Plant Archives Vol. 26, Supplement 1, 2026 pp. 2484-2493 e-ISSN:2581-6063 (online), ISSN:0972-5210

Plant Archives

Journal homepage: http://www.plantarchives.org
DOI Url : https://doi.org/10.51470/PLANTARCHIVES.2026.v26.supplement-1.333

TEMPORAL CHANGES IN CALCIUM AND BORON FRACTIONS IN ACIDIC LATERITE SOILS BY THE CO-APPLICATION OF LIME AND BORAX

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(Date of Receiving : 18-10-2025; Date of Acceptance : 30-12-2025)

ABSTRACT

The dynamics of calcium-boron interactions and nutrient fractionation in laterite soil of Kerala, India, was studied in a comprehensive 150-day laboratory incubation study. The experiment involved a 3x3 factorial randomized design with three levels of calcium oxide (C_1: 0, C_2: 1.0 and C_3: 2.0 t ha^{-1}) and three levels of boron (B_1: 0, B_2: 0.5 and B_3: 1.0 kg ha^{-1}), making a total of nine combinations of treatments in three replications. Findings indicated typical three step dynamics of the calcium transformation, in Phase I (1-30 days after incubation (DAI) rapid CaO dissolution with pH rising to maximum values of 6.83-6.86 at the highest lime rate, in Phase II (30-60 DAI) stabilization and establishment of a quasi-equilibrium, and Phase III (60-150 DAI) gradual reacidification and progressive change of labile to stable calcium forms. Exchangeable calcium reached its highest point of 773.09 mg kg^{-1} at 30 DAI and then decreased 24.2% at 150 DAI because of the conversion to organically complexed forms, which rose 166% during the incubation period. Boron showed fast fixation by soluble fraction that decreased by 63-67% and oxide-bound boron rose by 69-106%, and this indicated that boron was strongly adsorbed by Fe-Al oxides common in soils of laterite. There was no significant interaction between calcium and boron interaction on most of the parameters implying that the two nutrients have independent nutrient transformation pathways. The findings lead to a scientific justification of integrated calcium-boron management in the acidic laterite soils in Kerala and illustrate the significance of studying nutrient time dynamics in order to have optimal recommendations of fertilisers.

***Keywords* :** Adsorption; Boron fixation; Nutrient transformation; Acidic soils.

Introduction

Laterite soils are a product of extreme tropical weathering and therefore constitute one of the most difficult to produce agricultural soils because of their natural acidity, low base saturation as well as high aluminium toxicity and high iron-aluminium oxide levels (Chandran *et al.*, 2005). These are highly weathered soils that are classified as Oxisols and Ultisols in USDA taxonomy, occurring over an area of about 248 million hectares world-wide with large amounts in tropical areas such as Indian subcontinent, sub-Saharan Africa, South-East Asia and South America. Laterite soils in Kerala, India, cover a large portion of the midland and highland areas that are part of the region and are used as support for a wide range of crops such as plantation crops, vegetables, and food grains. The usual 4.5-5.5 pH of these soils drastically limits the availability of nutrients and introduces the conditions of the toxicity of aluminium that inhibits the growth of roots and the productivity of crops (Srinivasan *et al.*, 2012).

Recent studies have contributed much to the knowledge on the buffering of the pH of soils in tropical soils. The laterite soils have significant initial pH reaction to lime addition and are further prone to quick reacidification on depletion of buffering capacity (Liu *et al.*, 2022). Calcium plays several crucial roles in soil-plant networks on its part in relation to acidity amelioration. Being a structural constituent of cell walls and membranes, calcium is needed in large amounts by most crops with its deficiency leading to blossom-end rot in vegetables, bitter pit in apples and inadequate fruit quality in most crops. Although boron is needed in comparatively small amounts (0.5-2.0 mg kg^{-1} to provide proper crop nutrition), it is involved in fundamental cell wall structures and cell wall strength, carbohydrate metabolism, transport of sugars across phloem tissues, pollen tube growth, and reproductive activities of flowering plants. Boron is exceptionally sensitive with a deficiency (less than 0.5mgkg^{-1}) versus toxicity (greater than 5mg kg^{-1}) concentrations having a very narrow range, and thus difficult to manage in agro-ecosystems. Padbhushan and Kumar (2017) present a broad overview of boron fractions in the soils and outline the five pools of operationally defined fractions using sequential extractions. The dynamics and interconversions among these fractions are vital to the prediction of the availability of boron and the control of the fertilizer management strategies. With the high content of sesquioxides (>30% Fe_2O_3 + Al_2O_3) in the laterite soils, the fixation of boron by means of ligand exchange on Fe-Al (hydro)oxides, which are the major adsorbers (capacity of 24.55-30.63 mg g^{-1}) and pH-dependent (Van Eynde *et al.*, 2020; Ulatowska *et al.*, 2024) mechanisms, is the predominant process that leads to low boron

Despite of the significance of calcium and boron to soil fertility and enhancing crop productivity, their relationship in laterite soil systems has had insufficient studies. The use of calcium oxide alters the soil pH and this in turn affects the boron speciation, surface charge properties, and adsorption behaviour. Borate anion $(B(OH)_4)^-$ is the predominant form of the soil solution at pH values above 7.0 with greater affinity to the oxide surfaces than the undissociated boric acid $(B(OH)_3)$ at lower pH values. These pH-mediated interactions are necessary in understanding the development of integrated nutrient management practices which maximize calcium and boron availability in the laterite acidic soils. The current research was formulated to explore the dynamics of calcium-boron interaction of the laterite soil through a detailed 150 days incubation experiment to determine the dynamic nature of nutrient fractionation and transformation in order to come up with scientifically-grounded management guidelines for the agricultural systems of Kerala.

