



Fractionation and Availability of Calcium and Boron in Lateritic Soils of Kerala, India

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

This study investigated the fractionation patterns of calcium and boron in lateritic soils across four agro-ecological units of Kerala to assess their availability in relation to soil properties. The laboratory-based fractionation study with sequential extraction procedures was conducted at the Department of Soil Science and Agricultural Chemistry, College of Agriculture, Kerala Agricultural University, Vellanikkara, between 2023 and 2024. Forty soil samples from four lateritic agro-ecological units (AEU 8, 9, 10, and 11) of Kerala were analyzed. Calcium was fractionated using Mokwunye and Melsted (1972) method into water-soluble, exchangeable, organic complexed, acid soluble, and mineral-bound forms. Boron was fractionated following Datta et al. (2002) into readily soluble, specifically adsorbed, oxide-bound, organically bound, and residual forms. Correlation analysis was performed between fractions and soil properties. Calcium fractions ranged from 3.57 to 11.33 mg kg⁻¹ for water-soluble, 298.71 to 1895.43 mg kg⁻¹ for exchangeable, 18.59 to 268.53

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mg kg⁻¹ for organic complexed, 68.74 to 195.98 mg kg⁻¹ for acid soluble, and 89.64 to 635.01 mg kg⁻¹ for mineral calcium. Total calcium varied from 348.33 to 3425.44 mg kg⁻¹ across AEU. The contribution of calcium fractions followed the order: Ex. Ca > Min-Ca > Ac-s. Ca > Or-c Ca > WS. Ca. Boron fractions ranged from 0.41 to 1.86 mg kg⁻¹ for readily soluble, 0.12 to 1.83 mg kg⁻¹ for specifically adsorbed, 0.05 to 0.59 mg kg⁻¹ for oxide-bound, 0.41 to 2.87 mg kg⁻¹ for organically bound, and 44.42 to 90.23 mg kg⁻¹ for residual boron. Residual boron constituted the largest pool (54.98-60.08 mg kg⁻¹ across AEU). All calcium fractions showed highly significant positive intercorrelations ($P < .001$). Available boron fractions (RS-B, SA-B, OX-B, OR-B) exhibited strong negative correlations with soil pH ($r = -0.78$ to -0.97 , $P < .001$) and positive correlations with available iron ($r = 0.72$ to 0.91 , $P < .001$) and exchangeable aluminum ($r = 0.74$ to 0.92 , $P < .001$). A distinct antagonistic relationship was observed between calcium and available boron fractions, with exchangeable calcium showing the strongest negative correlation with all available boron forms ($r = -0.60$ to -0.76 , $P < .001$). Conversely, residual boron and total boron exhibited highly significant positive correlations with all calcium fractions ($r = 0.52$ to 0.83 , $P < .001$). The dominance of exchangeable and mineral-bound calcium fractions indicates moderate calcium availability in Kerala lateritic soils. The predominance of residual boron fraction with strong pH-dependent availability suggests potential risk of boron deficiency under acidic conditions typical of lateritic soils. The strong negative correlations between calcium and available boron fractions reveal significant Ca-B antagonism, necessitating balanced fertilization strategies including integrated organic matter management and split application of amendments. Soil pH, organic carbon, clay content, and exchangeable aluminum emerge as key factors governing calcium and boron fractionation patterns. These findings provide a scientific basis for developing AEU-specific nutrient management recommendations for lateritic soils of Kerala.

Keywords: *Lateritic soils; calcium fractionation; boron speciation; sequential extraction; bioavailability; agro-ecological units; Kerala; Ca-B interactions.*

1. INTRODUCTION

Lateritic soils are characterized by highly weathered conditions under humid tropical climates, occurring in nearly 70 percent of Kerala's geographic area. These soils are formed through the laterization process, which involves the intensive leaching of bases and desilication, followed by enrichment with iron and aluminium oxides, leading to physico-chemical characteristics that limit their fertility and productivity. The gravelly texture, acidic pH, and low nutrient retention capacity make lateritic soils poor in essential plant nutrients (Ghosh, 2019).

