

Endogenous Ca-driven phosphorus immobilization by sugarcane filter mud biochar: 21-month evidence from an acidic citrus soil

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Abstract

Background and Aims Whether endogenous minerals in biochar can be exploited for phosphorus (P) management without exogenous reagents remains largely unexplored. We investigated whether calcium (Ca)-rich sugarcane filter mud (SFM) biochar could achieve long-term P immobilization in acidic soil.

Methods SFM biochar (pyrolyzed at 500 °C) was granulated with compound fertilizer at substitution ratios of 20–100% (w/w). An optimized 40% formulation was tested in a 21-month citrus pot experiment (initial soil pH 6.11), monitoring soil P dynamics, leaching, enzyme activities, and plant P status. Independent field corroboration (13 months, initial soil pH 4.91) was also evaluated.

Results The optimized amendment increased available P by 38.7% (39.26 vs. 28.30 mg kg⁻¹) and reduced P leaching by 22.0–37.7% relative to the conventional fertilization treatment, despite a 30% fertilizer reduction. Soil water retention and organic matter content increased by ~40% and 75.6%, respectively. Leaf P concentrations and SPAD values remained comparable to full fertilization. Field data exhibited consistent but less pronounced trends. Convergent evidence—including a Ca/P molar ratio of ~1.08, elemental co-localization, sustained P retention, and concurrent leaching reduction—strongly suggests the formation of metastable Ca-phosphate phases, most probably amorphous calcium phosphate (ACP).

Conclusion This 21-month study provides robust evidence for an endogenous-mineral-driven strategy that achieves durable P immobilization while valorizing a globally significant industrial waste, eliminating the need for exogenous chemical modification.

1. Introduction

In subtropical orchards, decades of ammonium-based fertilization have driven severe soil acidification, locking phosphorus (P) into forms unavailable to plants and triggering a self-reinforcing cycle of excessive P application, further acidification, and eutrophication (Guo et al. 2010; Zhou et al. 2025). Breaking this cycle requires amendments that can concurrently neutralize acidity, retain P against leaching, and release it in synchrony with plant demand.

Parallel to this soil degradation crisis, the global sugar industry faces a massive waste challenge. Sugarcane filter mud (SFM), the solid residue from juice clarification, is generated at an estimated 60–100 million tonnes annually worldwide (FAO 2024). In major producing countries, disposal relies largely on landfilling or untreated field application, causing odour, groundwater contamination, and greenhouse gas emissions (Tan 2017; Zeng et al. 2018). However, SFM is intrinsically a resource: lime added during clarification endows it with unusually high calcium (Ca) content (2–5 wt.%), alongside abundant organic matter (30–40 wt.%) and essential nutrients (Carneiro et al. 2021; Yang et al. 2021). In SFM, a potential P-binding reagent is already present—built into the feedstock by the sugar clarification process itself.

Biochar has emerged as a promising amendment for acidic soils, because pyrolysis concentrates mineral constituents within a stable, porous carbon matrix (Lehmann et al. 2011; Nepal et al. 2023). Yet, after two decades of research, the prevailing paradigm for P retention still relies on post-synthesis loading or co-pyrolysis with external reagents such as MgO, CaO, or H₃PO₄ (Jetsrisuparb et al. 2022; Liang et al. 2026; Marcinczyk and Oleszczuk 2022). Such strategies add cost and chemical consumption. An alternative "built-in reagent" approach—granulating SFM biochar with fertilizers to allow endogenous Ca to precipitate Ca-phosphate phases in situ during wet granulation—has received little systematic study. Moreover, most biochar amendment evaluations are shorter than six months (Sim et al. 2025), leaving uncertainty about the durability of any P immobilization achieved.

Two interconnected questions remain unresolved: (i) can a waste-derived biochar, without any externally added binding reagents, sustain P immobilization over agronomically meaningful timescales, and (ii) what specific chemical mechanisms—particularly those involving endogenous mineral constituents—underpin such sustained performance? We hypothesized that granulating SFM biochar with compound fertilizer at an optimized ratio would enable in-situ formation of poorly soluble Ca-phosphate phases driven entirely by endogenous Ca.

The objectives of this study were to: (1) optimize the biochar substitution ratio; (2) evaluate the 21-month efficacy on soil P dynamics, leaching losses, and plant nutrition; and (3) infer the endogenous Ca-driven P immobilization mechanism using multiple converging lines of evidence. We deliberately employed robust classical techniques (SEM/EDS, FTIR, sequential extraction) to maintain method consistency across six sampling points, prioritizing a coherent temporal trajectory over molecular-level resolution at a single time point.

2. Materials and Methods

2.1. Raw materials

2.1.1. Sugarcane filter mud

SFM was obtained from Guangxi Funan Dongya Sugar Co., Ltd. (Nanning, China) during the 2022 crushing season. Samples were air-dried to < 15% moisture and homogenized. Initial properties (per kg dry weight): pH 7.72, organic matter 31.2 g, total N 1.21 g, total P 0.31 g, total K 4.28 g, Ca 2.15 g, Mg 1.83 g, EC 2.31 mS cm⁻¹.

2.1.2. Soil and plant material

Soil (0–20 cm) was collected from a slightly acidic citrus orchard in Guangxi. Properties: pH 6.11, organic matter 22.10 g kg⁻¹, total N 0.81 g kg⁻¹, total P 0.272 g kg⁻¹, total K 5.06 g kg⁻¹, alkali-hydrolyzable N 62.17 mg kg⁻¹, available P 9.4 mg kg⁻¹, available K 56.1 mg kg⁻¹. Plant material was 12-month-old 'Orah' mandarin (*Citrus reticulata* Blanco) grafted on trifoliolate orange (*Poncirus trifoliata* L. Raf.).

2.1.3. Field corroboration source

Field corroboration data were drawn from a previously published study (Hu et al. 2025), as described in Sect. 2.7.

2.2. Biochar production

Air-dried SFM was pyrolyzed in a muffle furnace at 500°C for 2 h under limited oxygen (heating rate 10°C min⁻¹). The biochar was ground to < 2 mm. Properties: pH 7.85, organic matter 27.46 g kg⁻¹, total N 1.03 g kg⁻¹, total P 0.285 g kg⁻¹, total K 5.39 g kg⁻¹, alkali-hydrolyzable N 86.91 mg kg⁻¹, available P 19.9 mg kg⁻¹, available K 70.3 mg kg⁻¹, BET surface area 48.6 m² g⁻¹. Yield (dry mass basis) was 42.6% ± 1.8% (mean ± SD, n = 3).

2.3. Biochar-based amendment preparation

Biochar-based amendments (BCAs) were prepared via coating–granulation. A commercial compound fertilizer (N–P–K = 21–10–10) was dissolved in deionized water (50% w/v). SFM biochar was mixed with the solution at substitution ratios of 20%, 40%, 60%, 80%, and 100% (by mass). The pastes were stirred at 60°C, granulated to 3–5 mm (ZL-200 granulator), dried at 50°C to < 5% moisture, coated with 2% polyvinyl alcohol (PVA) solution, and cured at 40°C for 24 h. For treatments B–E, the total N, P, K input was kept equivalent to that of the reduced-fertilization control (A, 100 g fertilizer pot⁻¹); treatment F contained biochar only. Details are given in Table 1

Table 1
Experimental treatments and fertilization regimes in the 21-month pot experiment.

