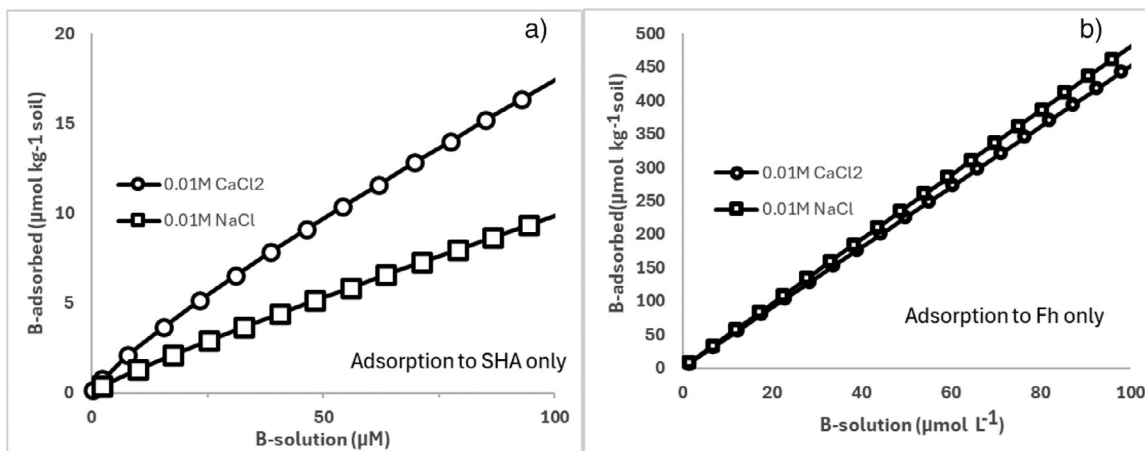


FIGURE 4 | B adsorption in Ca and Na electrolyte systems. The model data show the comparison if B would be adsorbed only in HA (a) and oxide fraction represented by Ferrihydrite (b). For the modeling, the conditions were kept as for the original soil sample; that is, RSA, R-PO₄, SSR, and pH were fixed to 5.0 for both reactive surfaces.

4 | Discussion

4.1 | Mineral Surface Reactivity

The abundance of SRO aluminosilicates and metal (hydr)oxides determined by the various Fe and Al extractions (AO and Py) is consistent with the dominant mineralogy reported for soils from this region (Nieuwenhuys et al. 1994, 2000; Buurman et al. 1997). The content of Fe and Al measured in DC and AO extractions has been used to estimate the RSA of soils for modeling purposes (Dijkstra et al. 2004, 2009; Van Eynde, Weng, et al. 2020), assuming explicit values of specific surface area (SSA) and molar masses for the reactive metal (hydr)oxide minerals. This approach presents substantial uncertainties as these values can largely vary across the reactive minerals in different soils (Mendez et al. 2020).

For this study, we applied a method that uses native PO₄ as probe ion (Hiemstra et al. 2010) to estimate the RSA (m² g⁻¹ soil). Although the use of the probe ion method interpreted with CD-MUSIC model using ferrihydrite as an oxide reference resulted in appropriate estimates of RSA and the R-PO₄ of Dutch soils (Mendez and Hiemstra 2020), it is important to consider whether this approach is applicable to soils with different mineralogical compositions, particularly in our case, for volcanic soils dominated by SRO aluminosilicates. For our volcanic soil, these fitted values of the RSA and R-PO₄, subsequently used as independent modeling input, correctly described the B adsorption isotherms without further modeling adjustments (Figure 1), suggesting that, as a first approximation, this is a valid approach for modeling the RSA of this type of volcanic soils.

4.2 | P–B Adsorption Interactions

P–B adsorption interaction was studied by two complementary approaches: first, by experiments and modeling of B adsorption isotherms and second, by analyzing the effect of PO₄ on native B concentrations.

The experimental and modeled isotherm data showed that without added PO₄, B adsorbed almost linearly across the eval-

uated B concentrations. However, the addition of PO₄ reduced the linearity of the B adsorption isotherm, indicating PO₄–B competition particularly at the highest concentrations of added B (Figure 1). The observed PO₄–B competition could be related to the reduction of inner-sphere complexation induced by PO₄, noticeable only at high B loadings (our dataset contains only one point at such high B concentrations where PO₄–B competition was observed). Conversely, the formation of outer-sphere B species is likely unaffected by PO₄ due to the absence of charge in boric acid molecule (H₃BO₃) that dominates the speciation of B at the pH values of the adsorption experiments.