Calcium and boron are essential plant nutrients that play critical roles in growth and development. Calcium is required for cell wall formation, membrane integrity, and enzyme activation (White & Broadley, 2003), while boron is essential for cell wall synthesis, membrane function, sugar transport, and reproductive development (Marschner, 2011). Both nutrients are particularly important in maintaining cell wall structure and function (Blevins & Lukaszewski, 1998). In lateritic soils, the acidic nature and high aluminium saturation levels adversely affect calcium availability (Wong et al., 1990). "Conversely, boron can be strongly adsorbed to

iron and aluminium oxides, thereby reducing its bioavailability" (Goldberg, 1997). Calcium deficiency causes tissue necrosis, stunted growth, and physiological disorders such as blossom end rot (Saure, 2001), while boron deficiency leads to death of growing points, poor fruit set, and reduced fertility (Shorrocks, 1997). The interaction between calcium and boron is complex, involving both synergistic effects in cell wall metabolism and antagonistic relationships in nutrient uptake (Cakmak & Römheld, 1997).

"Total nutrient content provides limited information about plant availability. Nutrients exist in various chemical forms with different accessibility. Sequential fractionation procedures partition nutrients into operationally defined fractions representing water-soluble, exchangeable, organic complexed, acid soluble, and mineral-bound forms for calcium" (Mokwunye & Melsted, 1972), and readily soluble, specifically adsorbed, oxide-bound, organically bound, and residual forms for boron (Hou et al., 1994, 1996). These fractions differ in their availability, with water-soluble and exchangeable forms being readily available while mineral-bound and residual forms remain largely unavailable (Shuman, 1991). Fractionation studies provide insights into nutrient dynamics,

transformation processes, and factors governing availability (McLaren & Cameron, 1996).

Kerala has been divided into agro-ecological units based on physiography, climate, soil characteristics, and land use patterns. Lateritic soils occur across several agro-ecological units, exhibiting considerable variability in properties due to differences in parent material, weathering intensity, and environmental conditions. This spatial variability necessitates agro-ecological unit-specific characterization to develop location-specific nutrient management recommendations (Gajbhiye & Mandal, 2000).

Despite the importance of calcium and boron in crop nutrition and the prevalence of lateritic soils in Kerala, comprehensive fractionation studies across different agro-ecological units remain limited. Most assessments have focused on total or extractable contents without investigating distribution among chemical fractions (Singh, 2008). Understanding fractionation patterns is critical for identifying bioavailable pools, dominant chemical forms, nutrient transformation processes, and developing targeted management strategies.

The present investigation was undertaken to determine the distribution of calcium and boron

among different fractions in lateritic soils across four agro-ecological units of Kerala, assess bioavailable pools, establish relationships between nutrient fractions and soil properties, examine calcium-boron interactions, and develop a comprehensive understanding of factors governing their availability to facilitate agro-ecological unit-specific nutrient management recommendations.

2. MATERIALS AND METHODS

2.1 Study Area and Sampling

The study was conducted at the Department of Soil Science and Agricultural Chemistry, College of Agriculture, Kerala Agricultural University, Vellanikkara, between 2024 and 2025. Forty soil samples were selected from four lateritic agro-ecological units of Kerala: southern laterites (AEU 8), south central laterites (AEU 9), north central laterites (AEU 10), and northern laterites (AEU 11). Ten samples were selected from each AEU based on variations in pH, organic carbon content, texture, cation exchange capacity, and initial calcium and boron status to ensure representation of diverse soil conditions across the lateritic regions. The geographical distribution of sampling locations across the four AEU is presented in Fig. 1.

