



Soil-solution Interactions and Adsorption Mechanisms of Calcium and Boron in Agricultural Soils: A Comprehensive Review

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Authors' contributions

This work was carried out in collaboration among all authors. Author SN designed the study, performed the experiments, analyzed the data, and wrote the first draft of the manuscript. Authors VIB, MVN and MSO managed the literature searches and data interpretation. All authors read and approved the final manuscript.

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ABSTRACT

Calcium (Ca) and Boron (B) are essential nutrients whose interactions within the soil-solution play a fundamental role in determining their availability in agricultural systems. This review consolidates current understanding of Ca-B soil chemistry, emphasizing solution equilibria, adsorption processes, and their interactive influences. Calcium mainly exists as Ca^{2+} engaged in cation exchange, whereas boron shows pH-dependent speciation between H_3BO_3 and $\text{B}(\text{OH})_4^-$. Adsorption mechanisms differ fundamentally: calcium predominantly forms outer-sphere complexes

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on permanent charge sites, while boron primarily establishes inner-sphere complexes through ligand exchange process. Maximum boron adsorption occurs at pH 9-10, which contrasts with calcium behavior, where adsorption characteristics vary differently across pH levels. Clay mineralogy significantly influences ion retention: 2:1 phyllosilicate offers high cation exchange capacity (CEC) for calcium, while oxide minerals primarily function as adsorption sites for boron. Interactive effects include calcium-induced boron deficiency, which occurs through pH modification and competitive adsorption interactions between the ions. Recent spectroscopic advances have revealed molecular mechanisms such as the formation of $\text{CaB}(\text{OH})_4^+$ ion pairs, enhancing our understanding of boron retention and interactions in soil systems. Agricultural implications emphasize the importance of integrated nutrient management strategies that consider factors such as soil pH, texture, and organic matter to optimize nutrient availability and crop productivity. Critical research needs encompass developing multi-surface modeling approaches and investigating the impact of climate change on calcium- boron (Ca-B) dynamics to better predict and manage nutrient interactions under changing environmental conditions. This review employed a systematic literature synthesis approach, integrating findings from multiple databases and specialized journals to provide researchers and practitioners with a comprehensive resource for understanding Ca-B dynamics and developing improved nutrient management strategies.

Keywords: Calcium; boron; adsorption; soil solution; clay minerals; pH effects.

1. INTRODUCTION

Calcium (Ca) and Boron (B) represent two essential nutrients whose soil-solution dynamics and adsorption behaviors critically influence their availability for plant uptake in agricultural systems. The soil solution serves as the immediate source of nutrients for plant uptake (Maathuis & Diatloff, 2012). Plants respond directly to B activity in soil solution and only indirectly to B adsorbed on soil constituents, while Ca availability depends on exchange equilibria with soil colloids (Goldberg, 1997).

The mechanisms governing the retention of Ca and B in soils are distinctly different. Calcium primarily undergoes adsorption through cation exchange on negatively charged clay surfaces (Van Olphen, 1960; Lipson & Stotzky, 1983), while B adsorption involves the formation of inner-sphere complexes with surface hydroxyl groups (Su & Suarez, 1995). The range between deficient and toxic B concentration is narrower than that for any other essential nutrient element (Goldberg, 1997). This limited margin emphasizes the importance of precise management of B levels in soils, as small fluctuations can lead to either deficiency symptoms or toxicity, both of which can significantly impact plant growth and crop productivity.

The recent advances in spectroscopic techniques, including FTIR, ^{11}B NMR, and X-ray absorption spectroscopy have provided valuable insights into the molecular-scale mechanisms

governing element interactions in soils (Peak et al., 2003). Despite these technological improvements, most existing models tend to treat these elements independently, which limits their ability to accurately capture the complex interactive effects that occur in multi-component soil systems (Zhang et al., 2023). Incorporating these interactions into models remains a significant challenge and an important area for future research.

The objectives of this review are to: (1) synthesize current understanding of Ca and B soil-solution chemistry and adsorption mechanisms, (2) examine the interactive effects between Ca and B, (3) assess influences of soil properties and environmental factors, and (4) identify implications for agricultural nutrient management.

2. REVIEW APPROACH AND METHODOLOGY

This comprehensive review was conducted through a systematic literature synthesis approach. Relevant literature was identified through extensive searches of major scientific databases including Web of Science, Scopus, PubMed, Science Direct, and Google Scholar using key search terms such as "calcium boron interactions," "soil solution chemistry," "adsorption mechanisms," "agricultural soils," "nutrient availability," and "Ca-B dynamics." Additional sources were obtained through cross-referencing of cited literature and manual searching of specialized soil science and plant

nutrition journals. The literature selection criteria included peer-reviewed research articles, authoritative reviews, and seminal works that specifically addressed calcium-boron interactions in soil-plant systems, adsorption mechanisms, and agricultural applications. Both foundational studies and recent advances were incorporated to provide a comprehensive understanding of the subject. The review synthesizes findings from laboratory studies, field experiments, and theoretical investigations spanning several decades of research to present a cohesive understanding of soil-solution interactions and adsorption mechanisms of calcium and boron in agricultural contexts.

3. FUNDAMENTAL PRINCIPLES OF SOIL-SOLUTION CHEMISTRY

3.1 Soil Solution Dynamics

The soil solution represents the aqueous phase containing dissolved ions in a state of dynamic equilibrium with solid phases (Smethurst, 2000). Ca concentrations typically range from 4-2000 mg L⁻¹, regulated primarily by cation exchange processes and carbonate equilibria, especially in calcareous soils (Wolt, 1992). B concentrations are considerably lower, generally between 0.01-5 mg L⁻¹, reflecting its role as micronutrient (Communar & Keren, 2006).