Treatment	Biochar substitution ratio (%)	Fertilizer (g pot ⁻¹)	Biochar (g pot ⁻¹)	Total BCA applied (g pot ⁻¹)	N (g pot ⁻¹)	P (g pot ⁻¹)	K (g pot ⁻¹)
T(Conventional)	0	150	0	150	31.5	15.0	15.0
A (Reduced)	0	100	0	100	21.0	10.0	10.0
B (BCA-20%)	20	100	25	125	21.0	10.0	10.0
C (BCA-40%)	40	100	66.7	166.7	21.0	10.0	10.0
D (BCA-60%)	60	100	150	250	21.0	10.0	10.0
E (BCA-80%)	80	100	400	500	21.0	10.0	10.0
F (BCA-100%)	100	0	100	100	0	0	0

Note: The compound fertilizer has an N–P–K ratio of 21–10–10. For B–E, total nutrient input equals that of A because biochar replaces an equivalent mass of fertilizer. The biochar amount is calculated as 100 × [ratio / (1 – ratio)]. Nutrient contributions from biochar itself are negligible.

2.4. Material characterization

Microstructure was examined by SEM (S-3400N, Hitachi, Japan) at 15 kV. Elemental composition was analysed by EDS. Surface functional groups were characterized by FTIR (Nicolet iS10; KBr pellet, 4000–400 cm⁻¹, 2 cm⁻¹ resolution). Surface area and porosity were measured by N₂ adsorption at 77 K (ASAP 2460, Micromeritics). Acid-neutralizing capacity (ANC) was determined by titration to pH 4.5 (Bolan et al. 2023).

2.5. Nutrient use efficiency indicators

The following indicators were calculated:

Biochar yield (%) = (mass of biochar / mass of dry SFM) × 100%

Phosphorus recovery efficiency (%) = (total P in biochar × biochar mass) / (total P in raw SFM × dry SFM mass) × 100%

Carbon retention rate (%) = (total C in biochar × biochar mass) / (total C in raw SFM × dry SFM mass) × 100%

Fertilizer replacement rate (%) = (chemical fertilizer input in conventional treatment – input in BCA treatment) / conventional input × 100%

2.6. Pot experiment design

The pot experiment ran for 21 months (March 2023 – December 2024) with seven treatments (T, A, B–F) and five replicates in a completely randomized block design. Each pot (50 cm diameter × 40 cm height) contained 25 kg soil and one citrus seedling. To minimize confounding by reproductive growth, plants were maintained in vegetative stage. Fertilizer was applied every two months by surface broadcasting, and irrigation maintained at ~ 60% field capacity.

2.7. Field corroboration

Field data were obtained from a 13-month study (July 2022 – August 2023) on highly acidic red soil (initial pH 4.91) planted with 'Jinxiang' mandarin (Hu et al. 2025). The same seven treatments were arranged in a randomized complete block design with three replicates. Key differences from the pot experiment were initial soil pH (4.91 vs. 6.11), cultivar ('Jinxiang' vs. 'Orah'), duration (13 vs. 21 months), and endpoints (fruit yield vs. vegetative growth). These contrasting conditions test the robustness of BCA effects across scales.

2.8. Sample collection and analysis

Soil was sampled at six time points (Sept, Nov 2023; Jan, Mar, May, Jul 2024). Physicochemical properties were determined by standard methods: pH (1:2.5 soil:water), organic matter (K₂Cr₂O₇ oxidation), total N (Kjeldahl), total P (NaOH fusion–Mo-Sb colorimetry), total K (NaOH fusion–flame photometry), available N (alkali diffusion), available P (NaHCO₃ extraction–Mo-Sb colorimetry), available K (NH₄OAc extraction–flame photometry). Enzyme activities (urease, sucrase, acid phosphatase) were

measured as described in Online Resource 6. Leaf SPAD values and nutrient concentrations were determined in Mar, May, Jul 2024.

Leachate was collected from trays beneath pots in Mar, May, Jul 2024 after irrigation. Total N and P were determined by alkaline potassium persulfate digestion–UV spectrophotometry and ammonium molybdate spectrophotometry, respectively (GB 11894-89, GB 11893-89). Nutrient leaching concentration ratios (LCR, %) were calculated as leachate concentration divided by soil total nutrient content $\times 100\%$. The limited leachate monitoring window is acknowledged as a limitation (Sect. 4.7).

2.9. Data analysis

One-way ANOVA with Duncan's multiple range test ($P < 0.05$) was performed using SPSS 27.0. Figures were prepared with Origin 2021.

3. Results

3.1. Structural and chemical evidence for Ca-P formation

Pyrolysis transformed the dense, irregular surface of raw SFM into a well-developed interconnected porous network (Fig. 1). BET surface area increased from 2.3 to 48.6 m² g⁻¹ and total pore volume from 0.008 to 0.097 cm³ g⁻¹. EDS showed enrichment of C, P (0.59% to 1.88% atomic fraction) and Ca (0.40% to 3.79%) (Online Resource 2). Biochar yield of 42.6% corresponded to P recovery efficiency of 68.4% and C retention rate of 52.3%. FTIR spectra confirmed retention of reactive functional groups after pyrolysis (Online Resource 1).

Among the BCAs, Treatment C (40% substitution) exhibited an optimal "mosaic" microstructure, with fertilizer crystallites uniformly filling biochar pores while maintaining partial pore connectivity (Fig. 2c,d). At higher substitution ratios, pores were incompletely filled (Fig. 3). EDS point analysis of the BCA granule gave Ca atomic fraction 4.63% and P 4.28%, yielding a Ca/P molar ratio of ~ 1.08 (Online Resource 2). EDS mapping confirmed spatial co-localization of P and Ca (Online Resource 3). This Ca/P ratio excludes stoichiometric hydroxyapatite (1.67) and β -tricalcium phosphate (1.5), pointing instead toward metastable, non-stoichiometric phases—most probably amorphous calcium phosphate (ACP, Ca/P ~ 1.0 –1.5) and/or dicalcium phosphate (CaHPO₄·2H₂O, Ca/P = 1.0)—precipitated during alkaline granulation (Combes and Rey 2010). ACP's higher solubility relative to crystalline phases enables it to function as a transient P reservoir responsive to rhizosphere acidification.

3.2. Long-term amelioration of soil physicochemical properties

Soil pH declined in all treatments over 21 months, but BCAs significantly attenuated acidification (Table 2). The non-biochar controls dropped from pH 6.11 to 5.15–5.17 (an ~ 9 -fold increase in H⁺ activity), whereas Treatment C maintained pH 6.36, which was 1.19 units higher than the reduced-

fertilization control ($P < 0.05$). The estimated ANC of SFM biochar was $0.42 \text{ kg CaCO}_3 \text{ eq t}^{-1}$. Treatment C also increased soil water-holding capacity by $\sim 40\%$ (7.66% to 10.72%) and organic matter by 75.6% (28.45 to 49.96 g kg^{-1}). The peak organic matter at 40% substitution, rather than at higher rates, may reflect either sampling variability or enhanced root turnover at optimal nutrient balance.