Materials and Methods

Sampling location and initial soil characterization

The samples taken are representative surface soil (0-20 cm) of agricultural fields, Thiruvananthapuram district, Kanjiramkulam village, Kerala, India (8.5 °N Latitude, 76.9 °E Longitude) which are typical of the midland laterite soils of the area. The climate is humid tropical with an average annual rainfall of more than 3000 mm that falls in the monsoon season of southwest and northeast. Prior to chemical analysis and incubation experiments, the soil was air-dried in the shade to avoid photodegradation of organic components, ground with wooden mallet to avoid the addition of metal and sieved through 2 mm stainless steel to remove fine particles.

Experimental Design and Treatments

The experiment was designed as a 3x3 factorial completely randomized design with three replications, which constituted 27 experimental units. The factors of treatment included three concentrations of calcium oxide (C_1: 0 t ha^{-1} as control, C_2: 1.0 t ha^{-1} and C_3: 2.0 t ha^{-1}) and three levels of boron (as borax) (B_1: 0 kg ha^{-1} as control, B_2: 0.5 kg ha^{-1}, and B_3: 1.0 kg ha^{-1}), which created nine treatment levels as reported in Table 2. The rates of calcium oxide were determined according to the standard lime requirement calculations to increase the pH of the soil starting at pH 5.4 to the desired pH 6.5 as a sub-optimal (C_2) and optimal (C_3) liming rate. Boron applications were in accordance with the Kerala Agricultural University soil test based recommendations.

The processed soil samples (500 g oven-dry equivalent each) were left in perforated plastic containers to be incubated under the conditions of controlled laboratory conditions (25 ± 2 °C, ambient humidity) over 150 days. The content of moisture was also kept through periodic weighing and adding deionized water every 3-4 days. The amendments were thoroughly mixed with the soil during the initial stages of incubation that guaranteed even distribution. Sampling was carried out in seven time points of 1, 15, 30, 60, 90, 120 and 150 days following incubation (DAI) with three samples of soil sampled at each individual date of sampling to obtain detailed chemical characterization.

Analytical Methods

The pH of soils was determined in 1:2.5 soil-water suspension by using digital pH meter after calibration with the standard buffers (pH 4.0 and pH 7.0) through standard procedures (Jackson, 1973). The conductivity of the same suspension was determined by a conductivity meter (temperature compensated). The estimation of organic carbon was done through wet oxidation using potassium dichromate in accordance with Walkley and Black (1934) procedure. The stock of the calcium was captured using 1M neutral ammonium acetate (pH 7.0) at 1:10 ratio of soil to extractant and was assayed using atomic absorption spectrophotometry (Thomas, 1982). Hot water (1: 2 ratio of soil and water, and 5 min boiling) was used to extract available boron and the amount was determined colorimetrically using azomethine-H method (Gupta, 1979).

Calcium fractionation was performed using the modified sequential extraction method of Tessier *et al.* (1979) with five operationally defined fractions, namely, (1) water-soluble Ca which was extracted using deionized water at the ratio of 1:5 soil-water and shaken over 30 minutes, (2) exchangeable Ca with 1 M NH_4OAc at pH 7.0 which lasted 2 hours, (3) organic complexed Ca with 0.5M NaOH which lasted 16 hours extracting calcium. Calculation of mineral calcium was done as the difference between the total calcium and the total of other fractions.

Boron fractionating was followed by sequential extraction procedure of Jin *et al.* (1987) having five fractions: (1) readily soluble B with 0.01M $CaCl_2$ representing immediately plant-available boron, (2) specifically adsorbed B with 0.05M KH_2PO_4 extracting phosphate-displaceable boron bound through ligand exchange, (3) oxide-bound B with 0.2M ammonium oxalate in darkness dissolving amorphous Fe-Al oxides and associated boron, (4) organically bound B with 0.02M HNO_3 + 30% H_2O_2 oxidizing organic matter and releasing complexed boron, and (5) residual B calculated by difference from total boron determined by alkali fusion. Factorial analysis of variance (ANOVA) was used to analyse the statistical analysis of means of the treatment with critical difference (CD) at the level of $p<0.05$ significance through the use of SPSS software version 26.

Results and Discussion

Initial soil characterisation

Table 1 describes the physico-chemical characteristics of the experimental soil, which contains the initial data that should be used to interpret the effects of the treatment. The soil had sandy loam texture consisting of 48.90%, 30.25%, and 20.85% sand, silt, and clay respectively, which reveals moderate water-holding capacities and drainage attributes of soils composed of crystalline basement materials (laterite). The pH of 5.4 (strongly acidic) and electrical conductivity 0.2 dS m^{-1} are indicative of acidic conditions with low soluble salt levels that are typical of highly weathered laterite soils that undergo high leaching of base cations as a result of high rainfall. The laterite soils have organic carbon content of 1.16% which is moderate because it indicates the ratio between the rapid decomposition under tropical conditions and the input of the organic matter into the soils via the vegetation cover.

