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Long-term Organic and Inorganic Fertilization Affect Soil pH, Humus Carbon Fractions, and Crop Yield in Three Soil Types

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Authors' contributions

This work was carried out in collaboration among all authors. Author PTS conceptualized the study, performed the methodology, did software and formal analysis, investigated the work, did data curation, data visualization and wrote the original draft. Author JH searched for resources, performed the methodology, investigated the work and did data validation. Authors ZS, NAD, and JL did data curation, data visualization, formal analysis, reviewed and edited the manuscript. Author KAT investigated the work, wrote, reviewed and edited the manuscript. Author LL performed the methodology, investigated the work, and searched for resources. Author HZ did funding acquisition, administered the project, did data validation and supervised the study. All authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

Context: Soil acidification and humus carbon depletion pose significant challenges to agricultural sustainability. Organic and inorganic fertilization influence soil pH, humus carbon, and crop yield, yet the effects in different soil types remain inadequately understood.

Objective: This study aimed to (i) measure soil pH changes under different long-term organic and inorganic fertilization in granite, Quaternary red, and purple sandy shale soils, (ii) quantify humus carbon content and humification degree, and (iii) explore the implications for crop yield in these soils.

Methods: A field experiment was conducted in 2023 based on a long-term study established in 1982 at the National Observation and Research Station of Farmland Ecosystem in Qiyang, south China. Six treatments were applied: CK-T (control with straw take away), CK-R (control with straw return), NPK-T (NPK with straw take away), NPK-R (NPK with straw return), OM-T (straw take away), and OM-R (straw return).

Results: Soil pH was highest under the OM-R treatment, while NPK-T and NPK-R significantly reduced pH in Quaternary red and granite soils compared to purple sandy shale soil. NPK-R and OM-R treatments significantly increased humus carbon fractions, humic acid carbon (HA-C), fulvic acid carbon (FA-C), and humin carbon (HU-C) in all three soils. The NPK-R treatment increased the soil organic carbon (SOC) and soil microbial biomass carbon (SMBC) in granite soil than in Quaternary red and purple sandy shale soils. The average humic acid to fulvic acid ratio (HA:FA) across all treatments was 1.46, with the purple sandy shale soil exhibiting the highest humification degree (HA:FA 1.51), surpassing Quaternary red (HA:FA 1.49) and granite soils (HA:FA 1.38). NPK-R treatment produced the highest sweet potato (*Ipomoea batatas* 'Beauregard') yields in granite (25,000 kg ha^{-1}) and Quaternary red soils (24,012 kg ha^{-1}) and the highest broad bean (*Vicia faba 'Aquadulce* Claudia') yield (632.8 kg ha^{-1}) in purple sandy shale soil. Both crop yields were strongly correlated with soil pH, humus carbon fractions, SOC, TN, AP, AK, BD, and SWC.

Conclusion: Straw return stabilizes soil pH, whereas NPK fertilizer reduces soil pH. Straw application with NPK fertilizer increases humus carbon content, nutrient concentrations, and crop yield. These findings provide valuable insights into the synergistic effects of straw and mineral fertilizers on soil properties, contributing to crop yield improvement in different soil types.

Keywords: Long-term fertilization; humus carbon fractions; soil pH; SOC; crop yield.