Table 2 Effect of SFM-derived BCA on final soil physicochemical properties (pot experiment, July 2024).			
Treatment	pH	Moisture (%)	Organic Matter (g kg^{-1})
E (BCA-80%)	6.68 ± 0.10 a	10.48 ± 1.19 a	38.65 ± 4.78 b
D (BCA-60%)	6.56 ± 0.09 b	8.55 ± 0.50 b	43.53 ± 6.29 b
C (BCA-40%)	6.36 ± 0.08 c	10.72 ± 1.12 a	49.96 ± 3.81 a
B (BCA-20%)	5.66 ± 0.08 d	7.75 ± 0.63 b	38.80 ± 2.60 b
A (Reduced)	5.17 ± 0.08 e	7.66 ± 0.77 b	37.36 ± 5.85 b
T (Conventional)	5.15 ± 0.10 e	7.42 ± 0.54 b	41.49 ± 1.68 b
Note: Values are means $\pm$ SD ($n = 5$). Different letters within columns denote significant differences ($P < 0.05$, Duncan's multiple range test).			

3.3. Long-term phosphorus management and the in-situ Ca-phosphate slow-release mechanism

Treatment C significantly increased soil available P over the reduced-fertilization control (39.26 vs. 28.30 mg kg^{-1} , $P < 0.05$; Table 3) and maintained higher numerical values across all six sampling points (Fig. 4). At the same time, total P concentrations in leachate from Treatment C were 0.152–0.238 mg L^{-1} , representing reductions of 22.0–37.7% relative to conventional fertilization (Fig. 5a). Estimated cumulative P leaching was reduced by $\sim 28\text{--}34\%$. Total N leaching was also reduced by 33.5–37.6% (Fig. 5b). This combination—elevated soil available P with significantly reduced leaching—constitutes strong functional evidence for a slow-release mechanism: P is retained in the root zone and released gradually rather than as a rapid pulse.

The multiple lines of evidence—EDS co-localization, Ca/P ratio of ~ 1.08 , sustained P elevation over 21 months, and significant leaching reduction—collectively support the conclusion that endogenous Ca drove the in-situ formation of metastable Ca-phosphate phases, most probably ACP.

Table 3

Effects of SFM-derived BCA on soil available nutrients (pot experiment, final sampling, July 2024).

Treatment	Available N (mg kg ⁻¹)	Available P (mg kg ⁻¹)	Available K (mg kg ⁻¹)
T (Conventional)	134.13 ± 7.91 b	30.98 ± 4.35 b	206.08 ± 8.25 a
A (Reduced)	105.69 ± 4.63 d	28.30 ± 3.82 b	179.12 ± 25.23 ab
B (BCA-20%)	104.94 ± 5.45 d	29.06 ± 7.94 b	190.20 ± 25.56 a
C (BCA-40%)	148.25 ± 9.92 a	39.26 ± 6.33 a	194.48 ± 18.45 a
D (BCA-60%)	116.43 ± 5.33 c	35.58 ± 8.47 ab	177.52 ± 17.49 ab
E (BCA-80%)	83.32 ± 11.26 e	26.86 ± 6.68 b	155.94 ± 27.84 b
F (BCA-100%)	68.98 ± 5.45 f	20.22 ± 5.57 c	149.74 ± 26.70 b
Values are means ± SD (n = 5). Different letters within columns denote significant differences (P < 0.05, Duncan's multiple range test). Treatment C had significantly higher available P than the			

reduced-fertilization control (A); treatments E and F showed the lowest values.

3.4. Biological feedback supporting sustained nutrient cycling

BCA treatments enhanced soil enzyme activities over the 21 months (Fig. 6). Urease activity peaked in Treatment B (20%), likely reflecting an optimal C/N ratio. Sucrase activity increased over time, with highest values in B and T. Notably, acid phosphatase activity—critical for organic P mineralization—was 7.8–14.3% higher in BCA treatments than under conventional fertilization. These enhancements are consistent with pH amelioration, substrate supply, and microbial habitat provision. A companion study on the same experiment (Huang 2025) demonstrated that BCA treatments maintained higher bacterial and fungal richness and diversity than conventional fertilization, providing ecosystem-level support for the observed enzyme activities..

3.5. Plant performance and field corroboration

Treatment C maintained leaf SPAD values and P concentrations statistically equivalent to full conventional fertilization and significantly higher than the reduced-fertilization control (Table 4), confirming that the 30% fertilizer reduction did not compromise P nutrition. Similar trends were observed for leaf N and K.

Independent field corroboration on a strongly acidic soil (pH 4.91) with 'Jinxiang' mandarin (Hu et al. 2025) showed that the 40% BCA increased soil pH by 0.35–0.52 units and available P by 22–36% relative to the reduced-fertilization control, while maintaining leaf P and fruit yield. As expected, the magnitude of available P enhancement was less pronounced than in the pot experiment, reflecting greater

environmental heterogeneity and shorter duration. These consistent directional trends support the robustness of the BCA effects across contrasting settings.

Table 4
Effects of SFM-derived BCA on leaf nutrients and SPAD values (pot experiment, July 2024).

Treatment	Leaf N (g kg ⁻¹)	Leaf P (g kg ⁻¹)	Leaf K (g kg ⁻¹)	SPAD
T (Conventional)	24.8 ± 1.1 a	1.82 ± 0.08 ab	12.3 ± 0.5 a	68.5 ± 2.8 a
A (Reduced)	22.1 ± 1.0 b	1.71 ± 0.07 b	11.5 ± 0.4 b	63.2 ± 2.5 b
B (BCA-20%)	24.5 ± 1.2 a	1.88 ± 0.09 a	12.5 ± 0.5 a	69.2 ± 2.9 a
C (BCA-40%)	25.3 ± 1.2 a	1.93 ± 0.09 a	12.8 ± 0.5 a	70.1 ± 3.0 a
D (BCA-60%)	24.1 ± 1.1 a	1.85 ± 0.08 ab	12.4 ± 0.5 a	68.9 ± 2.8 a
E (BCA-80%)	23.5 ± 1.1 ab	1.79 ± 0.08 b	12.0 ± 0.4 ab	67.5 ± 2.7 ab
F (BCA-100%)	22.8 ± 1.0 b	1.73 ± 0.07 b	11.8 ± 0.4 b	65.8 ± 2.6 b
Note: Values are means ± SD (n = 5). Different letters within columns denote significant differences (P < 0.05, Duncan's multiple range test).				

4. Discussion

4.1. An alternative strategy: from exogenous reagents to endogenous minerals

This study demonstrates a paradigm shift: endogenous Ca in a carefully selected waste feedstock can perform the same P-retention function conventionally achieved only by loading biochar with external reagents. The key advantage of SFM lies in its unique combination of high intrinsic Ca (enriched to 3.79 at.% after pyrolysis), abundant organic carbon, and massive annual production (60–100 million tonnes yr⁻¹, primarily in Brazil, India, China, Thailand, and Pakistan) as an industrial waste requiring disposal. This "built-in reagent" strategy, if generalizable to other mineral-rich wastes (e.g., bone char, eggshell biochar), could substantially reduce the cost and environmental footprint of biochar-based P management.