The data on fractionation of calcium presented in Table 1 show that the exchangeable calcium (299.10 mg kg^{-1}) is predominated in the labile pool and water-soluble calcium forms only 2.9% of the exchangeable calcium, which implies that there is high retention of calcium on the exchange sites. The organically complexed calcium amounts to 32.30 mg kg^{-1}, it represents 5.1% of total calcium and mineral calcium value was 213.25 mg kg^{-1}, it is 33.9% of total calcium, a characteristic of laterite soils in which all the primary minerals are highly weathered. The fractionation of boron exhibits presence of residual boron (8.00mg kg^{-1}, 89.1% of total) and readily soluble and specifically adsorbed fractions of total boron which only constitute 4.5% of total boron, suggest limited immediate activity, although total boron is sufficient.

Dynamics of Soil pH and Electrical Conductivity

The application of calcium oxide had very strong ($p<0.05$) effect on the soil pH during the 150 DAI, with the typical three-phase response dynamics, as shown in Figure 1a and described in Table 3. Initial pH values at 1st day had shown instant neutralization effects of CaO addition with the following values varying from 5.42 to 5.45 for control treatment (C_1), 5.92 to 5.95 for treatment with 1.0 t ha^{-1} of CaO (C_2) and 6.32 to 6.36 for treatment with 2.0 t ha^{-1} of CaO (C_3) at all levels of boron. The sharp rise of 0.50-0.94 units in pH in the initial 24 hours following application of the amendment indicates the high reactivity and solubility of calcium oxide which reacts instantly with moisture of the soil to form hydrated calcium oxide ($CaO + H_2O \quad Ca(OH)_2$) and later dissociates to release calcium ions and hydroxyl ions that neutralize the acidity of the soil.

The three-phase patterns of the temporal pH dynamics were observed during incubation. Phase I (1-30 DAI) involved a rapid neutralization phase where the pH was slowly rising as the dissolution of CaO was maintained and the balance between soil and exchange complex was reached. The highest pH values were reached at 30 DAI, which represents the end of the rapid neutralization stage. Control treatment (C_1) exhibited the slight rise of 5.55 to 5.61 indicating natural soil processes, whereas C_2 treatment attained the highest values of 6.39 to 6.45 and C_3 treatment with highest values of 6.79-6.86 indicating the optimum range of PH (6.5-7.0) that provided nutrient availability in agricultural soils. These maximum values are the results of 1.39 to 1.46 unit increments in the initial soil pH of the highest lime treatment, proving successful acidity amelioration according to the lime requirements calculations.

Phase II (30-60 DAI) was the stabilization phase where the quasi-equilibrium was achieved between the soil solution, exchange complex and precipitated calcium phases. The change in pH values was negligible during this period, decreasing by 0.02-0.04 units till the system reached a steady state. The phase III (60-150 DAI) had a gradual reacidification, where the pH decreased to 5.49-5.54 (C_1), 6.23-6.30 (C_2), and 6.64-6.70 (C_3) on 150 DAI, which is a decrease of 0.07-0.16 units as compared to the peak values. This reacidification indicates several simultaneous processes such as the formation of carbonic acid because of microbial respiration, the formation of organic acids as a result of the decomposition of organic substances, loss of protons as a result of reactions with calcium, and the conversion of the hydroxyl ions to structural water in mineral phases. Liu *et al.* (2022) found that lateritic red soils had the lowest pH buffering capacity across all the tropical soil types, which clarifies the high initial pH response and subsequent ease of reacidification in the current study. The statistical analysis showed the main effects of calcium to be highly significant on all the sampling days (Table 3), with the CD of calcium values of 0.061 on the 1st day and 0.098 on the 150 DAI indicating strong treatment differences during the study course.

The dynamics of electrical conductivity were also correlated with patterns of pH (Figure 1b) which were both significantly ($p<0.05$) affected by the calcium and boron treatments. Initial EC rose at 0.2 dS m^{-1} up to the maximum values of 0.41 dS m^{-1} in C_1B_3, 0.48 dS m^{-1} in C_2 mean, and 0.56 dS m^{-1} in C_3 mean at 30 DAI. This increment represents the ions that are liberated in the course of the dissolution of CaO (Ca^{2+}) and Borax (Na^+, $B(OH)_4^-$). The later EC drop to 0.29-0.47 dS m^{-1} at 150 DAI reflective of gradual ion loss in solution due to adsorption on the exchange site, precipitation reactions and adsorption of ions into organic complexes as described later on in the dynamics of calcium transformation.