1. INTRODUCTION

Soil acidification and humus carbon depletion pose significant challenges to agriculture sustainability in southern China (Liu et al., 2020; Renkou et al., 2018).This condition adversely affects soil fertility, emphasizing the need for effective soil amelioration practices. Among soil components, humus, a principal form of organic carbon, is crucial for improving soil quality. Soil humus is a form of carbon that is an essential component of the soil carbon pool, accounting for 60 to 80% of total SOM in soil (Stevenson, 1972). It improves soil physical, chemical, and biological characteristics Lehmann., (2015); Powlson et al., (2012), which can influence nutrient cycling and plant growth (Bhattacharyya et al., 2012; Rudrappa et al., 2006; Wang et al., 2015). Importantly, the interaction between soil humus carbon and soil pH is essential, as soil pH directly affect stabilization and degradation of organic matter (Chen et al., 2020). The relationship between soil pH and soil humus carbon has been identified as a key factor for improving soil quality. This is particularly relevant given the prevalent use of different fertilization, such as organic and inorganic fertilizers. These interventions have been documented to alter soil pH and increase humus carbon content over time (Nardi et al., 2004; Wu et al., 2023). Despite some research progresses on the long-term impacts of organic and inorganic fertilization, there are still gaps in our understanding of the underlining mechanisms through which they impact soil properties over a longer timescale, especially in different parent material soils, such as granite, Quaternary red and purple sandy shale. For instance, (Luo et al., 2023) reported improvements in soil pH and humus levels through combined organic and inorganic fertilization. However, the specific interactions and underlying mechanisms, particularly concerning different soil types, are not fully understood. Furthermore, soil humus plays a central role in stabilizing SOC pool (Smith et al., 2019; Xu et al., 2017). Based on their solubility in acidic and alkali solutions, soil humus is divided into three main fractions, Humic Acid (HA), Fulvic acid (FA), and Humin (HU) (Stevenson, 1972). Humic acid is insoluble under acidic condition (generally pH < 2), whereas Fulvic acid is soluble under all pH conditions, and Humin is the insoluble fraction (Sutton et al., 2005). Ferrari et al., (2011) reported that long-term application of farmyard manure increased soil humus carbon content. A study by Zhang et al., (2020) showed that the application of mineral fertilizers and straw increased soil humus content. Doane et al., (2003) also found that HA had greater turnover of carbon than FA and HU. Straw return, as an organic amendment, improves soil attributes by enhancing soil fertility, structure, and microbial activity (Akhtar et al., 2023; Liu et al., 2022; Wang et al., 2015; Zhang et al., 2023). The decomposition of straw adds organic matter to the soil. This increases soil organic carbon (SOC) and improve nutrient cycling, particularly nitrogen and phosphorus (Chen et al., 2023). This process not only replenishes essential nutrients but also improves soil pH (Wang et al., 2024). Straw return also enhances soil physical properties by improving aggregation and water retention, reducing erosion, and fostering better root penetration (Li et al., 2023; Zhao et al., 2022). Better organic matter in the soil also supports microbial diversity and activity (Yang et al., 2024). By serving as a renewable resource, straw return is a sustainable practice that improves long-term soil productivity and resilience, making it an essential component of integrated soil management systems (Sun et al., 2023). However, the reliance on chemical fertilization has been associated with soil acidification, limited organic matter, and decline in soil fertility (Li et al., 2017; Zhao et al., 2013). Researches covering various climatic and soil conditions have demonstrated benefits of straw return on enhancing soil organic carbon (Powlson et al., 2012). However, in the short- and mid-term field experiments, most of the research focused only on the responses of labile carbon pool to fertilization managements, with limited attention to changes in the recalcitrant carbon pool, like soil humus carbon. Moreover, most of the existing studies have been short-term and limited in their geographic scope, leaving a gap in our understanding of these processes over longer timescales and across different soil types (Iqbal et al., 2023). The long-term comparative effects of organic and inorganic fertilization on soil pH and soil humus, particularly in different parent material soils, such as granite, Quaternary red and purple sandy shale soils remain inadequately explored. Thus, it is necessary to assess the long-term impacts of different soil management practices on critical soil properties like, humus carbon fractions and soil pH, especially in field conditions.

This study aimed to (i) measure soil pH changes under long-term applications of straw and NPK fertilizer in granite, Quaternary red, and purple sandy shale soils, (ii) quantify humus carbon content and humification degree, and (iii) evaluate the implications for crop yield in these soils. We hypothesized that straw return would stabilize soil pH, while NPK fertilizer would reduce pH in the three soils. Straw combined with NPK fertilizer would increase humus carbon content, nutrient concentrations, and crop yields, with each soil exhibiting distinct humification degrees.