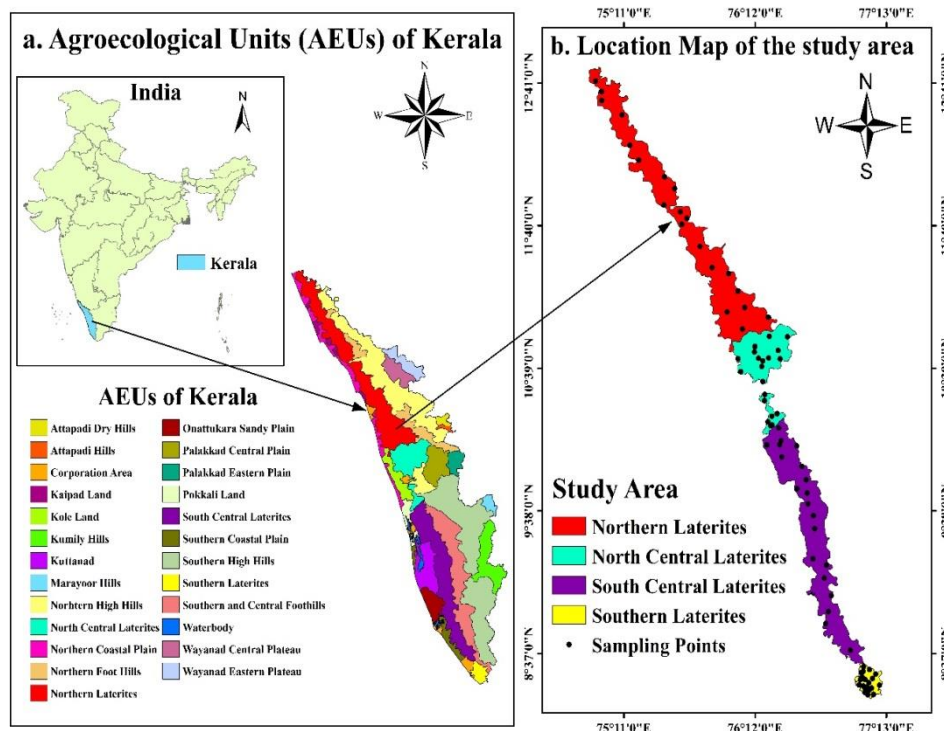


Fig. 1. Map showing sampling locations across four lateritic agro-ecological units of Kerala

2.2 Soil Characterization

Soil samples were air-dried, ground, and passed through a 2 mm sieve for physico-chemical analysis. Soil pH was determined in a 1:2.5 soil-water suspension using a glass electrode pH meter (Jackson, 1958). Electrical conductivity was measured in a 1:2.5 soil-water extract using a conductivity meter (Jackson, 1958). Organic carbon was estimated by the Walkley & Black wet oxidation method (Walkley & Black, 1934). Particle size distribution was determined by the international pipette method (Robinson, 1922), and textural class was assigned using the USDA textural triangle. Exchangeable cations and cation exchange capacity (CEC) were determined by following the barium chloride compulsive exchange method (Hendershot & Duquette, 1986). Available nitrogen was estimated by alkaline permanganate method (Subbiah & Asija, 1956). Available phosphorus was determined by Bray's method (Bray & Kurtz, 1945) and available potassium by neutral normal ammonium acetate extraction followed by flame photometry (Jackson, 1958). Available calcium and magnesium were extracted using neutral normal ammonium acetate and determined by atomic absorption spectrophotometry (Jackson, 1958). Available boron was determined by the hot water extraction method using azomethine-H reagent (Berger & Truog, 1939). Available iron, manganese, copper, and zinc were extracted by DTPA extractant and determined by atomic absorption spectrophotometry (Lindsay & Norvell, 1978).

2.3 Fractionation of Calcium

Sequential extraction following Mokwunye and Melsted (1972), with modifications, was employed to partition calcium into five fractions. Soil samples were ground and passed through a 0.417 mm sieve before analysis.

2.4 Water Soluble Calcium

Five grams of soil was extracted with 25 ml of distilled water by shaking for one hour, centrifuged at 2000 rpm for 10 minutes, and the extraction was repeated until 100 ml of extract was obtained.