Our modeling results for the isotherm adsorption experiments (Table S4) and literature data (Van Eynde, Weng, et al. 2020) suggest that B adsorption at the experimental pH values occurs mainly on metal hydroxide surfaces as outer-sphere species when PO₄ is present.

In the system without PO₄ addition, the implemented model (purely predictive approach) performed very well describing the almost linear B adsorption and suggesting adsorption principally to the (hydr)oxide surfaces, likely including both inner- and outer-sphere species. This assumption about the presence of both species is supported by literature on pure goethite and ferrihydrite systems (Goli et al. 2011; Van Eynde, Mendez, et al. 2020).

The model also performed well for the +1.6 mM P system up to B solution concentrations close to 45 µmol L⁻¹ (Figure 1). The deviation from linearity observed at the highest B concentration could be related to a decrease in the formation of inner-sphere B species. Van Eynde, Mendez et al. (2020), considering a pure ferrihydrite system, observed that at P concentrations of 0.1 mM, inner-sphere B species are practically negligible, whereas the outer-sphere species dominated the adsorption of B.

The good agreement between modeled and measured data (Figure 1) is remarkable because our modeling approach is fully predictive and does not include the fitting of any adsorption parameters. It correctly predicted B solution concentrations despite such low micromolar B concentrations observed for this volcanic soil.

Although our dataset includes just one data point with such elevated B concentrations in which PO_4 -B competition was experimentally observed, this finding provides valuable insight into the complex interactions governing B adsorption at elevated concentrations and suggests a potential opportunity for further study about the behavior of B adsorption under such condition. To further investigate this, we also tested other modeling scenarios to explore possible causes about the differences between modeled and measured data at the highest B concentrations (Figure S1).

These explorative scenarios showed that decreasing the log K for the formation of outer-sphere species (i.e., $\Delta \log K = -0.20$) and increasing inner-sphere complexation contribution (i.e., by increasing the site density of reactive groups that form inner-sphere with B) (Figure S1) described the PO_4 -B competition observed at high B concentrations. This explorative scenario also predicted reasonably well B adsorption without PO_4 .

Furthermore, the good performance of this purely predictive modeling approach enables the assessment of the effects of changing chemical conditions on B adsorption, such as variations in soil pH, counter ions, and surface reactivity.

For the second approach, we studied the effect of PO_4 on native B concentrations. Measured data indicate that PO_4 additions do not affect equilibrium B concentrations for native B levels (Figure 2). The red point in Figure 2 represents the “native phosphate” present in the soil, that is, no extra P added.

The lack of relationship between B adsorption and PO_4 loading at natural B levels is probably related to the mechanisms of PO_4 and B adsorption. Phosphate adsorbs with a higher affinity as an inner-sphere species, introducing negative charges to the 1-plane (Hiemstra and Van Riemsdijk 2006), reducing extra anion adsorption related to the expected electrostatic repulsion and site competition. However, B at low natural loadings can adsorb as both inner-sphere and outer-sphere complexes, and due to its neutral electrostatic behavior, the outer-sphere complexes are not affected by these negative charges present at the 1-plane derived from the inner-sphere PO_4 adsorption. Van Eynde, Mendez et al. (2020) suggest that B adsorption under the presence of PO_4 occurs principally as an outer-sphere species. However, at high B concentrations for this soil, part of the B is adsorbed as inner-sphere complexes, as it was affected by the presence of PO_4 (Figure 1).

In soil systems, there is also present interfacial NOM adsorbed at the surfaces of metal oxides (Mendez et al. 2020). The interfacial NOM through different functional groups (i.e., phenolic and carboxylic groups) could compete with nutrients like PO_4 for adsorption sites at the surfaces of metal oxides (Deng et al. 2019). For our soil without added B, the expected competitive effect of PO_4 additions on B adsorption was masked effectively by the NOM already adsorbed to the oxide surfaces (Figure 2b). Modeling calculations (Figure 2b) show that considering the presence of SOM interacting with the oxide surfaces at an effective density of 1.19 sites/nm⁻² (as found for our soil), there is almost no effect on B solution concentration when the PO_4 loading increases from ~0.5 to 1.5 $\mu\text{mol}/\text{m}^2$. Conversely, without interfacial SOM, an increase in B solution concentration is predicted when increasing PO_4 loading. In this case, B solution concentrations achieve

similar values at high PO_4 loadings compared to the observed values for the condition in which it is considered the effect of the NOM.