2. MATERIALS AND METHODS

2.1 Experimental Design and Management

The long-term experimental field was established in 1982 at the National Observation and Research Station of Farmland Ecosystem in Qiyang, south China (26°45′42″N, 111°52′32″E). The field was made of three soil types: Quaternary red, granite and purple sandy shale soils, according to World Reference Base for soil resources (WRB) (FAO, 2014) and the Chinese soil classification (Baxter, 2007). The site is in a subtropical monsoon zone characterized by hot summers and cold winters. The mean annual temperature (MAT) is 18 ℃ and mean annual precipitation (MAP) is 10 ℃, with an annual rainfall of 1290mm from April to end of June. The frost-free season is 300 days with an annual radiation of 108.66 kcal/cm^2. Annual evaporation and sunshine durations are 1470mm and 4550mm for 1610 hours, respectively. The climate data were collected from the county weather station, where weather data of dry- and wet-bulb temperature, minimum and maximum air temperature, and precipitation are recorded daily at 0800 following the National Standard of

Specifications for Surface Meteorological Observations (1979). The study had six treatments: CK-T (control with straw take away), CK-R (control with straw return), NPK-T (NPK with straw take away), NPK-R (NPK with straw return) OM-T (straw take away) and OM-R (straw return). The experimental field consisted of 18 plots, each measuring 8m² with a depth of 1 meter, arranged in unsealed cement pools in a randomized block design with three replications. The plots were divided into three strata, each containing six plots for the six treatments. Each plot was separated from adjacent plots by 60-cm cement barriers. The inorganic N, P, and K fertilizers were applied as 175 kg N ha^{-1}, 75 kg P_2O_5 ha^{-1}, and 75 kg K_2O ha^{-1} every year. The N, P, and K fertilizers were applied as urea, ammonium phosphate, and potassium chloride, respectively. 1,251 kg ha^{-1} of organic straw (dry rice straw) was applied with nutrient contents of 8.23 g kg^{-1} N, 2.72 g kg^{-1} P_2O_5, 20.62 g kg^{-1} K2O, and 15.00% water content on average (Table 2). All the inorganic fertilizers and organic straw were applied as a basal application, before sowing broad bean seeds and planting sweet potato slips. ANOVA and post-hoc Tukey's HSD-test were used to measure the treatment effects on sweet potato (*Ipomoea batatas* 'Beauregard') and broad bean (*Vicia faba* 'Aquadulce Claudia') yields from each soil.

2.2 Soil Sampling and Analysis

The initial physical and chemical properties of the three soils at the start of the study are presented in (Table 1). Soil samples were collected from a 0–20 cm depth in 2023, following the harvest of sweet potato (*Ipomoea batatas* 'Beauregard') and broad bean (*Vicia faba* 'Aquadulce Claudia') crops. A minimum of six soil cores were taken from each plot using a soil auger and combined to form a composite sample. The sampling points were the meeting points of two diagonals of the adjoining plants making a rectangle, and S-shaped sampling method. The soil samples were packaged in clean polythene bags and conveyed to the laboratory, where plant residues were removed, separated into fresh and air-dried portions, crushed and sieved for analysis. Subsamples were passed through a 0.153-mm mesh to determine SOC, TN, TP, AP, and AK contents, using routine methods (Nelson and Sommers 1996; Murphy and Riley 2002). Total potassium (TK) was extracted with 1N ammonium acetate (NH4OAc) and measured using a flame photometer. Soil pH was measured using a water-soil ratio of 5:1 with a potentiometer (Rukun et al., 2000). Cation exchange capacity (CEC) was determined by ammonium oxalate-barium chloride method (Lu et al., 2000). Bulk density (BD) and soil water content (SWC) were measured by using a short core (5 cm in diameter and 5.1 cm in height) to obtain undisturbed soil of the same depth of each soil (Grossman and Reinsch, 2002). Soil Microbial Biomass Carbon (SMBC) and Nitrogen (SMBN) were quantified using the fumigation-extraction method (Jenkinson and Powlson, 1976; Vance et al., 1987). The protocols of the International Humic Substances Society (IHSS) and Preston et al., (1994) were used for the extraction and purification of humus carbon fractions. Briefly, the procedure involved acidifying 5.0 g of soil with 1M HCl and treating it with 0.1M HCl, followed by centrifugation to collect the supernatant and cleansing the soil residue with deionized water. Humic and fulvic acids were extracted with a combination of 0.1M NaOH and 0.1M $Na_4P_2O_7$, and then separated three times by centrifugation. The alkaline extract was acidified to precipitate humic acid, which was separated from fulvic acid by centrifugation and purified until the supernatant was colorless. Fulvic acids were further purified through a DAX-8 resin column and Amberlite IR 120H+ resin, followed by freeze-drying. The residual soil (humin) was de-ashed using an HF solution, rinsed, and freeze-dried. The end products were quantified as Fulvic Acids Carbon (FA-C), Humic Acids Carbon (HA-C), and Humin Carbon (HU-C).