Fractionation and Dynamics of Calcium Transformation

The main treatment effect over the incubation period was produced by exchangeable calcium, a major plant-available pool, and the predominant labile fraction that was significantly ($p<0.05$) affected by treatment (Table 4, Figure 2a). The control treatment (C_1) was relatively steady in terms of exchangeable calcium of 296-302 mg kg^{-1} during incubation, which is the measure of the equilibrium situation in the soil. Comparatively, lime-amended treatments exhibited strong time dynamics where the treatments initially increased with time, which decreased progressively with time. The C_2 treatment (1.0 t ha^{-1} CaO) exhibited exchangeable calcium rising between 469-478 mg kg^{-1} to maximum values of 533-539 mg kg^{-1} at Day 30 (mean of 537.05mg kg^{-1}) and thereafter falling to 441-443mg kg^{-1} at Day 150 (mean of 442.50mg kg^{-1}). The most pronounced dynamics were observed with C_3 treatment, where the exchangeable calcium started with 641-642 mg kg^{-1} and reached the maximum value of 770-774mgkg^{-1} at the end of 30 DAI (mean value 773.09 mg kg^{-1}), which is 2.6 times higher than the initial amount of exchangeable calcium in the soil.

After the peak values at 30 DAI, the exchangeable calcium in C_3 treatments (mean value) decreased continuously up to Day 150 (mean 586.47 mg kg^{-1}), which is 24.2% of the peak values decreased during the 120 days. Such massive decrease brings significant concerns on the fate of calcium in the closed incubation system. Mass balance analysis indicates that this degradation is caused by conversion to less reactive, non-exchangeable calcium species instead of a true loss of the system, and is in agreement with the mass conservation laws in closed experimental systems. The pathways of transformation include a series of progressive incorporation of exchangeable calcium into organically complexed as well as acid-soluble fractions. This happens by means of cation bridging with the functional groups of organic matter, co-precipitation with iron-aluminium hydroxides, and production of the secondary minerals of calcium (Rowley *et al.*, 2018; Shabtai *et al.*, 2023).

Dynamic water-soluble calcium (Figure 2b) demonstrated high initial increases after the addition of CaO, which indicates instant dissolution reactions. The C_3 treatment recorded optimum water-soluble calcium amounts of 29.74- 30.05 mg kg^{-1} at 30 DAI relative to control with 8.49- 8.57 mg kg^{-1} which is a 3.5-fold enhancement. Later reduction to 9.69-9.86 mg kg^{-1} at 150 of DAI indicates that it is partitioned to exchangeable sites via mass action and is incorporated in organic complexes.

Calcium that was organically complexed (Figure 2c) also rose steadily during the incubation time and shows that organic matter is essential in the long-term calcium retention and cycling. The C_3 treatment exhibited progressive increment (32.28 mg kg^{-1} on 1st day) up to 85.93 mg kg^{-1} on Day 150, which is an increment of 166% during the incubation. This high amount is evidence of binding of calcium to soil organic matter functional groups, especially carboxylic (-COOH) and phenolic (-OH) groups, via inner-sphere cation bridging and outer-sphere electrostatic processes. Shabtai *et al.* (2023) established by isotope labelling that calcium enhances persistent soil organic matter by means of physicochemical associations with calcium additions leading to a 45% rise in microbial carbon utilization as well as mineral-organic associations. These mechanisms were validated by Rowley *et al.* (2023) through STXM NEXAFS spectroscopy, which revealed that calcium selectively bonds with aromatic and phenolic carbon functional groups in acidic soils. Gong *et al.* (2024) also showed that exchangeable calcium has a pronounced effect on organic carbon loss by leaching and microbial mineralization, which explains the gradual calcium-organic matter complexation process that was recorded in our incubation experiment.

The three-phase model of calcium transformation with highlighted areas is given in Figure 2d, giving a conceptual picture of calcium dynamics after lime application. Phase I (1-30 DAI) involves rapid dissolution and early equilibration in which CaO dissolves, releases calcium ions, neutralizes acidity, and calcium partitions across the solution, exchangeable, and early organic complexation pools. Phase II (30-60 DAI) is the stabilization phase when quasi-equilibrium is formed between the various pools of calcium, dissolution is mainly achieved and transformation reactions start to predominate. Phase III (60-150 DAI) is the transition phase where the transformation of the labile calcium forms (water-soluble and exchangeable) to the organically complexed forms and acid-soluble forms takes place in a gradual manner. This transformation pattern is kinetically first-order typical of calcium reactions in acidic soils and is indicative of thermodynamic preference of stable calcium-organic matter complexes within the conditions of the prevailing soil.

Changes in the fractionation of calcium during incubation are shown quantitatively in Figure 3 with stacked bar charts at 1, 30, and 150 DAI under selected treatments of control and highest amendment levels. On 1st day, the exchangeable calcium prevailed in the labile calcium pool with 45-65 % of overall calcium based on treatment. Nevertheless, even 150 DAI, significant redistribution had taken place, with organically complexed calcium rising to about 12% of total calcium in C_3 treatment, whereas a corresponding decrease in the proportion of exchangeable calcium occurred. This redistribution of calcium over time shows that the availability of calcium is a changing process that is controlled by competing reactions such as adsorption-desorption equilibria, organic matter complexation, precipitation-dissolution reactions and mineral transformation reactions.

Fractionation and fixation dynamics of boron

Easily soluble boron, the immediately available pool, which could be extracted by dilute calcium chloride, exhibited rapid and very considerable ($p<0.05$) decline upon boron treatment (Table 5, Figure 4a). The B_3 treatment (1.0 kg ha^{-1} boron) showed a reduction of initial values of 0.36-0.42 mg kg^{-1} at 1st day to final values of 0.12-0.15 mg kg^{-1} at 150 DAI, which was 63-67% reduction at the incubation period owing to the level of calcium treatment. This quick and large fixation is indicative of the high boron retention capacity of the laterite soils and is indicative of the several simultaneous adsorption reactions referred to as ligand exchange reaction with the oxide surfaces of Fe-Al and complexation with functional groups associated with organic matter, and the incorporation into secondary mineral structures.