For our modeling approach (considering the NOM), most B was adsorbed as an outer-sphere species, which is not affected by PO_4 adsorption, whereas under the absence of NOM (no-HNOM simulations), part of the B could adsorb as an inner-sphere species, and consequently this fraction could be affected by the PO_4 loadings. This situation does not occur for the natural condition of our volcanic soil due to the presence of organic matter.

4.3 | Modeling B Adsorption in Ca vs. Na Systems

According to Goli et al. (2019), the adsorption mechanisms of trigonal B species (species dominant at pH values below 9.24) to NOM (i.e., humic acids) require the deprotonation of sites for the B binding, as shown in the following equation:



The findings of Goli et al. (2019) in model systems with humic acids are relevant for understanding the mechanisms of B adsorption to NOM and in this way to also understand B adsorption mechanisms in volcanic soils. Our modeled data show that there is more adsorption of B to the humic acids present in our soil in CaCl_2 0.01 M than in NaCl 0.01 M systems (Figure 4). As explained in depth by Goli et al. (2019), this result is a combination of both the counter ion effect and the ionic strength effect on B adsorption.

The increase of the ionic strength produces a reduction in the electrostatic potential at the Donnan phase, and consequently, it would reduce the local H^+ concentration, and B binding is facilitated by a weaker proton competition.

The effect of changing from a monovalent cation to a divalent cation also favors the deprotonation of the reactive groups of the humic acids, as the Ca^{2+} ions can better screen the charge of the humic acids reducing the competition of the protons with the B. At the same time, calcium can compete with B for specific adsorption to humic acids (Goli et al. 2019). However, this competition is compensated by the effect of Ca in decreasing the negative electrostatic potential at the Donnan phase as compared to the Na systems.

On the other hand, when we applied the same modeling exercise exclusively to the (hydr)oxide fraction, it showed no effect of either the ionic strength or the change in the cation valence of the electrolyte solution (Figure 4b). As our adsorption isotherms did not show differences in B adsorption at different electrolyte solutions, it suggests that B adsorption is dominated by the oxides fraction in this volcanic soil.

4.4 | Surface Speciation of Boron

The predicted B adsorption (Figure 3) showed a sorption increase with increasing the pH; this result agrees with literature (Van

Eynde, Mendez, et al. 2020) and was principally related to the more important role of organic matter for B adsorption at high pH.

The modeling speciation suggests that most of the B is present as a soluble fraction at the typical pH values found in volcanic soils of this region (4.5–6.0). For this pH range, about 31% of the B is adsorbed to the soil particles for both background electrolytes (Figure 3a,b and Table S4).

According to the B adsorption modeling results (Figure 3), a reduction of the oxide fraction of the soil (e.g., a volcanic soil with lower oxide contents) is not fully compensated by the increased B adsorption to the organic fractions. The increase of B adsorption with the increase of pH was more significant for the Ca-dominated background solution.

A possible reason for the more important role of the organic fractions in B binding as the soil pH increases could be the increased difficulty of forming (hydr)oxide protonated species (such as $\equiv\text{FeOH}_2^{+0.5}$) as the soil pH increases. Boron adsorption for this soil was significantly related to outer-sphere adsorption, and the higher pH values could affect the formation of protonated species that adsorb B as an outer-sphere species.

Additionally, at higher pH, the deprotonation of the organic matter binding sites (as shown in Section 4.3, Equation 1) could increase the importance of the organic matter for B binding. For our volcanic soil in a Ca-dominated system (Figure 3a), the simulation also suggests a more important role of the organic fractions as the soil pH increases. These results appear to be related to the better screening of the charge in Ca systems that promotes the proton desorption and facilitates the B binding to the organic fractions, as described in Section 4.3 and explained in detail by Goli et al. (2019).