2.5 Exchangeable Calcium

One gram of soil was extracted with 20 ml of neutral 1 N NH_4OAc by shaking for 40-60

minutes, centrifuging, and repeating until 100 ml of extract was collected.

2.6 Organic Complexed Calcium

The residue from the exchangeable fraction was treated with 10 ml of 10 per cent H_2O_2 until foaming ceased, centrifuged, and washed with neutral 1 N NH_4OAc until 100 ml was obtained.

2.7 Acid-Soluble Calcium

The residue was treated with 30 ml of 1 N HNO_3 , boiled gently for 15 minutes, cooled, filtered, and washed with 0.2 N HNO_3 to make 100 ml extract.

2.8 Mineral Calcium

The residue with filter paper was digested with 25 ml of tri-acid mixture ($\text{HNO}_3:\text{H}_3\text{PO}_4:\text{HClO}_4$ in a 23:23:54 ratio) until complete digestion. After cooling, 5 ml of 5 N HCl was added, and the volume was made to 100 ml.

2.9 Total Calcium

One gram of soil was digested with 25 ml of 70 per cent HClO_4 until the appearance of white fumes and clear residue. After cooling, 5 ml of 5 N HCl was added, and the volume was made to 100 ml.

All calcium determinations were performed using atomic absorption spectrophotometry with strontium (4000 ppm) added to suppress interference.

2.10 Fractionation of Boron

Sequential extraction following Datta et al. (2002) with modifications from Hou et al. (1994, 1996) was employed to partition boron into five fractions. Soil samples were ground and passed through a 0.5 mm sieve.

2.11 Readily Soluble Boron

Five grams of soil was extracted with 10 ml of 0.01 M CaCl_2 by shaking for 16 hours, centrifuged at 10,000 rpm for 30 minutes, and filtered. Boron was determined using the azomethine-H method.

2.12 Specifically Adsorbed Boron

The residue was extracted with 10 ml of KH_2PO_4 by shaking for one hour, centrifuged, filtering,

and boron was determined using the azomethine-H method.

2.13 Oxide-Bound Boron

The residue was extracted with 20 ml of 0.175 M ammonium oxalate (pH 3.25) by shaking for 4 hours. The colored extract was treated with NaOH and HClO₄ to eliminate color, and boron determined using the carmine method.

2.14 Organically Bound Boron

The residue was extracted with 20 ml of 0.5 M NaOH by shaking for 24 hours. The dark extract was treated with HClO₄, and boron determined using the carmine method.

2.15 Total Boron

Exactly 0.2 g of soil was pre-digested overnight with 3 ml freshly prepared aqua regia (HCl: HNO₃ in a 3:1 ratio), then digested at 135°C for 2 hours until a white residue appeared. After cooling, the digest was diluted, filtered, and made to 50 ml. Boron was determined using the carmine method with absorbance measured at 585 nm.

2.16 Residual Boron

Calculated by subtracting the sum of readily soluble, specifically adsorbed, oxide-bound, and organically bound fractions from total boron.

2.17 Statistical Analysis

Descriptive statistics were computed for all fractions. Pearson correlation analysis was performed to establish relationships between different fractions of calcium and boron, and between fractions and soil properties. Statistical analyses were conducted using appropriate software, and significance was tested at $P = .05$, $P = .01$, and $P = .001$ levels.

3. RESULTS AND DISCUSSION

3.1 Calcium Fractionation in Lateritic Soils

The distribution of calcium fractions across four lateritic agro-ecological units of Kerala is presented in Table 1. Exchangeable calcium emerged as the dominant fraction, accounting for 50-60% of total calcium, with mean values ranging from 703.89 to 907.96 mg kg⁻¹ across AEUs. Water-soluble calcium constituted less than 1% of total calcium, reflecting limited immediately available pools susceptible to leaching under humid tropical conditions (Bhattacharyya et al., 2009). Organic complexed calcium ranged from 66.54 to 116.29 mg kg⁻¹, with north central laterites showing the highest values, likely due to greater organic matter content (Sharma et al., 2017). Mineral calcium exhibited high spatial variability (CV 0.47-0.71), representing slowly available reserves occluded within oxide structures (Srinivasarao et al., 2009). Total calcium varied from 348.33 to 3425.44 mg kg⁻¹, with the fractionation order: Ex Ca > Min-Ca > Ac-s Ca > Or-c Ca > WS Ca (Pal et al., 2001).