4.2. In-situ Ca-phosphate formation as a self-regulated P reservoir

The Ca/P molar ratio of ~ 1.08 provides specific stoichiometric evidence for the formation of metastable Ca-phosphate phases, most probably ACP, within the BCA granule. This ratio effectively excludes hydroxyapatite (1.67) and β-tricalcium phosphate (1.5), which are often assumed but require Ca loadings incompatible with SFM's endogenous content. ACP's thermodynamic metastability ($K_{sp} \approx 10^{-25} - 10^{-26}$) enables pH-responsive dissolution under mild rhizosphere acidification, releasing orthophosphate in

approximate synchrony with plant demand (Combes and Rey 2010). The slow-release behaviour is further corroborated by the concurrent increase in soil available P and decrease in leaching—a functional signature that a significant portion of P is held in a solid-phase reservoir rather than being immediately solubilized.

We recognize that the analytical techniques employed—while appropriate for a 21-month multi-timepoint design—do not provide the molecular-level resolution of synchrotron-based XANES or isotopic tracing. Direct crystallographic confirmation and quantification of the Ca-P pool remain priorities for future work.

4.3. Pot-to-field translation

The field corroboration showed consistent directional trends but with attenuated effect sizes, a pattern commonly observed when transitioning from controlled pot conditions to open fields (Poorter et al. 2016). The fact that BCA effects remained detectable across contrasting soil types, cultivars, durations, and endpoints strengthens the inference that the underlying mechanisms are robust. Multi-year field trials across diverse agroecosystems are needed to fully assess commercial viability.

4.4. Synergistic rhizosphere mechanisms

Sustained P availability likely reflects a synergy of five mechanisms: (i) pH-driven desorption of Fe/Al-fixed P; (ii) competitive sorption by biochar surface functional groups; (iii) endogenous Ca-driven ACP formation and gradual dissolution; (iv) enhanced acid phosphatase activity (7.8–14.3%), promoting organic P mineralization; and (v) reduced leaching through physical encapsulation and chemical retention. This multi-mechanistic nature distinguishes the SFM-derived BCA from amendments relying on a single retention pathway.

4.5. The 21-month dataset

To the best of our knowledge, this is one of the longest continuous monitoring datasets for a granular biochar amendment in acidic soil, providing confidence that the observed improvements are not transient. The six sequential sampling points reveal a consistent trajectory rather than an initial pulse followed by decline.

4.6. Plant growth and nutrient acquisition

The maintenance of leaf P and SPAD values at levels comparable to full fertilization, despite a 30% fertilizer reduction, confirms that the slow-release mechanism translated effectively into plant P uptake. This decoupling of crop performance from excessive fertilizer input has important implications for sustainable orchard management.

4.7. Limitations and future directions

Important limitations remain. The pot experiment used a single soil type and non-fruiting trees; generalizability to fruit-bearing mature orchards requires multi-site evaluation. Leachate was collected only during the final three months, and fertilization via surface broadcasting may not represent optimal

commercial practice; high-frequency, year-round monitoring is needed. The anomalous organic matter pattern (C > D > E) warrants further investigation. Direct confirmation of ACP via XRD/XANES, isotopic tracing, and comprehensive life-cycle assessment are recommended next steps.

5. Conclusion

This 21-month study demonstrates that an endogenous Ca-driven mechanism in SFM biochar provides durable P immobilization and acidic soil remediation. The principal advances are:

1. **A "built-in reagent" strategy** that eliminates the need for exogenous chemical additives by exploiting the intrinsic Ca in a globally abundant industrial waste (60–100 million tonnes yr⁻¹).
2. **Long-term validation** showing enhanced plant-available P pools and reduced P leaching (22.0–37.7%), sustaining plant nutrition under 30% reduced chemical fertilizer input, with consistent field trends.
3. **Mechanistic specificity** from a Ca/P ratio of ~ 1.08, strongly suggesting the formation of metastable ACP rather than stoichiometric crystalline phases.
4. **Global applicability**: This valorization route offers a scalable circular-economy solution addressing industrial waste disposal, soil acidification, and non-point source P pollution simultaneously.

Abbreviations

ACP

Amorphous calcium phosphate

ANC

Acid–neutralizing capacity

BCA

Biochar–based amendment

EDS

Energy–dispersive X–ray spectroscopy

FTIR

Fourier–transform infrared spectroscopy

P

Phosphorus

PVA

Polyvinyl alcohol

SEM

Scanning electron microscopy

SFM

Sugarcane filter mud

TP

LCR–Total phosphorus leaching concentration ratio

Declarations

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Author Contributions Huang SZ: Investigation, Data curation, Formal analysis, Writing – original draft, Visualization. Tang XH: Investigation, Data curation, Writing – original draft, Validation. Hu CF: Investigation, Data curation, Validation. Wei HJ: Investigation, Formal analysis. Cheng XR: Methodology, Resources. Li SL: Conceptualization, Supervision, Writing – review & editing. Li ZG: Conceptualization, Methodology, Supervision, Project administration, Writing – review & editing, Funding acquisition.

Declaration of generative AI and AI-assisted technologies No generative AI or AI-assisted technologies were used in the preparation of this work.

Data Availability The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

References

1. Ahmad S, Zhai XX, Wang MR, Shi YJ, Chen YM, Liang QM, He B, Wen RH (2024) Sugarcane bagasse biochar enhances soil enzyme activities and plant growth in acidic soil. *Chem Biol Technol Agric* 11:28. <https://doi.org/10.1186/s40538-024-00546-4>
2. Bolan N, Sarmah AK, Bordoloi S, Bolan S, Padhye LP, Van Zwieten L, Sooriyakumar P, Khan BA, Ahmad M, Solaiman ZM, Rinklebe J, Wang HL, Singh BP, Siddique KHM (2023) Soil acidification and the liming potential of biochar. *Environ Pollut* 317:120632. <https://doi.org/10.1016/j.envpol.2022.120632>
3. Carneiro JSD, Ribeiro ICA, Nardis BO, Barbosa CF, Lustosa Filho JF, Melo LCA (2021) Long-term effect of biochar-based fertilizers application in tropical soil: Agronomic efficiency and phosphorus availability. *Sci Total Environ* 760:143955. <https://doi.org/10.1016/j.scitotenv.2020.143955>
4. Combes C, Rey C (2010) Amorphous calcium phosphates: Synthesis, properties and uses in biomaterials. *Acta Biomater* 6(9):3362–3378. <https://doi.org/10.1016/j.actbio.2010.02.017>
5. FAO (2024) World Food and Agriculture – Statistical Yearbook 2024. Food and Agriculture Organization of the United Nations, Rome. <https://doi.org/10.4060/cd2971en>
6. Guo JH, Liu XJ, Zhang Y, Shen JL, Han WX, Zhang WF, Christie P, Goulding KWT, Vitousek PM, Zhang FS (2010) Significant acidification in major Chinese croplands. *Science* 327:1008–1010. <https://doi.org/10.1126/science.1182570>