The effects of the addition of calcium on the fixation of boron were amplified by the pH-mediated effects on the characteristics of the surface charges of minerals and borate speciation. The borate anion ($B(OH)_4^-$) is the major aqueous species at pH values greater than 7.0 in C_3 treatment and has a much stronger affinity towards oxide surfaces than does the undissociated boric acid ($B(OH)_3$) found at lower pH values. This pH effect is observed in the differential readily soluble boron values at 150 DAI where C_3B_3 treatment was lower (0.12 mg kg^{-1}) than C_1B_3 treatment (0.15 mg kg^{-1}) indicating a better adsorption at higher pH despite identical initial boron usage. Ulatowska *et al.* (2024) showed that the gibbsite, kaolinite, and montmorillonite soil minerals had the highest adsorption capacities of boron of 24.55-30.63 mg g^{-1}, and adsorption was controlled by pH-dependent processes of changing the boron adsorption capacity of the surface hydroxyl group to achieve protonation or deprotonation.

Precisely adsorbed boron (Figure 4b), which is phosphate-displaceable boron held by ligand exchange on mineral surfaces, advanced steadily with incubation time and speed of boron application. The mean values were found to rise between 0.29-0.33mg kg^{-1} at 1st day to 0.32-0.37mg kg^{-1} at 150 DAI with higher calcium treatments demonstrating accumulation. Padbhushan and Kumar (2017) observed that the specifically adsorbed boron is generally 0.01-0.61% of the entire soil boron and a significant slowly available reserve that can sustain the replenishment of solution boron as the readily soluble pool fades away with uptake by plants. This fraction is sensitive to solution chemistry and can be used as a buffer to allow boron to persist over long-term intervals.

Boron-treated soils showed the strongest accumulation over the incubation period with oxide-bound boron (Figure 4c) rising between 0.16-0.17mg kg^{-1} at the 1st day to 0.23-0.35mg kg^{-1} at 150 DAI. This 69-106 % gain is a high affinity of amorphous Fe-Al hydroxides to boron by utilizing inner-sphere complexation by way of ligand exchange with borate that substitutes surface hydroxyl groups on oxide minerals. The multi-surface geochemical model created by Van Eynde *et al.* (2020) indicates that the adsorption of boron in tropical soils is dominated by iron and aluminum (hydr)oxides, with ferrihydrite being the principal adsorbent because of its high surface area and the quantity of active hydroxyl groups. Laterite soils of Kerala are high in sesquioxide content, which is usually above 30% (Fe_2O_3 + Al_2O_3), so they have a large capacity of fixation of boron that should be specifically taken into consideration when preparing fertilizer management recommendations. Das *et al.* (2024) verified that adsorption with aluminium and iron oxide minerals is the major process that results in low boron levels in acidic soils in areas of heavy rainfall as is typical of tropical India such as Kerala.

Stable boron (Figure 4d) rose gradually to 0.44-0.47 mg kg^{-1} at 1st day to 0.51-0.71 mg kg^{-1} at 150 DAI with higher amounts accumulating in the soils treated with calcium which allowed more binding sites due to enhanced organic matter preservation by calcium bridging. This fraction depicts the boron complexed with soil organic matter due to diol complexation using cis-hydroxyl group on carbohydrate and polyol compounds. The interaction between calcium and Boron proved to be significant ($p<0.05$) at various boron fractions on certain dates of sampling, demonstrating that the pH alteration due to liming does impact boron distribution among pools via impact on surface chemistry and organic matter dynamics.

The total boron content was relatively constant during incubation (8.86-9.78 mg kg^{-1} all treatments and sampling date) indicating that the mass balance was maintained in the closed experimental system. The remaining portion of boron (about 8.0mg/kg) was found to be essentially the same, showing that this lattice-incorporated boron is inaccessible to transformation reactions within the existing experimental conditions and time scale. All these results indicate that the management of boron in laterite soils should have the consideration of the fast fixation kinetics and the prevailing role played by sesquioxides in the control of boron availability.

Conclusion

The incubation study revealed that there were specific three-phase dynamics of calcium transformation in the laterite soil. In the phase I (Day 1-30) which was marked by intensive CaO dissolution with an increase in pH. Phase II (Day 30-60) which was marked by stabilization including the establishment of the quasi-equilibrium. The phase III (Day 60-150) which was marked by gradual reacidification (0.16 units loss) with the gradual transformation. The dynamics of boron were dominated by fast fixation mechanisms, and readily soluble fraction decreased by 63-67 % and oxide bound boron by 69-106 %, which was indicative of high adsorption by Fe-Al oxides that are typical in laterite soils. The non-significant interaction between calcium and boron suggests that there are independent nutrient transformation pathways, making the design of experiments to be simpler to validate in field. These laboratory results form critical baseline information in the development of field experiments to test lime persistence, re-liming periods, borrowing of boron application techniques and how crops respond to the real agro- climatic conditions within the laterite soils areas of Kerala.