Our modeling suggests that for a condition with a lower RSA and lower R- PO_4 , while keeping the same P-loading and HNOM, more B will be present in the solution (a more prone to leaching condition). The latter means that under the reduction of the importance of the (hydr)oxide fraction (e.g., volcanic soils with lower content of (hydr)oxides), at low pH, the organic matter could not compensate for the reduction in the B adsorption. However, the compensation effect is more evident for high pH and Ca-dominated systems and less perceptible for Na-dominated systems.

As our experimental adsorption data (Figure 1) and the multi-surface modeled data implemented for the soil (considering all the adsorption surfaces) (Figure 3) did not show important differences in B adsorption for different background solutions (NaCl 0.01 M and CaCl_2 0.01 M) for the common pH range of this volcanic soil, the results suggest that under the experimental conditions, B is adsorbed principally by the (hydr)oxide fraction (Table S4 and Figure 3).

Despite the differences between modeled and measured data, the approach using only consistent, intrinsic, and previously determined parameters from pure systems was shown to be functional for predicting B adsorption and soluble concentrations in volcanic soils. The good agreement between pure prediction and

measured data gives confidence in the model and its assumptions, supporting extrapolation to other soils and variable chemical conditions (e.g., electrolyte background).

4.5 | Synthesis of Findings and Implications for B Management

The integration of all experimental and modeling results obtained for this volcanic soil evidenced a limited B adsorption capacity, a predominance of the SRO minerals as the primary B-adsorbing surface, minimal B adsorption to OM, and weak B- PO_4 interaction. All these findings suggest that effective boron management in this volcanic soil requires frequent applications to compensate for B losses through leaching. Furthermore, the results suggest that effective B management requires the application of low B rates to minimize losses and improve B use efficiency, as B is likely to remain in solution in this type of agricultural systems.

5 | Conclusions

This study provides insights into the adsorption behavior and surface speciation of boron (B) in volcanic soils from a humid tropical region and its interaction with phosphate. At the natural pH conditions of the soil, the reactive minerals, mainly SRO minerals, are the major binding surfaces for B. Phosphorous additions had no significant effect on the solubility of native B, which was modulated by the influence of interfacial NOM. For added B, the influence of PO_4 on B adsorption varied with B concentration. At low B concentrations, PO_4 had a negligible effect on adsorption, whereas at higher B concentrations, PO_4 caused moderate competitive interactions for adsorption sites. The advanced multi-surface ion adsorption model implemented in this study successfully described the adsorption of B and the interaction with phosphate (PO_4). This mechanistic approach, using intrinsic adsorption parameters and independently derived modeling inputs, highlights the potential applications of this framework for predicting B adsorption processes in other volcanic soils with similar chemical and mineralogical properties. Overall, the combination of experimental data and advanced mechanistic modeling contributes to our understanding of B adsorption processes in volcanic soils rich with an abundance of SRO minerals. The limited B adsorption observed in experiments and modeling for this volcanic soil, combined with the high precipitation rates common in the sampled area, and the typically high permeability of volcanic soils, suggests that B management in this agricultural system should be carried out through recurrent applications of low B rates. All these findings are relevant for improving B management in systems where both B deficiencies and high P fertilizer applications are common.

Acknowledgments

We are very grateful to professor and friend Sjoerd E.A.T.M. van der Zee of the Wageningen University, who initially supervised this study but sadly passed away before its completion. The first author acknowledges to the Ministry of Science and Technology of Costa Rica (MICITT), contract number PINN-MICITT 2-1-4-17-1-014, and the University of Costa Rica for its partial complementary funding, contract number: OAICE-53-2018.

Disclosure

The principal author declares that artificial intelligence (AI) tools (Copilot Microsoft) were used solely to improve grammar and readability of this manuscript. All text and content were written by the authors. Funding sources had no role in study design, in the collection, analysis, and interpretation of data, in the writing of the report, nor in the decision to submit the article for publication.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Datasets and the implemented ORCHESTRA files (i.e., ferrihydrite) are available upon request from the corresponding author. The implemented ORCHESTRA code is available at the ORCHESTRA webpage (<https://orchestra.meeussen.nl>) after the publication of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supplementary File 1: jpln70012-sup-0001-SuppMat.docx.

Supplementary File 2: jpln70012-sup-0002-SuppMat.docx.