7. Hu CF, Huang SZ, Liu CR, Zhang CQ, Li SL, Li ZG (2025) Effect of sugar mill filter mud biochar-based fertilizer on soil physicochemical properties and leaf nutrient content in citrus orchards. *J Plant Nutr Fertil* 31(3):147–156 (in Chinese)
8. Huang SZ (2025) Effects of sugarcane filter mud-base fertilizer on soil micro-ecological and nitrogen and phosphorus loss of potted citrus. Master's Thesis. Guangxi University, Nanning, China (in Chinese)
9. Jantapa W, Jetsrisuparb K, Macquarrie D, Kasemsiri P, Chindaprasirt P, Knijnenburg JTN (2025) Temperature-dependent phosphorus speciation and release from magnesium-rich biochars. *Waste Biomass Valor* 16:2287–2300. <https://doi.org/10.1007/s12649-024-02851-3>
10. Jetsrisuparb K, Jeejaila T, Saengthip C, Kasemsiri P, Ngernyen Y, Chindaprasirt P, Knijnenburg JTN (2022) Tailoring the phosphorus release from biochar-based fertilizers: role of magnesium or calcium addition during co-pyrolysis. *RSC Adv* 12:30539–30548. <https://doi.org/10.1039/d2ra05848k>
11. Lehmann J, Rillig MC, Thies J, Masiello CA, Hockaday WC, Crowley D (2011) Biochar effects on soil biota – A review. *Soil Biol Biochem* 43:1812–1836. <https://doi.org/10.1016/j.soilbio.2011.04.022>
12. Li HW, Huang YM, Zhang JT, Liang YX, Wu JL, Liu KX (2026a) Valorizing pruning residues into biochar for remediating acidified cropland soil: Effects on fertility, enzymes, and bacterial communities. *Agronomy* 16(3):296. <https://doi.org/10.3390/agronomy16030296>
13. Li HX, Li YX, Xu Y, Lu XQ (2020) Biochar phosphorus fertilizer effects on soil phosphorus availability. *Chemosphere* 244:125471. <https://doi.org/10.1016/j.chemosphere.2019.125471>
14. Liang P, Han JY, Liu XC, Deng ZH, Tian F, Wu ZS (2026) Phosphoric acid-triggered phosphorus transformation: Structural regulation and long-term phosphorus release mechanism of biochar slow-release phosphate fertilizer. *Environ Res* 301:124494. <https://doi.org/10.1016/j.envres.2026.124494>
15. Luo Y, Wu X, Xiao HB, Toan N-S, Liao B, Wu X, Hu RG (2023) Leaching is the main pathway of nitrogen loss from a citrus orchard in Central China. *Agric Ecosyst Environ* 356:108559. <https://doi.org/10.1016/j.agee.2023.108559>
16. Marcinczyk M, Oleszczuk P (2022) Biochar and engineered biochar as slow- and controlled-release fertilizers. *J Clean Prod* 339:130616. <https://doi.org/10.1016/j.jclepro.2022.130616>
17. Nepal J, Ahmad W, Munsif F, Khan A, Zou ZY (2023) Advances and prospects of biochar in improving soil fertility, biochemical quality, and environmental applications. *Front Environ Sci* 11:1114752. <https://doi.org/10.3389/fenvs.2023.1114752>
18. Neumann G, Römheld V (2012) Rhizosphere processes and management for improving nutrient use efficiency and crop productivity. In: Sparks DL (ed) *Advances in Agronomy*, Vol 114. Academic Press, pp 1–70
19. Pei L, Yang F, Xu XY, Nan HY, Gui XY, Zhao L, Cao XD (2021) Further reuse of phosphorus-laden biochar for lead sorption from aqueous solution: Isotherm, kinetics, and mechanism. *Sci Total Environ* 792:148550. <https://doi.org/10.1016/j.scitotenv.2021.148550>

20. Poorter H, Fiorani F, Pieruschka R, Wojciechowski T, van der Putten WH, Kleyer M, Schurr U, Postma J (2016) Pampered inside, pestered outside? Differences and similarities between plants growing in controlled conditions and in the field. *New Phytol* 212(4):838–855.
<https://doi.org/10.1111/nph.14243>
21. Sim DHH, Tan IAW, Lim LLP, Yeo FKS, Phornvillay S, Abat M, Lam SS, Hameed BH (2025) Biochar-based slow/controlled-release fertilizer for sustainable agriculture: Recent advances, challenges and future prospects. *J Environ Chem Eng* 13(5):118826.
<https://doi.org/10.1016/j.jece.2025.118826>
22. Tan HW (2017) Fermentation of sugar mill filter mud to produce bio-organic fertilizer. *J South Agric* 48(3):428–432 (in Chinese)
23. van der Ploeg JD, de Roo N, Hilhorst T, van der Zee SEATM (2020) The gap between pot and field experiments in soil science: Causes, consequences, and solutions. *Geoderma* 374:114425.
<https://doi.org/10.1016/j.geoderma.2020.114425>
24. Yang L, Wu YC, Wang YC, An WQ, Jin J, Sun K, Wang XK (2021) Effects of biochar addition on the abundance, speciation, availability, and leaching loss of soil phosphorus. *Sci Total Environ* 758:143657. <https://doi.org/10.1016/j.scitotenv.2020.143657>
25. Zeng CC, Su TM, Qin F, et al (2018) Effect of sugarcane sugar mill filter mud organic fertilizer on the growth of flowering Chinese cabbage. *Southwest China J Agric Sci* 31(4):796–801 (in Chinese)
26. Zhang SW, Zhu QC, de Vries W, Ros GH, Chen XH, Muneer MA, Zhang FS, Wu LQ (2023) Effects of soil amendments on soil acidity and crop yields in acidic soils: A world-wide meta-analysis. *J Environ Manage* 345:118531. <https://doi.org/10.1016/j.jenvman.2023.118531>
27. Zhou Q, Zhou LH, Zhang H, Li J, Zeng QC (2025) Microbial phosphorus cycling shaped by citrus-induced soil acidification and phosphorus accumulation in fertilized orchards. *J Environ Manage* 395:127885. <https://doi.org/10.1016/j.jenvman.2025.127885>