Table 1 : Initial physico-chemical properties and nutrient fractions of laterite soil used in the incubation study

Property	Value
Sand (%)	48.90
Silt (%)	30.25
Clay (%)	20.85
pH (1:2.5 soil:water)	5.4
EC (dS m^{-1})	0.2
Organic carbon (%)	1.16
Water-soluble Ca (mg kg^{-1})	8.62
Exchangeable Ca (mg kg^{-1})	299.10
Organically complexed Ca (mg kg^{-1})	32.30
Acid-soluble Ca (mg kg^{-1})	47.34
Mineral Ca (mg kg^{-1})	213.25
Total Ca (mg kg^{-1})	628.81
Readily soluble B (mg kg^{-1})	0.14
Specifically adsorbed B (mg kg^{-1})	0.26
Oxide-bound B (mg kg^{-1})	0.15
Organically bound B (mg kg^{-1})	0.43
Residual B (mg kg^{-1})	8.00
Total B (mg kg^{-1})	8.98

Table 2 : Treatment combinations in the 3×3 factorial completely randomized design

Treatment Code	Calcium (CaO t ha^{-1})	Boron (kg ha^{-1})
C_1B_1	0 (Control)	0 (Control)
C_1B_2	0	0.5
C_1B_3	0	1.0
C_2B_1	1.0	0
C_2B_2	1.0	0.5
C_2B_3	1.0	1.0
C_3B_1	2.0	0
C_3B_2	2.0	0.5
C_3B_3	2.0	1.0

Table 3 : Effect of calcium and boron treatments on soil pH at different incubation periods (mean values)

Treatment	1 DAI	15 DAI	30 DAI	60 DAI	90 DAI	120 DAI	150 DAI
C_1 Mean	5.44	5.50	5.58	5.60	5.56	5.53	5.51
C_2 Mean	5.94	6.24	6.42	6.38	6.33	6.29	6.27
C_3 Mean	6.34	6.65	6.83	6.79	6.73	6.70	6.67
CD (0.05) C	0.061	0.072	0.079	0.083	0.088	0.094	0.098
CD (0.05) B	NS	NS	NS	NS	NS	NS	NS
CD C×B	NS	NS	NS	NS	NS	NS	NS

DAI = Days after incubation; NS = Non-significant; CD = Critical difference

Table 4 : Effect of calcium and boron treatments on exchangeable calcium (mg kg^{-1}) at different incubation periods

Treatment	1 DAI	15 DAI	30 DAI	60 DAI	90 DAI	120 DAI	150 DAI
C_1 Mean	296.79	299.67	300.69	299.47	299.17	299.08	298.31
C_2 Mean	474.69	511.92	537.05	518.18	495.86	471.48	442.50
C_3 Mean	642.05	722.47	773.09	735.34	697.97	645.52	586.47
CD (0.05) C	3.216	3.873	5.550	4.650	3.347	5.397	3.522
CD (0.05) B	NS	NS	NS	NS	NS	NS	NS

Table 5 : Effect of calcium and boron treatments on readily soluble boron (mg kg^{-1}) at different incubation periods

Treatment	1 DAI	15 DAI	30 DAI	60 DAI	90 DAI	120 DAI	150 DAI
C_1B_1	0.14	0.13	0.12	0.12	0.12	0.11	0.10
C_1B_3	0.42	0.26	0.20	0.17	0.17	0.15	0.15
C_3B_1	0.12	0.11	0.10	0.10	0.09	0.09	0.09
C_3B_3	0.36	0.22	0.19	0.16	0.14	0.13	0.12
CD (0.05) C	0.019	0.013	0.009	0.006	0.006	0.006	0.006
CD (0.05) B	0.019	0.013	0.009	0.006	0.006	0.006	0.006