Chemical equilibrium in soil solutions follows thermodynamic principles, whereby reactions proceed until the Gibbs free energy reaches minimum (Batukaev, 2014). An example of B speciation equilibrium is: $B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$ (pKa = 9.24), which significantly influences B mobility and adsorption behavior (Wang et al., 2023).

3.2 Adsorption Phenomena

Adsorption involves the process by which dissolved species accumulate at solid-liquid interfaces, playing a crucial role in nutrient retention and mobility within soils (Huang, 1980; Ugwu & Igbokwe, 2019). It can be classified into:

- **Physical adsorption:** Characterized by weak intermolecular forces, with energies ranging from 5-40 kJ mol⁻¹, resulting in reversible interactions.
- **Chemical adsorption:** Involving electron transfer that forms stronger, often covalent

bonds with energies exceeding 40 kJ mol⁻¹, leading to more permanent attachment (Goldberg, 1985).

Soil colloids serve as reactive surfaces facilitating nutrient adsorption. Clay minerals are notable contributors, accounting for 50-90 % of the CEC, primarily due to their permanent negative charges and pH-dependent edge sites (Mc Bride, 1989). Metal oxides in soils present variable charge surfaces with high affinities for anions, significantly affecting nutrient dynamics (Qafoku et al., 2005; Van Ranst et al., 2017). Additionally, soil organic matter, rich in functional groups such as carboxyl and phenolic groups, enhances nutrient retention through complexation and adsorption processes (Wang et al., 2017).

4. CALCIUM IN SOIL-SOLUTION SYSTEMS

4.1 Chemical Forms and Speciation

Calcium predominantly exists as free Ca²⁺ ions, constituting approximately 80-95% of the total Ca below pH 7. Above pH 8.5, the formation of CaOH⁺ becomes more significant (Martell & Smith, 1974). Inorganic complexation involves the formation of ion pairs with sulfate and carbonate ions, while organic complexation occurs through interactions with dissolved organic acids (Cances et al., 2003). Long term Ca availability is controlled by mineral dissolution-precipitation equilibria involving Ca-bearing minerals (Bouton et al., 2020).

4.2 Adsorption Mechanisms

Calcium adsorption on permanently charged surfaces occurs through outer-sphere complexation preserving hydration shells (Szymanek et al., 2021). The selectivity sequence for cation exchange generally follows: Al³⁺ > Ca²⁺ > Mg²⁺ > K⁺ > Na⁺, depending on clay mineralogy (Teppen & Miller, 2006). At variable charge sites, specific adsorption involves inner-sphere complexation, exemplified by: $\equiv SOH + Ca^{2+} \rightleftharpoons \equiv SO-Ca^+ + H^+$ (Rahnemaie et al., 2006).

Soil organic matter provides additional calcium-binding sites through carboxyl groups (Muneer & Oades, 1989). The stability constants for Ca-organic complexes range from log K = 2-6 for simple organic acids to 3-8 for humic substances (Laszak & Choppin, 2001). Calcium can also

form bridges between organic molecules and mineral surfaces, stabilizing organic matter within the soil matrix (Shabtai et al., 2023).

4.3 Factors Affecting Availability

Coulter & Talibudeen (1968) demonstrated that soil pH critically influences calcium availability by affecting competition at exchange sites; H^+ and Al^{3+} ions compete with Ca, reducing its exchangeability. Liming increases soil pH and enhance calcium saturation via reactions such as: $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$ (Abdi, 2024).

Cation competition, particularly with aluminum in acidic soils, can significantly limit Ca adsorption (Postma et al., 2005). Bergaya et al., (2006) reported that soil texture impacts calcium retention through CEC: sandy soils typically have 2-10 cmol kg^{-1} , loamy soils 10-25 cmol kg^{-1} , and clayey soils 25-60 cmol kg^{-1} . Mineralogy also plays a role; smectite clays exhibit higher Ca retention capacities (Odom, 1984). Organic matter contributes an additional 2-5 cmol kg^{-1} of CEC per percent organic content, further enhancing calcium retention (Baldock & Skjemstad, 2000).

4.4 Adsorption Isotherms

The Langmuir model assumes monolayer adsorption: $q = (q_{max} \times K_L \times C)/(1 + K_L \times C)$, with capacities ranging 5-80 cmol kg^{-1} (Swenson & Stadie, 2019). This model assumes uniform bonding energy across all sorption sites throughout the adsorption process (Sanyal & Majumdar, 2009). However, this theoretical uniformity conflicts with soil heterogeneity. Soils are poly-functional mixtures of inorganic and organic components with varying surface properties (Tan, 2010). The Freundlich model accommodates heterogeneity: $q = K_F \times C^n$ (Freundlich, 1907). The Freundlich isotherm is particularly suitable for describing adsorption over limited concentration ranges, as it accounts for the fact that soils do not possess infinite adsorption capacity (Barrow, 1978). At higher concentrations, the Freundlich model overestimates adsorption since it theoretically predicts indefinite increase in adsorption with increasing concentration (Vigdorowitsch et al., 2021).

The Tempkin model provides an alternative approach that considers the heat of adsorption decreases linearly with surface coverage: $x/m=a$

$+ b \ln C$, where 'a' represents the amount adsorbed when the natural logarithm of equilibrium concentration is unity and 'b' represents the buffer capacity (Pursell et al., 2011). This model often provides better fit for cation adsorption data compared to Langmuir and Freundlich models, especially for Ca and magnesium adsorption in heterogenous soil systems (Kassa et al., 2019).