Figures

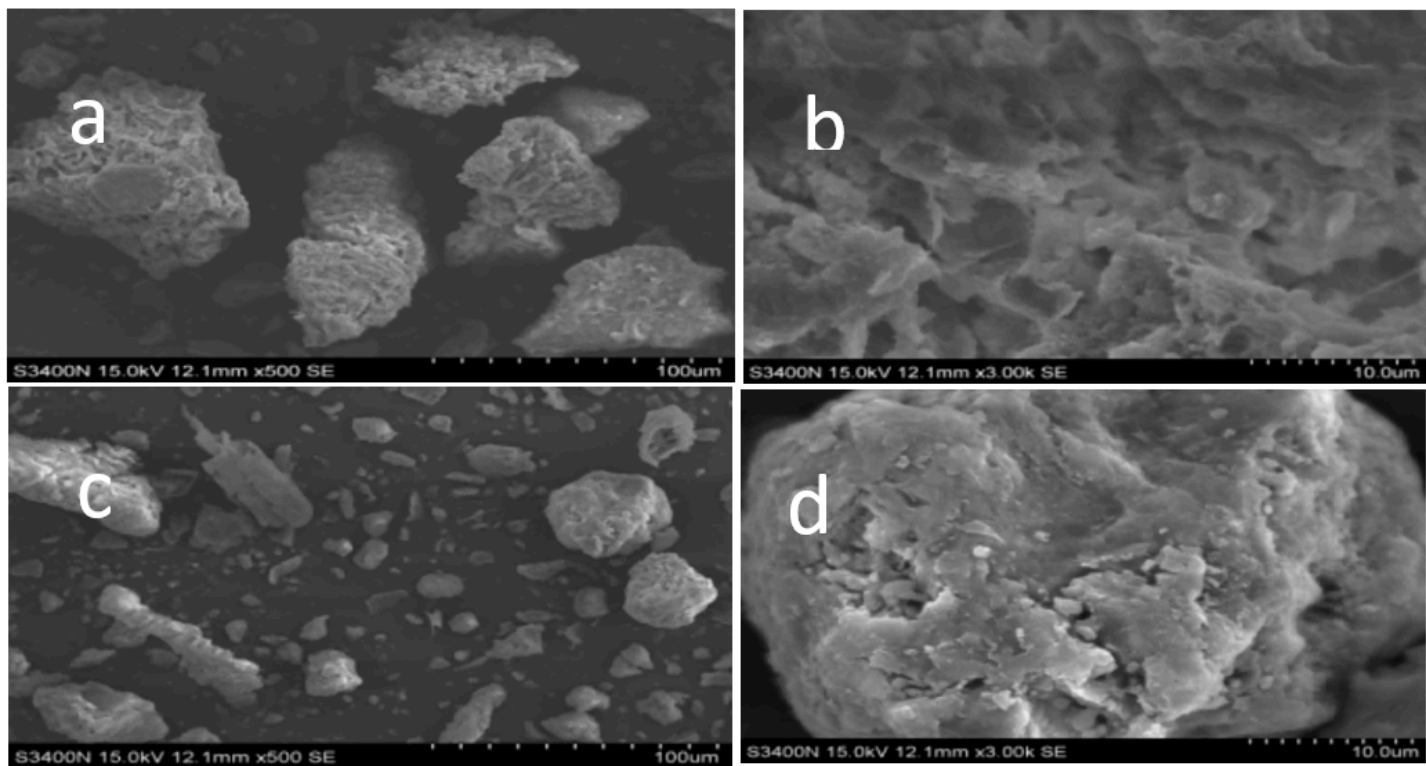


Figure 1

SEM images of raw SFM at (a) 500× and (b) 3000× magnification; SFM-derived biochar at (c) 500× and (d) 3000× magnification, showing the transformation from a dense, irregular surface to a well-developed interconnected porous network after pyrolysis.

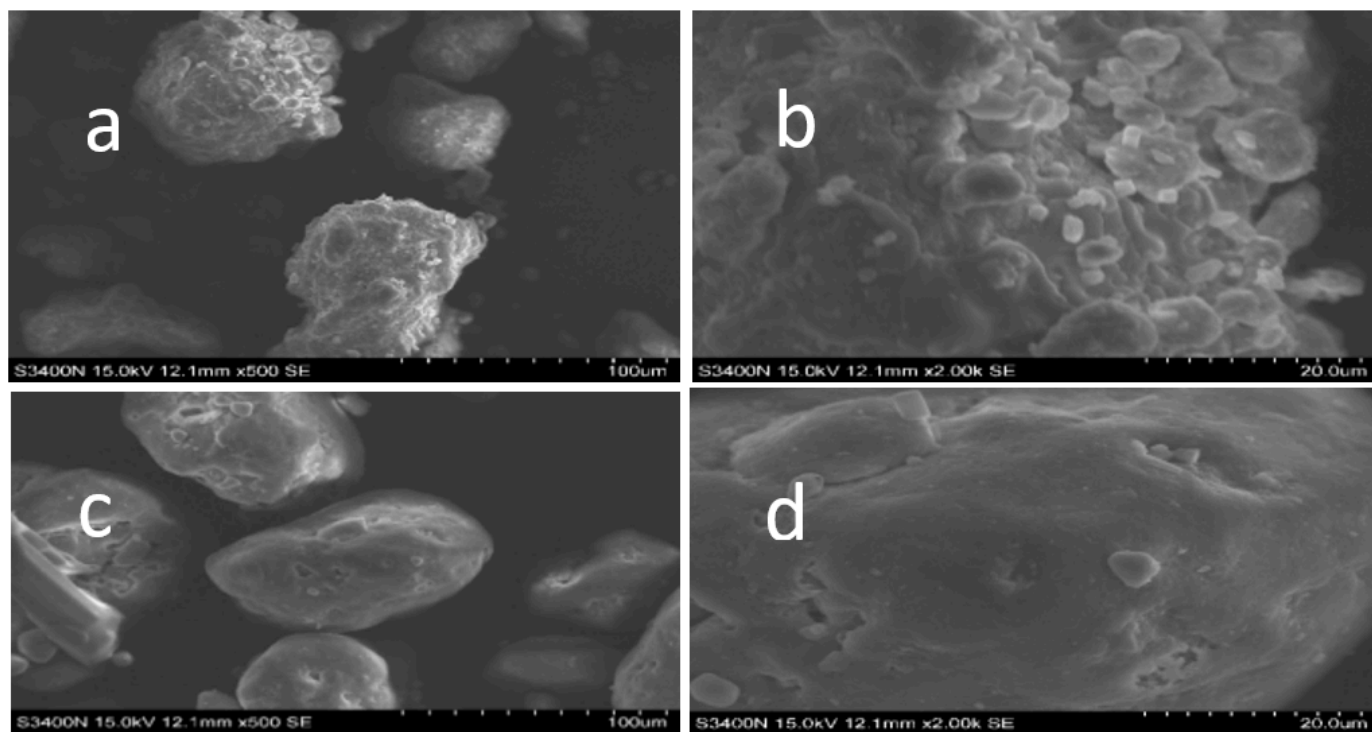


Figure 2

SEM images of BCAs: (a, b) BCA-20% at 500× and 2000× magnification, showing excess fertilizer crystallites on the biochar surface; (c, d) BCA-40% at 500× and 2000× magnification, exhibiting the optimal "mosaic" microstructure with fertilizer crystallites uniformly filling the biochar pores while maintaining a partially interconnected pore network.