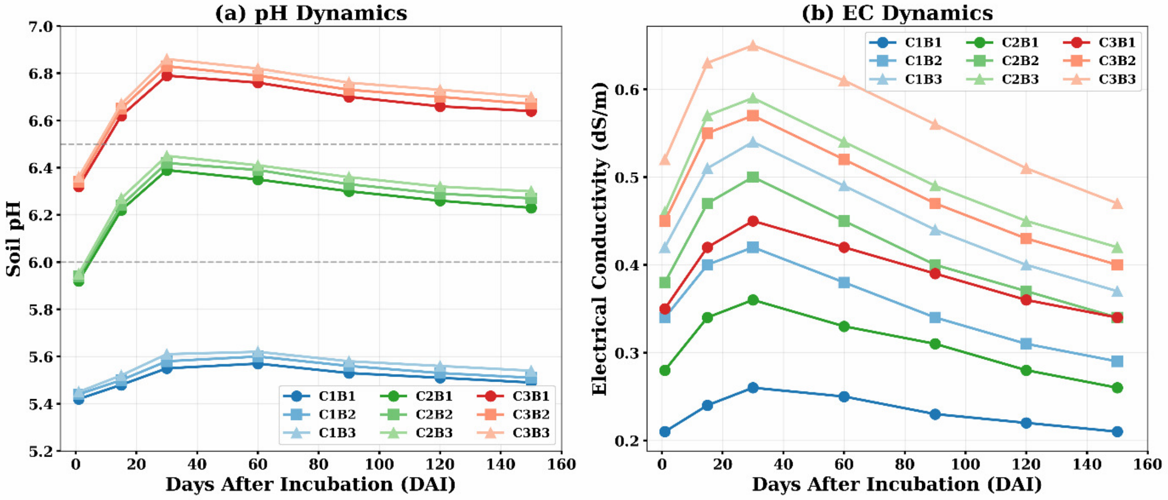

Fig. 1 : Temporal dynamics of (a) soil pH and (b) electrical conductivity under different calcium-boron treatment combinations during 150-day incubation. Treatment notations: C_1, C_2, C_3 = 0, 1.0, 2.0 t ha^{-1} CaO; B_1, B_2, B_3 = 0, 0.5, 1.0 kg ha^{-1} boron. Horizontal dashed lines in panel (a) indicate optimal pH range (6.0–6.5) for nutrient availability. The three-phase response pattern is evident: Phase I rapid neutralization (Days 1–30), Phase II stabilization (Days 30–60), and Phase III gradual reacidification (Days 60–150).

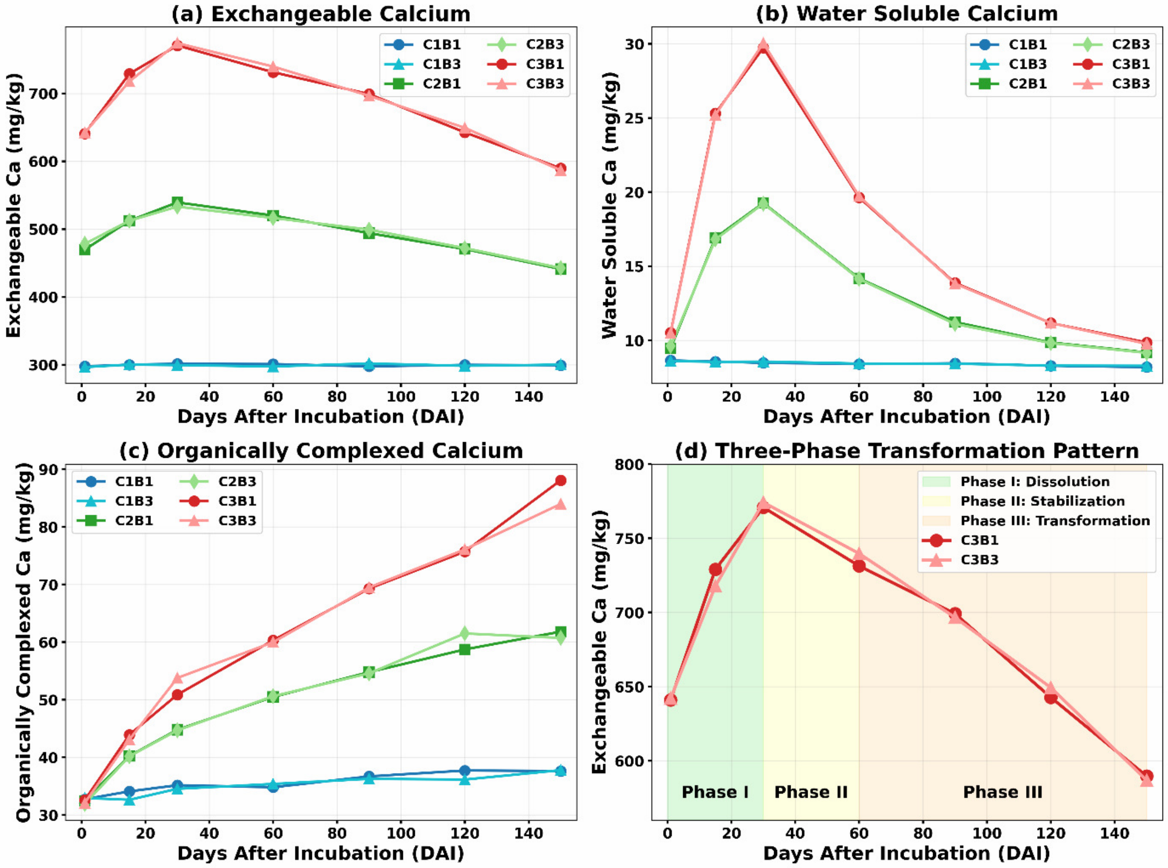

Fig. 2 : Temporal dynamics of calcium fractions during 150-day incubation: (a) Exchangeable Ca showing peak values at Day 30 followed by progressive 24.2% decline in C_3 treatment, (b) Water-soluble Ca exhibiting rapid 3.5-fold increase followed by decline as calcium partitions to exchange sites, (c) Organically complexed Ca demonstrating continuous 166% increase reflecting calcium-organic matter complexation, and (d) Three-phase calcium transformation pattern with Phase I dissolution (green shading), Phase II stabilization (yellow), and Phase III transformation (orange) clearly delineated.