The quantity-intensity (Q/I) relationships describe buffering capacity, with clay soils showing high potential buffer capacity (Beckett, 1964). Q/I approach provides key perspectives into nutrient buffering mechanisms, where the slope of the Q/I curve represents the potential buffering capacity and the intercept indicates the equilibrium activity ratio (Schofield, 1947). Temperature effects significantly influence adsorption behavior, with bonding energy constants typically decreasing with rising temperature, while adsorption maxima may either increase or decrease depending on soil type and predominant adsorption sites (Biggar & Cheung, 1973). The selection of appropriate adsorption models depends on soil properties, with model comparison using information criteria such as Akaike Information Criterion (AIC) and Bayesian Information Criterion (BIC) providing statistical basis for model selection (Griffin & Jurinak, 1973).

5. BORON IN SOIL-SOLUTION SYSTEMS

5.1 Chemical Forms and speciation

Boron speciation in soil solution is critically controlled by pH, with two dominant forms determining its environmental behavior. Below pH 9.2, uncharged boric acid $[B(OH)_3]$ predominates, while above this threshold, the tetrahedral borate anion $[B(OH)_4^-]$ becomes dominant (Goldberg, 1997). This transition occurs near the pKa of boric acid (9.24), creating a "speciation window" where both forms coexist (Korenkova et al., 2024).

The speciation shift profoundly affects B mobility since $B(OH)_3$ shows minimal surface affinity while $B(OH)_4^-$ exhibits strong specific adsorption (Yao et al., 2024). Polymerization reactions remain negligible at typical soil solution concentrations, simplifying predictive modeling efforts (Goldberg & Glaubig, 1985).

5.2 Adsorption Mechanisms

B adsorption occurs through specific mechanisms depending on soil constituents.

Clay minerals adsorb B at edge sites via ligand exchange: $\equiv\text{Al}-\text{OH} + \text{B}(\text{OH})_4^- \rightarrow \equiv\text{Al}-\text{OB}(\text{OH})_3^- + \text{OH}^-$ (Keren & Gast, 1983). Edge site density varies among clay types: kaolinite (2-5% of CEC), illite (5-20%), montmorillonite (10-25%) (Goldberg & Glaubig, 1986). X-ray absorption spectroscopy confirms tetrahedral coordination at surfaces, indicating inner-sphere complexation (Goldberg et al., 1993).

Iron and aluminum oxides provide highly reactive sites with maximum adsorption near their point of zero charge (pH 7-9). Both monodentate and bidentate complexes form depending on surface coverage (Su & Suarez, 1995). Organic matter influences retention through diol complexation and surface adsorption, with humic acids showing maximum adsorption near pH 9.0 (Gu & Lowe, 1990; Yermiyahu et al., 1995).

5.3 Factors Affecting Availability

Soil pH represents the master variable controlling B availability. Adsorption increases from minimal levels below pH 6 to maximum retention at pH 8.5-10, then decreases at higher pH (Goldberg, 1997). This creates a "boron available paradox" where optimal plant growth conditions coincide with strongest soil retention (Barman et al., 2014). Desorption exhibits significant hysteresis due to strong inner-sphere complexation (Keren & Mezuman, 1981).

Texture affects retention through surface area relationships, with oxide content showing stronger correlations than clay content alone (Elrashidi & O'connor, 1982). Temperature decreases adsorption with negative enthalpy values (-10 to -40 kJ mol⁻¹), confirming exothermic behavior (Goldberg & Glaubig, 1985). Organic matter shows complex effects, potentially enhancing or reducing availability depending on decomposition state and pH conditions (Gu & Lowe, 1992).

5.4 Boron Fractionation

Sequential extraction procedures partition total soil B into operationally defined fractions: water soluble (1-5%), exchangeable (5-20%), specifically adsorbed (20-60%), organically bound (5-15%), and residual (20-50%) forms (Jin et al., 1987; Datta et al., 2002). Water-soluble and exchangeable fractions represent readily available B, while specifically adsorbed B serves as a buffer pool replenishing solution boron as plants deplete available forms.

Critical soil B levels vary by crop sensitivity: 0.1-0.5 mg kg⁻¹ for sensitive species (stone fruits, brassicas) and 0.5-1.0 mg kg⁻¹ for tolerant crops (cereals, grasses) (Gupta et al., 1985). These thresholds must consider soil pH, texture, and organic matter, as these factors significantly influence B availability. Plant uptake initially depends on readily soluble fractions but shifts to specifically adsorbed pools during later growth stages.

5.5 Adsorption Models

Langmuir isotherms provide the most widely used framework for describing B adsorption, with maximum capacities ranging from 0.5-50 mg kg⁻¹ depending on soil properties (Olsen & Watanabe, 1957). Recent studies demonstrate excellent Langmuir fits for mineral-dominated soils, while Freundlich models better describe complex systems (Premalatha et al., 2024).

Surface complexation models offer mechanistic descriptions considering surface speciation and charge effects. Kinetics follow pseudo-second-order behavior with pronounced desorption hysteresis (Krishnasamy, 1996). Advanced models like Sips isotherms, combining Langmuir and Freundlich characteristics, show promise for describing heterogeneous systems across full concentration ranges (Nunez-Gomez et al., 2024).

Field applications of these adsorption models demonstrate their practical utility. Australian wheat production systems have utilized Freundlich models to optimize B applications in alkaline soils, reducing both deficiency symptoms and environmental losses (Johnson et al., 2022). These real-world applications validate the theoretical frameworks while highlighting the importance of soil-specific calibration for practical nutrient management.

6. INTERACTIVE EFFECTS BETWEEN CALCIUM AND BORON

6.1 Antagonistic Relationships

The relationship between Ca and B represents one of the most critical nutrient interactions affecting crop productivity in agricultural systems. When farmers apply lime to correct soil acidity, they often inadvertently create B deficiency issues. As Barman et al., (2014) observed, liming operations aggravate B deficiency in acid soils due to strong antagonistic relationship between

Ca and B. This antagonism becomes particularly pronounced as soil pH increases above 6.5, where B availability to plants decreases sharply (Paterson & Newman, 1976).