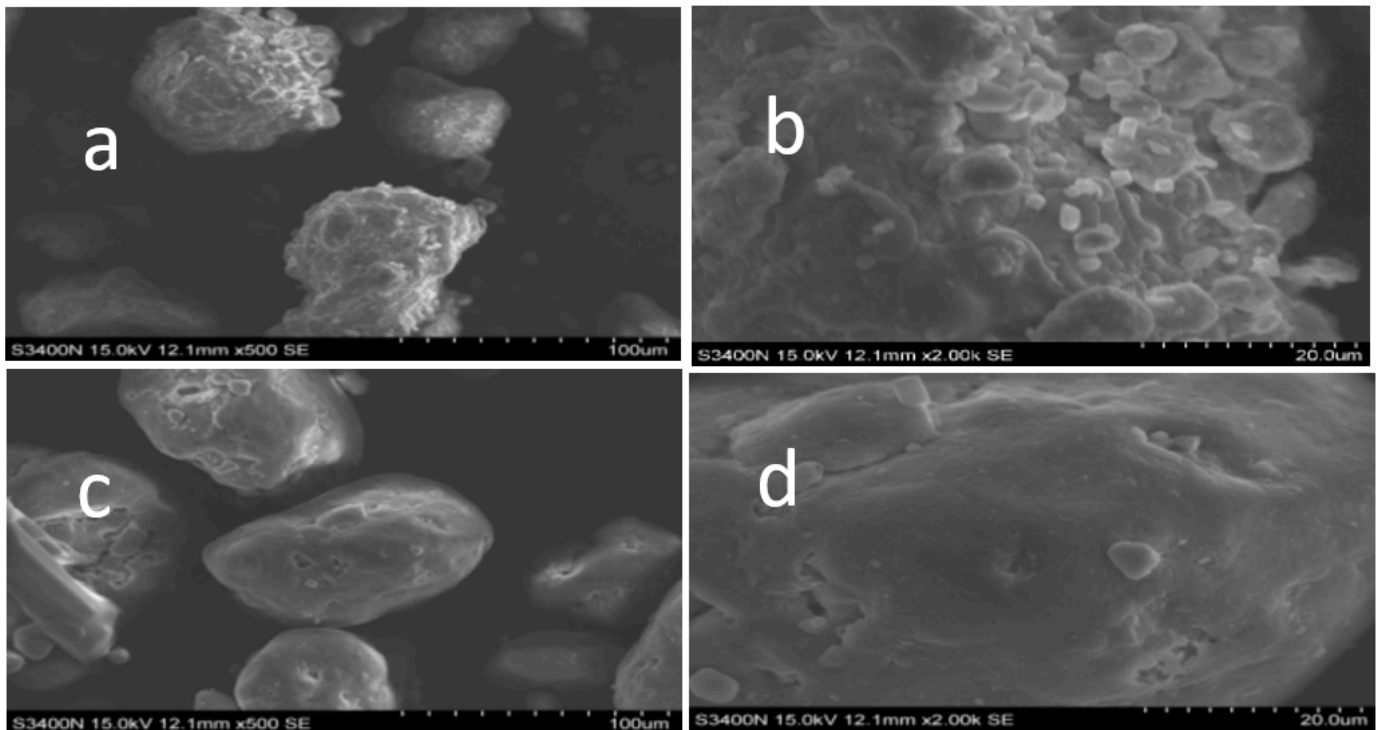


Figure 3

SEM images of BCAs: (a, b) BCA-60% at 500× and 2000× magnification; (c, d) BCA-80% at 500× and 2000× magnification. At higher biochar substitution ratios, the biochar pores are incompletely filled by the reduced amount of fertilizer, leaving more exposed pore structures.

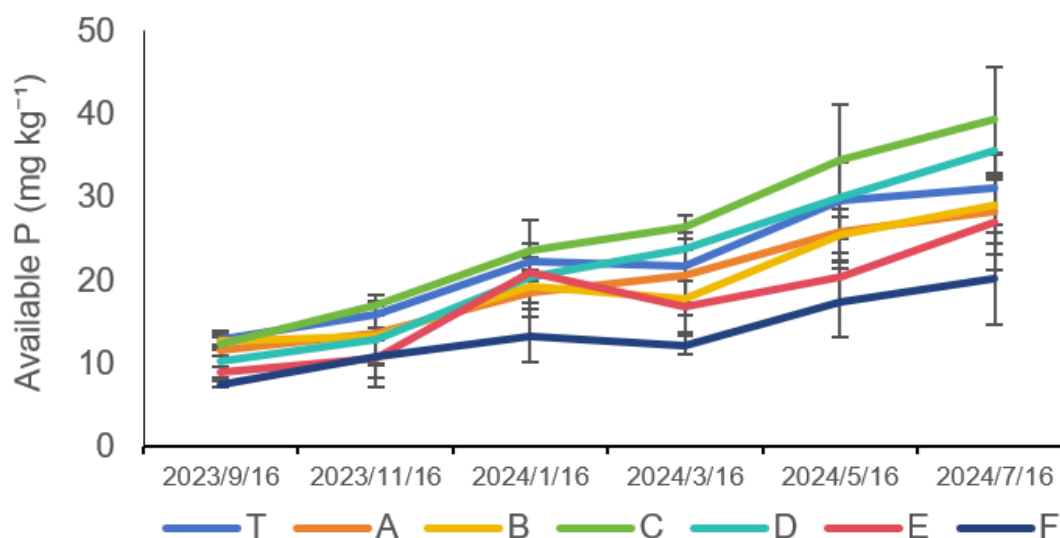


Figure 4

Temporal dynamics of soil available P over the 21-month pot experiment under different treatments. Data are means $\pm$ SD ($n = 5$). Standard deviations are provided in Online Resource 4. Treatment C (BCA-40%) maintained elevated available P throughout the experimental period, whereas Treatment A (reduced fertilization) showed consistently lower P levels. Different letters at each time point indicate significant differences among treatments ($P < 0.05$, Duncan's multiple range test; see Online Resource 4 for complete statistical annotations).