All calcium fractions showed significant positive intercorrelations (Table 2), indicating dynamic equilibrium among pools. Exchangeable calcium exhibited the strongest correlation with total calcium ($r = 0.93$, $P < .001$), confirming its role as the primary determinant of overall calcium status (Sanyal & De Datta, 1991). Soil pH, CEC, and organic carbon showed highly significant positive correlations with all calcium fractions, while exchangeable aluminium exhibited strong negative correlations (Table 2), reflecting acidic soil conditions limiting calcium availability (Pal et al., 2000; Ritchey et al., 1982). The inverse relationship with exchangeable aluminium is characteristic of acid soils where aluminium occupies exchange sites, displacing calcium and reducing its availability (Mandal & Mitra, 1982). The positive correlation with CEC reflects the fundamental role of cation exchange capacity in calcium retention (Razzaghi et al., 2021).

Table 1. Mean calcium fractions (mg kg⁻¹) across four lateritic AEUs

AEU	WS Ca	Ex Ca	Or-c Ca	Ac-s Ca	Min-Ca	Total Ca
AEU 8 (n=10)	9.06	835.61	66.54	117.11	215.26	1287.68
AEU 9 (n=10)	7.83	740.58	88.24	113.58	194.70	1369.96
AEU 10 (n=10)	9.67	907.96	116.29	127.22	226.91	1615.30
AEU 11 (n=10)	9.43	703.89	78.65	97.92	148.46	1172.12

WS Ca: Water-soluble; Ex Ca: Exchangeable; Or-c Ca: Organic complexed; Ac-s Ca: Acid soluble; Min-Ca: Mineral calcium

Table 2. Key correlations of calcium fractions

Parameter	Ex Ca	Or-c Ca	Total Ca
pH	0.81***	0.47**	0.64***
CEC	0.88***	0.93***	0.95***
OC	0.56***	0.84***	0.68***
Ex. Al	-0.76***	-0.46**	-0.64***
Clay	0.58***	0.73***	0.66***

*** $P < .001$, ** $P < .01$; OC: Organic carbon; CEC: Cation exchange capacity; Ex. Al: Exchangeable aluminium

3.2 Boron Fractionation in Lateritic Soils

Boron fractionation revealed a strikingly different pattern, with residual boron dominating (>90% of total), ranging from 54.98 to 60.08 mg kg⁻¹ across AEUs (Table 3). “Available fractions (readily soluble, specifically adsorbed, oxide-bound, and organically bound) collectively constituted less than 10% of total boron. Readily soluble boron ranged from 0.90 to 1.06 mg kg⁻¹, representing the immediately available pool highly susceptible to leaching” (Gupta et al., 1985). Total boron (48.75-91.94 mg kg⁻¹) showed relatively uniform distribution across AEUs compared to calcium. The predominance of residual boron indicates strong fixation in unavailable forms, explaining why boron deficiency can occur despite adequate total boron content (Goldberg, 1997; Hou et al., 1996; Kumar et al., 2018).

Residual boron showed extremely strong correlation with total boron ($r = 0.99$, $P < .001$) but no correlation with available fractions, indicating limited transformation between unavailable and available pools (Das et al., 2023). Soil pH exhibited highly significant negative correlations with all available boron fractions ($r = -0.78$ to -0.97 , $P < .001$) (Table 4), reflecting pH-dependent boron chemistry where acidic conditions favor uncharged boric acid formation, enhancing availability (Keren & Bingham, 1985; Xu et al., 2001). Conversely, residual boron showed strong positive correlations with organic carbon ($r = 0.96$, $P < .001$) and clay content ($r = 0.86$, $P < .001$), indicating enhanced retention in fine-textured, organic matter-rich soils

(Communar & Keren, 2006; Goldberg & Forster, 1991).