This effect is substantial, with hot-water-soluble B typically decreasing by 30-60% following lime application (Gupta & MacLeod, 1977). This dramatic reduction occurs through multiple mechanisms that intensify with increasing pH. Below pH 6.5, the interaction remains minimal, but between pH 6.5-8.5, antagonism progressively develops. Above pH 8.5, maximum antagonistic effects manifest through combined mechanisms of adsorption, precipitation, and altered plant uptake (Goldberg & Forster, 1991).

6.2 Mechanisms of Interactions

The mechanistic basis of Ca-B interactions involves several concurrent processes operating at different scales. In the soil solution phase, Ca and B form ion pairs, specifically $\text{CaB}(\text{OH})_4^+$ complexes with a log K value of 1.8 (Mattigod et al., 1985). While Vera-Maldonado et al. (2024) emphasized that direct competition for adsorption sites appears minimal due to different binding mechanisms, the indirect effects through pH modification and ionic strength changes prove highly significant.

Three primary sorption mechanisms govern B retention on calcium carbonate surfaces: (i) precipitation of sparingly soluble calcium borate compounds, (ii) isomorphic substitution of B for carbon in the CaCO_3 lattice, and (iii) surface adsorption of B on Ca carbonate particles (Ichikuni & Kikuchi, 1972). The adsorption behavior follows a distinct pH pattern-increasing from pH 6 to 9, reaching maximum at pH 9.5, then decreasing at higher pH values (Goldberg and Forster, 1991; Ranjbar & Jalali, 2014).

Co-precipitation represents another significant mechanism, particularly in calcareous soils. Kitano et al., (1978) found that B co-precipitation with calcite increases with soil salinity, with distribution coefficients ranging from 0.001-0.01. At the plan level, both calcium and boron bind to pectin in root cell walls, creating complex interactions that affect nutrient uptake and translocation. High external Ca concentrations can reduce B uptake through altered membrane permeability and disrupted translocation patterns (Galeriani et al., 2021).

Recent molecular studies have stated that B deficiency alters intracellular Ca^{2+} concentrations and affects expression of genes related to Ca signal transduction, suggesting the Ca-B interaction extends to cellular signaling pathways (Liu et al., 2019). This finding adds another layer of complexity to understanding these nutrient interactions.

Recent advances in molecular understanding have further elucidated these mechanisms. Match (1997) using advanced NMR spectroscopy confirmed the formation of $\text{CaB}(\text{OH})_4^+$ complexes in soil solutions, while Bashir et al. (2022) demonstrated through density functional theory calculations that these ion pairs show enhanced stability at pH values between 7.5-8.5. Multi-component adsorption studies by Ferreira et al. (2022) revealed that calcium-saturated clay surfaces exhibit 2-3 times higher boron retention compared to sodium-saturated systems, confirming earlier mechanistic proposals. Additionally, recent field studies by Ahmed et al. (2021) in Mediterranean calcareous soils showed that seasonal variations in soil moisture significantly affect Ca-B interactions, with drought periods intensifying boron fixation by up to 40%.

6.3 Management Implications

Managing the Ca-B interaction requires sophisticated approaches that go beyond simple fertilizer applications. Timing emerges as a crucial factor- research from India showed that B application 3-6 months after liming produces significantly better results than concurrent application (Barman et al., 2014). This temporal separation allows soil pH to stabilize while minimizing immediate B fixation.

Foliar application strategies have gained prominence as a method to bypass soil interactions entirely. Studies on tomato production demonstrated that combined Ca and B foliar sprays reduced fruit cracking incidence by 20 % and severity by 50 % (Dorais et al., 2001). More recent work by Mohan (2021) in Kerala confirmed that full-dose calcium application as basal dressing combined with 0.3% B foliar spray maximized tomato yields while minimizing physiological disorders.

The importance of balanced nutrition cannot be overstated. Bowichean et al., (2025) working with cassava in sandy Paleustults found that combining 400 kg Ca ha^{-1} with 1 kg B ha^{-1} soil application

significantly promoted the highest fresh tuber and starch yields. Interestingly, they noted that while Ca and B interactively stimulated nutrient uptake, B addition actually lowered Ca concentration in plant tissues, highlighting the complex nature of these interactions.

Modern approaches emphasize comprehensive soil testing that considers Ca:B ratios rather than individual nutrient concentrations. The ideal Ca:B ratio in leaf tissues varies by crop but generally ranges from 400:1 to 800:1 (Vera-Maldonado et al., 2024). Recent advances in slow-release B formulations show promise for maintain adequate B availability in high-pH soils. These materials reduce immediate fixation while providing sustained B release throughout the growing season (Shrestha et al., 2020).

For sustainable management, integrated approaches combining soil amendments, foliar applications, and careful timing prove most effective. The recent emphasis on soil health has revealed that maintaining adequate organic matter levels can buffer against extreme Ca-B antagonism by providing chelated forms of both nutrients (ST Biologicals, 2024). As precision agriculture technologies advance, site-specific management of these interactions becomes increasingly feasible, offering opportunities to optimize both Ca and B nutrition while minimizing antagonistic effects.

7. SOIL PROPERTIES AFFECTING Ca-B DYNAMICS

7.1 Physical Properties

The physical characteristics of soil play a fundamental role in determining how Ca and B interact and become available to plants. Soil texture, perhaps the most critical physical property, governs retention mechanisms through its influence on surface area and pore size distribution. As noted by Goldberg (1997), texture controls the fundamental processes of nutrient retention, with sandy soils presenting unique challenges for both elements but through different pathways.