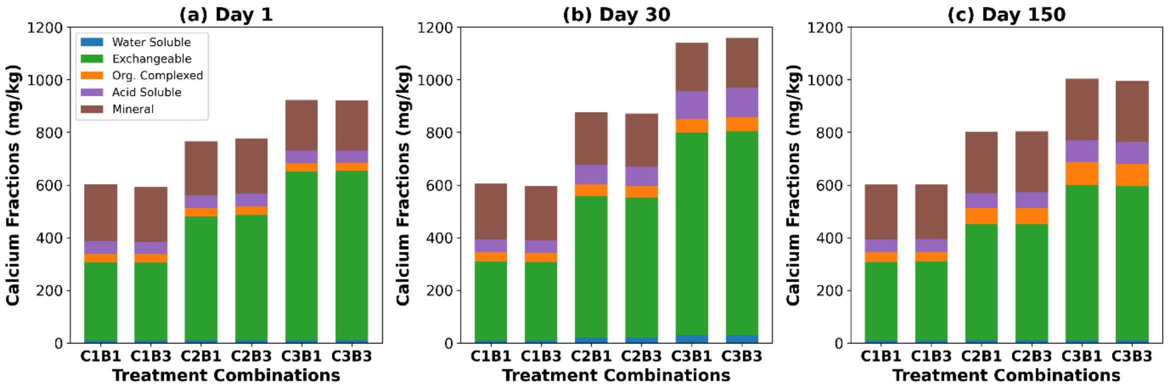

Fig. 3 : Proportional distribution of calcium among different fractions (water-soluble, exchangeable, organically complexed, acid-soluble, and mineral) at Days 1, 30, and 150 for selected treatments (C_1B_1 control and C_3B_3 highest amendment), illustrating progressive transformation from labile exchangeable forms to stable organically complexed forms over the incubation period.

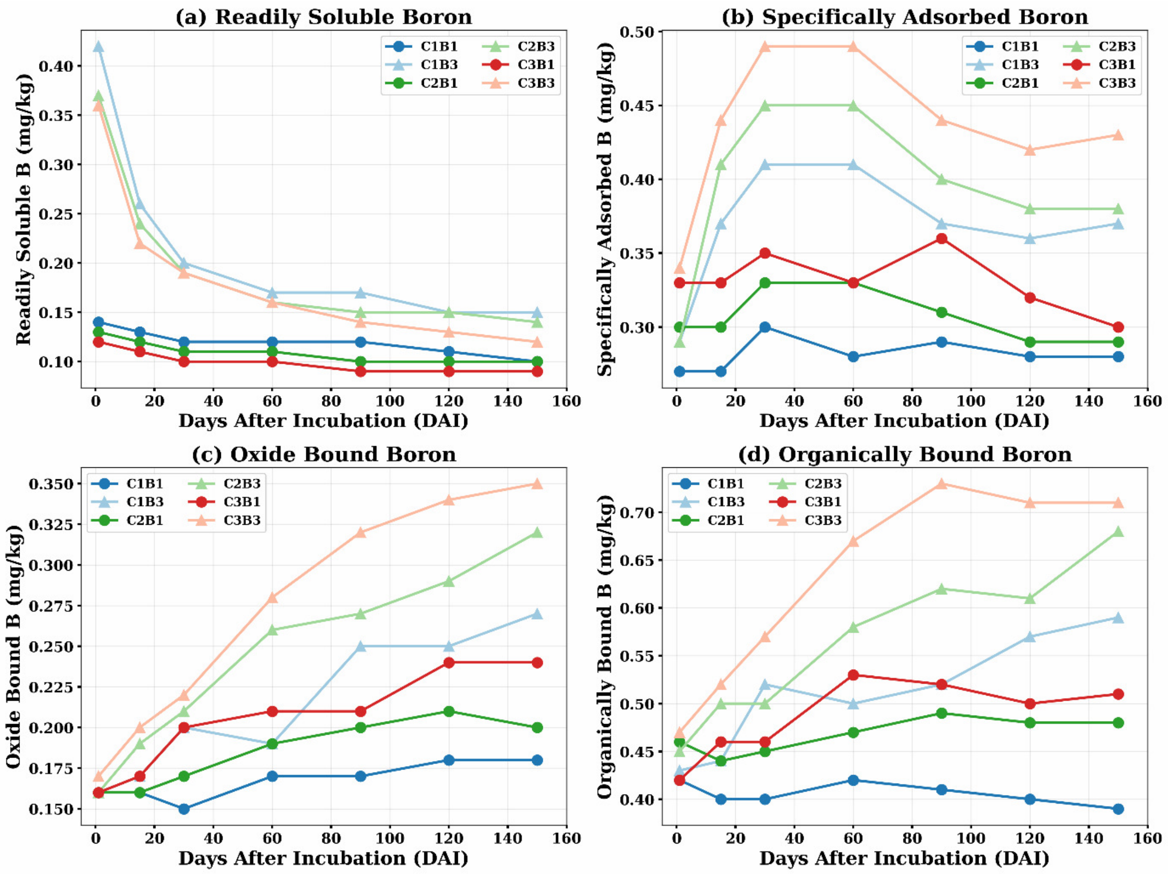

Fig. 4 : Temporal dynamics of boron fractions during 150-day incubation: (a) Readily soluble B showing rapid 63–67% decline reflecting strong fixation by laterite soil minerals, (b) Specifically adsorbed B with gradual accumulation representing ligand-exchange-bound pool, (c) Oxide-bound B demonstrating pronounced 69–106% increase through adsorption on Fe-Al oxide surfaces, and (d) Organically bound B exhibiting steady accumulation through diol complexation with organic matter functional groups.

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