3.3 Calcium-Boron Interactions

Significant antagonistic relationships were observed between calcium and boron fractions (Table 5). Exchangeable calcium showed the strongest negative correlations with all available boron fractions ($r = -0.60$ to -0.76 , $P < .001$), operating through multiple mechanisms: formation of insoluble calcium borate complexes, competitive adsorption on soil colloids, pH-mediated effects, and physiological antagonism at plant uptake level (Okazaki & Chao, 1968; Ruiz et al., 1998). In striking contrast, residual boron exhibited highly significant positive correlations with all calcium fractions ($r = 0.59$ to 0.83 , $P < .001$), with the strongest correlation observed with organic complexed calcium ($r = 0.83$, $P < .001$), suggesting common retention mechanisms involving organic matter and oxides (Goldberg & Glaubig, 1986; Yermiyahu et al., 1995).

The contrasting correlations—negative with available boron but positive with residual and total boron—create complex management scenarios. Liming to correct calcium deficiency may inadvertently reduce boron availability through direct antagonism, pH increase, and enhanced fixation (Bingham et al., 1964; Elrashidi & O'Connor, 1982). This necessitates integrated calcium-boron management strategies, with boron supplementation recommended as an integral component of liming programs, particularly in intensively managed systems (Gupta, 1993; Shorrocks, 1997).

Table 3. Mean boron fractions (mg kg⁻¹) across four lateritic AEUs

AEU	RS-B	SA-B	OR-B	RES-B	Total B
AEU 8 (n=10)	0.96	0.66	1.12	54.98	58.03
AEU 9 (n=10)	1.06	0.79	1.45	57.65	61.31
AEU 10 (n=10)	0.93	0.66	1.12	59.26	62.26
AEU 11 (n=10)	0.90	0.75	1.17	60.08	63.16

RS-B: Readily soluble; SA-B: Specifically adsorbed; OR-B: Organically bound; RES-B: Residual boron

Table 4. Key correlations of boron fractions with soil properties

Parameter	RS-B	SA-B	RES-B	Total B
pH	-0.78***	-0.95***	NS	NS
OC	NS	NS	0.96***	0.96***
CEC	-0.32*	-0.43**	0.68***	0.65***
Av. Fe	0.72***	0.89***	NS	NS
Ex. Al	0.74***	0.92***	NS	NS
Clay	NS	NS	0.86***	0.86***

*** $P < .001$, ** $P < .01$, * $P < .05$; NS: Not significant; OC: Organic carbon; CEC: Cation exchange capacity; Av. Fe: Available iron; Ex. Al: Exchangeable aluminium

Table 5. Correlations between calcium and boron fractions

B Fraction	Ex Ca	Or-c Ca	Total Ca
RS-B	-0.60***	-0.32*	-0.44**
SA-B	-0.75***	-0.42**	-0.58***
OR-B	-0.76***	-0.45**	-0.60***
RES-B	0.60***	0.83***	0.68***
Total B	0.52***	0.79***	0.62***

*** $P < .001$, ** $P < .01$, * $P < .05$; Ex Ca: Exchangeable calcium; Or-c Ca: Organic complexed calcium

4. CONCLUSION

This fractionation study of calcium and boron in lateritic soils across four agro-ecological units of Kerala revealed that exchangeable calcium dominated the calcium pool (50-60% of total), while boron was predominantly locked in residual forms (>90%), with soil pH, CEC, and organic carbon as key governing factors. Strong calcium-boron antagonism was evident, with exchangeable calcium showing significant negative correlations with all available boron fractions, necessitating integrated management strategies where liming programs use split applications and boron fertilization is synchronized with lime application to prevent induced deficiencies. Future research should establish critical calcium-boron ratios for major crops and develop AEU-specific nutrient management recommendations for sustainable agricultural intensification in Kerala's lateritic regions.

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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