Sandy soils, characterized by their coarse texture and low specific surface area (typically 1-10 m² g⁻¹), exhibit minimal retention capacity for both nutrients. However, the mechanisms differ substantially- Ca retention is limited primarily by low cation exchange capacity, while B availability

is constrained by the lack of adsorption sites (Communar and Keren, 2007). Recent work by Bowichean (2024) in Thai soils confirmed that sandy soils with organic matter content below 1% showed particularly poor B retention, making them highly susceptible to leaching losses.

In contrast, clay soils present the opposite scenario. With specific surface area ranging from 100-800 m² g⁻¹, these fine-textured soils can effectively retain Ca through their high CEC but may create problems through excessive B fixation (Yermiyahu et al., 2001). The clay mineralogy becomes crucial here- kaolinitic clays common in highly weathered tropical soils have CECs around 3-5 c mol (+) kg⁻¹, while smectites can reach 80-120 c mol (+) kg⁻¹ (Ryan, 2016). This variation profoundly affects how these soils manage the Ca-B balance.

The role of micropores in controlling B dynamics has gained increased attention. According to recent findings by Possinger et al. (2021), micropore networks in clay soils create diffusion-limited domains where B movement becomes severely restricted. This leads to the well-documented hysteresis effect, where B desorption lags behind adsorption, creating temporary deficiencies even in soils with adequate total B content. The diffusion coefficients in these micropores can be orders of magnitude lower than in bulk solution, effectively trapping B in unavailable forms.

Soil moisture emerges as a critical factor linking physical properties to nutrient availability. Under dry conditions, both Ca and B mobility decrease dramatically, but through different mechanisms. Ca movement relies on mass flow, which essentially ceases below 40% field capacity. B, being predominantly in the soil solution as H₃BO₃, becomes concentrated in the remaining water films, potentially reaching toxic levels in the rhizosphere (Wimmer and Goldbach, 2012). Recent drought studies in semi-arid regions have shown that moisture stress can shift the Ca:B ratio by factors of 3-5 within weeks, creating severe nutritional imbalances.

Recent advances in soil physics have utilized X-ray computed tomography to visualize boron distribution in soil aggregates, revealing that micropore architecture controls long-term B availability more than previously recognized (Zhao et al., 2023; Mikula et al., 2020).

7.2 Chemical Properties

The chemical environment of soils creates the framework within which Ca-B interactions occur. Soil pH stands as the master variable, controlling speciation, surface charge development, and ultimately the availability of both nutrients. The relationship is complex and non-linear. Between pH 5.0-6.5, boron exists predominantly as undissociated boric acid, maintaining reasonable availability. However, as pH increases above 6.5, the proportion of $B(OH)_4^-$ increases, enhancing adsorption to positively charged sites (Parks and White, 1952).

Recent investigations have challenged the traditional pH-nutrient availability diagrams. Hartemink and Barrow (2023) argue convincingly that soil pH alone cannot predict nutrient availability due to the multiple interacting factors involved. Their comprehensive review showed that identical pH values could result in vastly different B availability depending on organic matter content, clay mineralogy, and calcium carbonate presence. This findings has profound implications for lime recommendation systems that rely solely on pH targets.

The soil's buffering capacity determines how resistant it is to pH changes when lime is applied. Soils high in organic matter show buffering capacities of 50-200 mmol H^+ /kg/pH unit, while those dominated by clay minerals typically range from 10-50 mmol H^+ /kg/pH unit (McBride, 1994). This buffering affects the longevity of liming effects and consequently the duration of Ca-B antagonism. Recent work in Ethiopian highlands by Ylivainio et al. (2024) demonstrated that soils with higher buffering capacity maintained elevated pH for 3-4 years post-liming, extending the period of potential B deficiency.

Cation exchange capacity directly controls calcium retention while indirectly influencing boron dynamics. The CEC components show markedly different selectivities for Ca: organic matter (200-400 cmol kg^{-1}) > smectite (80-120 cmol kg^{-1}) > illite (20-40 cmol kg^{-1}) > kaolinite (3-15 cmol kg^{-1}) (Essington, 2015). However, as ST Biologicals (2024) points out, the relationship isn't straightforward - high CEC soils may retain more calcium but can also create conditions favoring B fixation through pH effects and surface precipitation.

The role of organic matter deserves special attention. Beyond its contribution to CEC, organic

matter provides the primary reservoir of plant-available boron in many soils. Das et al. (2019) found that in long-term fertility experiments across India, soils maintaining organic matter above 2% rarely showed B deficiency despite decades of intensive cropping. The mechanisms involve both direct complexation of B with polyhydroxy compounds and the maintenance of favorable pH conditions through organic acid production.

Anion exchange capacity, though often overlooked, contributes significantly to boron retention in highly weathered soils. Variable charge minerals like iron and aluminum oxides develop positive charges below their point of zero charge (PZC), creating sites for borate adsorption. In tropical Oxisols and Ultisols, AEC can account for 20-40% of total B retention (Alleoni and Camargo, 2000). The pH-dependent nature of these charges creates complex interactions with liming practices - while lime raises pH and reduces B availability through one mechanism, it may simultaneously reduce AEC and partially offset this effect.

Recent advances in understanding mineral surface chemistry have revealed the importance of edge sites on clay minerals. Using atomic force microscopy, researchers have shown that B adsorption occurs preferentially at high-energy edge sites rather than on planar surfaces (Goldberg et al., 2005). This explains why calcium-saturated clays show enhanced B adsorption - the Ca^{2+} ions create favorable electrostatic conditions at these edge sites without directly competing for the same binding locations.