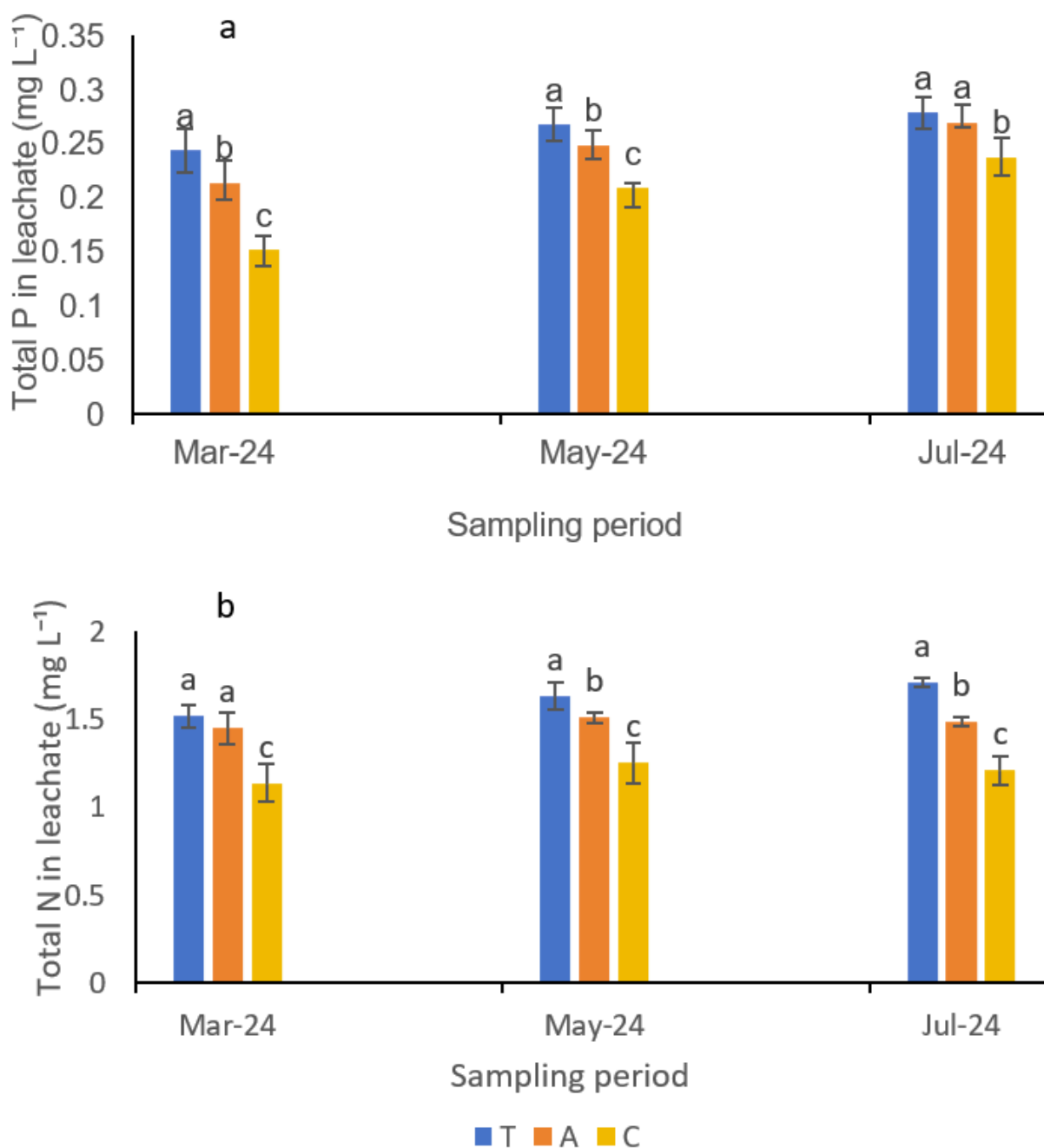


Figure 5

Concentrations of total P (a) and total N (b) in leachate from potted citrus under conventional fertilization (T), reduced fertilization without biochar (A), and the optimized BCA with 40% biochar substitution (C). Leachate was collected in March, May, and July 2024. Values are means $\pm$ SD ($n = 5$). Different lowercase letters denote significant differences among the three shown treatments within the same sampling period ($P < 0.05$, Duncan's multiple range test). Complete leachate data and statistical comparisons for all seven treatments are provided in Online Resource 5.

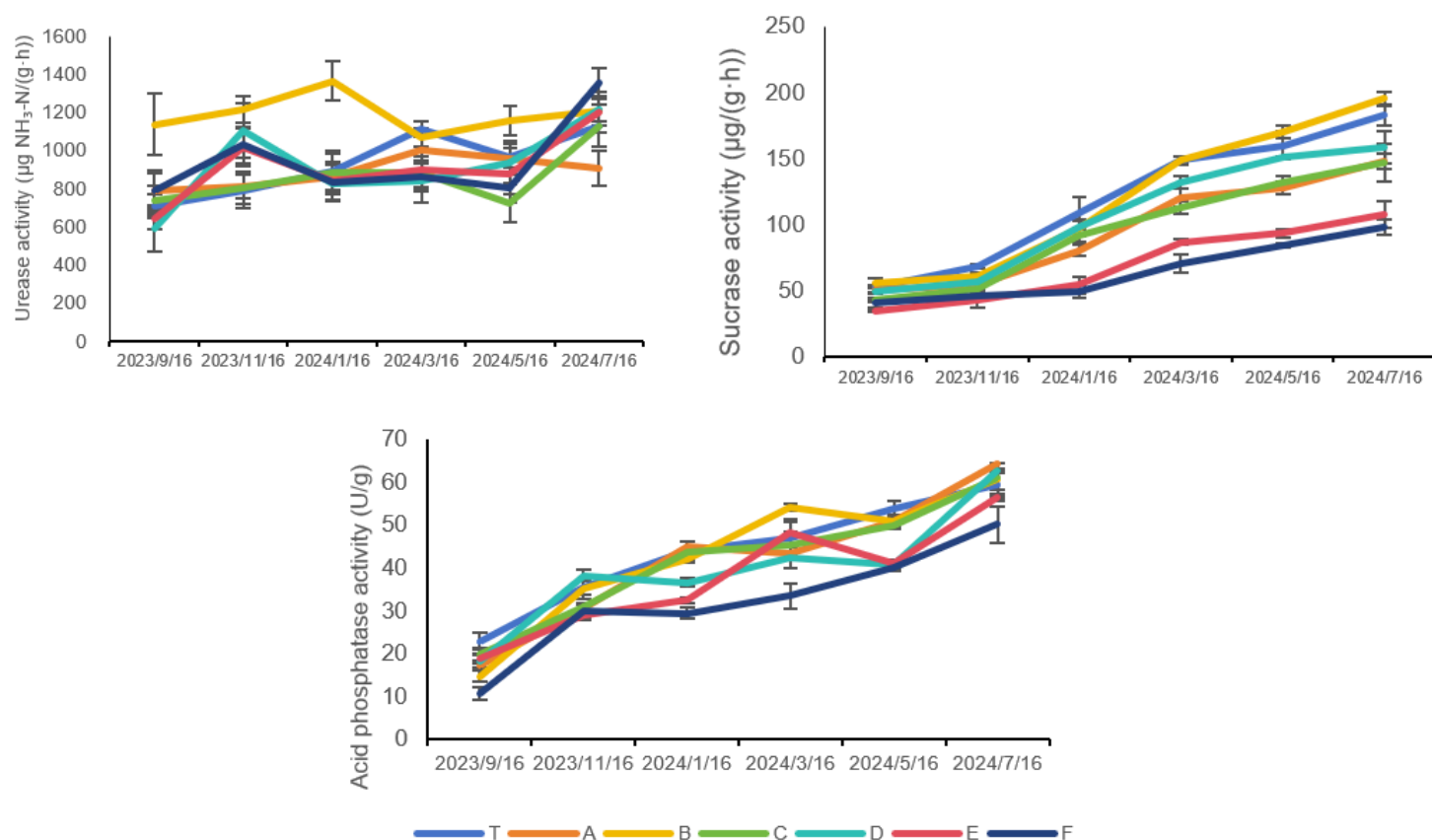


Figure 6

Soil enzyme activities under different treatments over the 21-month pot experiment: (a) urease, (b) sucrase, (c) acid phosphatase. Data are presented as means $\pm$ SD ($n = 5$). Different lowercase letters indicate significant differences among treatments within the same sampling period ($P < 0.05$, Duncan's multiple range test). T = conventional fertilization; A = reduced fertilization; B–F = BCAs with 20%, 40%, 60%, 80%, and 100% biochar substitution, respectively. Period (P), fertilization strategy (S), and their interaction ($P \times S$) all significantly affected enzyme activities ($P < 0.05$). The complete dataset is provided in Online Resource 6.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementaryMaterial78.docx](#)