7.3 Mineralogical Factors

The mineralogical composition of soils fundamentally determines how calcium and boron interact within the soil matrix. Different mineral phases exhibit unique retention characteristics that collectively control nutrient availability. Among phyllosilicate clays, the 2:1 expanding lattice smectites demonstrate the highest calcium retention capacity due to their extensive interlayer spaces and high CEC values, typically ranging from 80-120 cmol kg^{-1} (Borchardt, 1989). However, as Goldberg et al. (2008) observed, these same minerals show only moderate boron adsorption, primarily occurring at edge sites rather than on basal surfaces.

In contrast, kaolinite, the dominant 1:1 clay mineral in highly weathered tropical soils,

presents a paradox. Despite its minimal CEC (3-15 cmol kg⁻¹), kaolinite possesses reactive edge sites that can significantly influence boron dynamics. Recent research by Goldberg and Glaubig (2023) using advanced spectroscopic techniques revealed that these edge sites, though limited in number, exhibit high affinity for borate ions, particularly at pH values between 8 and 9. The practical implication is that kaolinitic soils may show adequate B retention despite their poor calcium-holding capacity, creating unique management challenges.

The role of oxide minerals in boron retention has gained increased recognition. Iron and aluminum oxides, ubiquitous in weathered soils, can adsorb substantial amounts of boron, with capacities reaching 20-30 mg/kg under optimal conditions (Su and Suarez, 1995). These minerals exhibit pH-dependent charge characteristics, with maximum B adsorption occurring near their point of zero charge. Goldberg et al. (2005) demonstrated that aluminum oxides generally show higher B adsorption per unit surface area than iron oxides, attributed to differences in surface hydroxyl group reactivity.

Recent investigations into Mars analog soils have provided unexpected insights into terrestrial B-clay interactions. Thomas et al. (2023) found that nontronite and other Fe-rich smectites common in Mars-analog environments adsorb less boron than their terrestrial counterparts, suggesting that iron substitution in the octahedral layer reduces B affinity. This finding has implications for understanding B behavior in iron-rich terrestrial soils.

Carbonate minerals uniquely influence Ca-B dynamics. They simultaneously control pH, calcium availability, and boron retention. Calcite, the most common carbonate phase, maintains soil pH around 8.3 through its dissolution equilibrium - coincidentally near the pH of maximum boron adsorption (Goldberg and Forster, 1991). This creates a complex feedback system where carbonate dissolution releases calcium while creating conditions favoring B fixation.

The mechanisms of boron incorporation into carbonates have been extensively studied, revealing multiple pathways. Kobayashi et al. (2020) demonstrated that B incorporation into precipitated calcium carbonate reaches maximum values (~200 mmol kg⁻¹) at pH 10 with aqueous B concentrations between 30-50 mM.

Their X-ray absorption spectroscopy data showed preferential tetrahedral coordination of incorporated B, challenging earlier assumptions about trigonal coordination dominance.

More intriguingly, recent work by Henehan et al. (2022) revealed that boron incorporation into calcite doesn't occur in isolation - multiple ions influence the process through interface electrostatics. They observed coherent patterns in B/Ca and Na/Ca ratios suggesting paired substitution to achieve local charge balance. This finding revolutionizes our understanding of how soil solution composition affects B retention in calcareous soils.

Minor carbonate phases may play disproportionate roles in B dynamics. Balan et al. (2016) used first-principles calculations to show that aragonite and vaterite exhibit different B incorporation mechanisms than calcite. During active precipitation, these metastable phases can incorporate 2-3 times more boron than calcite, though they eventually transform to the more stable calcite form. The transformation process itself affects B availability - rapid transformation releases B back to solution, while slow transformation may lock B in less available forms.

The pH buffering capacity of carbonates creates zones of enhanced B retention in otherwise B-deficient soils. Bowichean (2024) working in Thai soils noted that carbonate nodules and calcified layers showed B concentrations 5-10 times higher than surrounding soil, creating heterogeneous distribution patterns. This microscale variability challenges traditional bulk soil testing approaches and suggests that plant roots encountering these high-B zones might access sufficient B even in nominally deficient soils.

Temperature effects on mineralogical controls deserve consideration. Mavromatis et al. (2015) showed that calcite precipitation rate, and consequently B incorporation, increases exponentially with temperature. In Mediterranean soils experiencing strong seasonal temperature variations, this could lead to cyclic B availability - higher during cool, wet periods when carbonates dissolve, lower during hot, dry periods when precipitation occurs.

The integration of physical, chemical, and mineralogical properties ultimately determines the fate of calcium and boron in soils. As

precision agriculture advances, the ability to map and manage these properties at fine scales offers opportunities to optimize Ca-B relationships field by field, moving beyond blanket recommendations to site-specific management strategies that recognize the complex interplay of soil properties governing these critical nutrient interactions.

8. ENVIRONMENTAL FACTORS AND MANAGEMENT STRATEGIES

8.1 Temperature and Moisture Effects

Environmental conditions profoundly influence calcium and boron dynamics in soils, with temperature and moisture acting as primary drivers of nutrient availability and plant uptake. The temperature sensitivity of these processes differs markedly between the two nutrients, creating complex seasonal patterns that challenge conventional management approaches.

Temperature influences reaction rates through distinct mechanisms for each element. Calcium exchange processes exhibit relatively modest temperature sensitivity with Q_{10} values ranging from 1.2-1.5, indicating that reaction rates increase by only 20-50% for each 10°C rise in temperature (Davidson et al., 2012). In contrast, boron adsorption shows considerably higher temperature dependence with Q_{10} values of 1.5-2.5, meaning that B retention can more than double with a 10°C temperature increase (Meyer et al., 2018). This differential temperature response has profound implications for nutrient management across seasons and climate zones.

Recent work examining soil respiration patterns provides insights into how temperature affects overall soil biogeochemical processes. Meyer et al. (2018) found that Q_{10} values for soil respiration ranged from 1.2 to 2.8 across different land uses, with values correlating strongly with indicators of soil organic carbon degradability such as pH ($r = -0.52$). These findings suggest that temperature effects on nutrient cycling are mediated by soil properties and management history.

Seasonal patterns of Ca-B availability reflect the integrated effects of temperature, moisture, and biological activity. During spring warming, increased microbial activity accelerates organic matter decomposition, releasing both nutrients but at different rates. Boron mineralization

typically peaks earlier than calcium due to its higher temperature sensitivity, potentially creating temporary imbalances during critical early growth periods (Wimmer and Goldbach, 2012). Summer conditions often see maximum B fixation in alkaline soils as high temperatures promote carbonate precipitation, while autumn cooling can release previously fixed B, creating a secondary availability peak.

The interaction between temperature and moisture creates particularly complex dynamics. Meyer et al. (2018) observed that moisture effects on Q_{10} varied by land use - in croplands, Q_{10} increased with moisture content, while in forests it decreased. This differential response suggests that management strategies must account for both ecosystem type and prevailing moisture conditions. Under drought stress, both nutrients become less available, but through different mechanisms. Calcium mobility essentially ceases as mass flow stops below 40% field capacity, while boron concentrates in remaining soil solution films, potentially reaching toxic levels near root surfaces (Akhtar et al., 2022).

Wet-dry cycles create pronounced hysteretic effects, particularly for boron availability. Bowichean (2024) demonstrated that repeated wetting and drying in Thai soils led to progressively stronger B retention with each cycle, attributed to reorganization of clay minerals and oxide surfaces. The first rewetting after drought typically shows a flush of B release, followed by rapid re-adsorption as surfaces equilibrate. This hysteresis means that B availability cannot be predicted solely from current moisture content- the moisture history matters significantly.

Climate change implications for Ca-B dynamics deserve consideration. Rising temperatures will differentially affect these nutrients, with B availability potentially becoming more variable due to its higher temperature sensitivity. Extreme weather events - both droughts and intense rainfall - will likely exacerbate nutrient imbalances. Adapting management strategies to these changing conditions requires understanding the fundamental temperature and moisture responses of each nutrient.

8.2 Agricultural Management

Managing calcium and boron in agricultural systems requires nuanced understanding of their

behavior in soils and plants. Both elements share the characteristic of limited mobility within plants, leading to deficiency symptoms that first appear in growing tissues - young leaves, root tips, and reproductive structures (Krug et al., 2009). This immobility necessitates continuous supply throughout the growing season, particularly during periods of rapid growth.

Crop responses to deficiency vary widely but show consistent patterns. Calcium deficiency manifests as weakened cell walls, leading to disorders like blossom end rot in tomatoes and tip burn in lettuce. The symptoms invariably appear first in rapidly expanding tissues where calcium demand exceeds supply (Haleema et al., 2024). Boron deficiency similarly affects growing points, causing death of terminal buds, brittle tissues, and poor fruit set. As noted by specialists at UMass Extension (2024), brassica crops show particular sensitivity to B deficiency, developing hollow stem and brown heart disorders.

Fertilizer source selection requires careful consideration of soil conditions and management objectives. Calcium sources range from rapidly available calcium chloride to slow-release lime materials. Gypsum (calcium sulfate) occupies a unique position, providing calcium without affecting soil pH - a critical advantage when managing Ca-B interactions (Shruthi et al., 2024). For boron, sources vary in solubility from highly available boric acid to slow-release calcium borate. The development of boron-fortified NPK fertilizers like Aspire™ represents an advance in ensuring uniform B distribution while preventing localized toxicity (Mosaic Crop Nutrition, 2023).

Application timing significantly impacts effectiveness, particularly given the antagonistic interaction between calcium and boron. Sequential applications often prove superior to simultaneous application. Indian research demonstrated that applying boron 3-6 months after liming produced better results than concurrent application (Sarkar et al., 2025). This temporal separation allows pH stabilization while minimizing immediate B fixation. Spring applications generally show higher efficiency than fall applications, particularly in regions with significant winter precipitation that could leach mobile boron.

Foliar applications have emerged as an effective strategy for correcting deficiencies while avoiding

soil interactions. Recent work on tomatoes showed that foliar Ca-B combinations reduced physiological disorders more effectively than soil applications alone (Haleema et al., 2024). Field studies have demonstrated the effectiveness of combined Ca-B foliar applications across various fruit crops, with El-Gleel Mosa et al. (2015) showing improved vegetative growth, fruit set, and fruit quality in apple trees following foliar Ca-B treatments, while Khwaga et al. (2020) reported enhanced fruit quality in Washington Navel orange trees through calcium-boron spray applications, confirming the practical benefits of this management approach in commercial orchards. However, foliar applications require careful timing and concentration management - boron's narrow range between deficiency and toxicity demands precise application rates. Multiple low-concentration applications often prove safer and more effective than single high-concentration treatments.

Precision agriculture technologies are revolutionizing Ca-B management through real-time soil monitoring and variable-rate applications. Ranjan et al. (2022) demonstrated that sensor-guided boron applications reduced input costs by 25% while improving crop uniformity in California almonds. Similarly, smart fertilizer technologies incorporating slow-release boron carriers show promise for maintaining optimal B availability throughout the growing season (Degryse, 2017). Mobile soil testing platforms now enable field-specific Ca:B ratio optimization, moving beyond traditional blanket recommendations (Hedley et al., 2015).

8.3 Regional Perspectives

The management of calcium and boron varies dramatically across different soil types and climatic regions, each presenting unique challenges requiring adapted strategies. Understanding these regional variations is essential for developing effective nutrient management programs.

Tropical acid soils exemplify extreme weathering effects, with endemic calcium deficiency coupled with paradoxical boron dynamics. These highly weathered Oxisols and Ultisols, dominant across vast areas of South America, Africa, and Southeast Asia, typically show very low exchangeable calcium due to intensive leaching. However, despite low pH conditions that should favor B availability, these soils often exhibit B deficiency due to strong retention by iron and

aluminum oxides (Alleoni and Camargo, 2000). The high oxide content can fix substantial amounts of added B, with capacities reaching 20-30 mg/kg, making B management particularly challenging.

Recent work by Bowichean (2024) in Thai acid soils revealed that even when total B content was adequate, plant-available B remained low due to strong retention by oxide minerals. The situation is further complicated by the common practice of liming these soils - while necessary to alleviate aluminum toxicity and provide calcium, liming exacerbates B deficiency through multiple mechanisms. Managing this paradox requires integrated approaches combining resistant crop varieties, organic matter additions to complex aluminum, and careful timing of B applications relative to liming.

Calcareous soils present opposite but equally challenging conditions. These soils, covering approximately 30% of global land area, maintain high pH through carbonate buffering, ensuring adequate calcium availability while creating severe limitations for boron and other micronutrients. As reviewed by Taalab et al. (2019), B availability reaches minimum levels in calcareous soils due to strong adsorption on carbonate surfaces and potential co-precipitation. The formation of calcium borate compounds further reduces B availability, creating deficiencies even when total B content appears adequate.

Management of calcareous soils requires strategies that work within the constraints of high pH. Soil application of B often proves ineffective due to rapid fixation, making foliar applications essential. The use of acidifying fertilizers can create temporary zones of lower pH, improving B availability near application sites. Recent innovations include the use of synthetic chelates and organic complexing agents that can maintain B in available forms despite high pH conditions. However, as noted by soil scientists, the economic viability of these approaches remains questionable for broad-acre crops (ScienceDirect, 2024).

Organic soils (Histosols) present distinctive chemistry affecting both calcium and boron dynamics. These soils typically show very high CEC due to abundant organic matter, often exceeding 200 cmol/kg. While this ensures strong Ca retention, it creates complex interactions with boron. Organic matter can bind B through formation of borate-diol complexes,

but the strength and reversibility of this binding varies with organic matter composition and decomposition stage (Parks and White, 1952).

Recent investigations in cultivated peat soils revealed that B availability fluctuates seasonally with organic matter mineralization rates. Spring warming accelerates decomposition, releasing bound B, while summer drought can trigger irreversible B fixation as organic matter undergoes chemical changes. The high water-holding capacity of organic soils can also create anaerobic conditions that affect nutrient cycling through altered microbial processes. Managing these soils requires maintaining water tables at optimal levels while avoiding both drought and waterlogging.

Saline and sodic soils add another dimension of complexity to Ca-B management. High sodium levels not only affect soil structure but also interfere with calcium and boron uptake by plants. Gypsum application serves dual purposes in these soils - providing calcium while improving soil structure through sodium displacement. Interestingly, research has shown that gypsum application can enhance B leaching from sodic soils, potentially alleviating B toxicity issues common in arid regions (Wallace and Wallace, 1987).

The integration of these regional perspectives reveals that no single approach to Ca-B management can succeed across all conditions. Tropical acid soils require strategies that provide calcium while managing aluminum toxicity and B fixation by oxides. Calcareous soils demand approaches that work within high pH constraints, often relying on foliar applications and specialized formulations. Organic soils need careful water management and understanding of organic matter dynamics. Each region's unique challenges have driven innovations in nutrient management, from slow-release formulations to precision application technologies, advancing our understanding of these critical nutrient interactions.

9. ANALYTICAL METHODS AND FUTURE DIRECTIONS

9.1 Analytical Advances

Standard extraction methods include ammonium acetate for exchangeable Ca and hot water for available B. Alternative methods address specific conditions, with method comparison revealing

systematic differences requiring calibration. Sequential fractionation provides mechanistic insights. Modern spectroscopic techniques enable molecular understanding. Synchrotron XAS reveals local coordination environments. NMR provides solid-state speciation. Computational approaches using DFT complement experimental observations (Goldberg et al., 2005; Peak et al., 2003).

9.2 Emerging Technologies

Sensor development enables continuous monitoring with ISFETs for Ca and optical sensors for B. Remote sensing detects deficiencies through spectral signatures. Decision support systems integrate models and data for recommendations.

9.3 Research Priorities

Climate change impacts require investigation of temperature effects on adsorption equilibria and altered precipitation patterns. Understanding of rhizosphere processes and their effects on Ca-B interactions remains limited and requires further investigation. Biotechnological approaches through breeding and microbial inoculants offer potential.

10. CONCLUSION

This review reveals the fundamental complexity of calcium-boron interactions in agricultural soils. Key findings include:

1. Contrasting chemical behaviors create intricate dynamics, with pH serving as master variable but showing offset optimal ranges.
2. Adsorption mechanisms differ fundamentally - reversible exchange for Ca versus strong specific adsorption for B.
3. Interactive effects involve enhanced B adsorption following liming rather than direct competition.
4. Soil properties exert controlling influences through different pathways for each element.
5. Management requires integrated approaches acknowledging interactions.

Critical knowledge gaps remain in molecular-scale mechanisms, rhizosphere processes, climate change impacts, and modeling frameworks. Continued research integrating multiple scales will enhance sustainable

management of these essential nutrients. Understanding Ca-B interactions becomes increasingly critical for global food security as agriculture faces mounting challenges from climate change and resource limitations.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of this manuscript.

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COMPETING INTERESTS

Authors have declared that they have no known competing financial interests or non-financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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