2.3 Statistical Analysis

All data were analyzed using analysis of variance (ANOVA) in SPSS software, version 22 (SPSS, Inc., USA) and Tukey's HSD test at a 5% probability level were employed to determine significant differences between treatment means. Relative importance of fertility factors in the three soils was quantified based on the Random Forest Model, with feature scores normalized and scaled into percentages. Principal Component Analysis (PCA) and Correlation Analysis were employed to examine patterns and relationship between soil properties and crop yields. Partial Least Squares Path Modeling (PLS-PM) was used to identify pathways and main factors affecting response variables using the R package plspm.

3. RESULTS

3.1 Impact of Fertilization on Soil Physicochemical Properties and Humus Carbon Fractions

Soil pH exhibited significant variations under the treatments in the three soils. The single straw return (OM-R) treatment stabilized pH in all three soils, while the NPK with straw take away (NPK-T) treatment caused the greatest reductions, with pH decreases of -2.5 units in granite and -3.0 units in Quaternary red soils (Fig.1 and Table 4).The NPK with straw return (NPK-R) also reduced the soils' pH, but to a lesser extent than NPK-T treatment. The pH was more stable in purple sandy shale soil compared with Quaternary red and granite soils under all treatments (Fig.1 and Table 4). Meanwhile, granite soil accumulated the highest humus carbon content, humic acid carbon (HA-C 48.64%) fulvic acid carbon (FA-C 37.97%), humin carbon (HU-C 2.73%) and the highest soil organic carbon (SOC 15.9 g kg^{-1}) under NPK-R treatment (Tables 3 and 4). In Quaternary red soil, HA-C, FA-C, and HU-C accounted for 48%, 21.35%, and 11.60%, respectively, with a higher SOC of 12 g kg^{-1}. In purple sandy shale soil, HA-C was 45%, FA-C 33%, and HU-C 16.81%, with a higher SOC of 8.2 g kg^{-1} under the NPK-R treatment. Across all treatments and soils, the average humic acid to fulvic acid ratio (HA/FA) was 1.46, with purple sandy shale soil exhibiting the highest humification degree (HA/FA 1.51), followed by Quaternary red (1.49) and granite soil (1.38) (Table 3). Additionally, OM-R and NPK-R showed significantly higher ($P<0.01$) concentrations of soil available phosphorus (AP), available potassium (AK), total nitrogen (TN), soil microbial biomass carbon (SMBC), soil microbial biomass nitrogen (SMBN), and soil water content (SWC), in the three soils compared to other treatments (Table 4).

3.2 Relationships Among Soil Properties, Humus Carbon Fractions and Crop Yields

In granite soil, available phosphorus (AP), total phosphorus (TP), total nitrogen (TN), and soil organic carbon (SOC) were positively correlated, and negatively correlated with soil pH (Fig. 4). In Quaternary red soil, TP, TN, AP, available potassium (AK), exchangeable calcium (Ca^{2+}), magnesium (Mg^{2+}), aluminum (Al^{3+}), and hydrogen ion (H^+) exhibited significant ($P < 0.05$) positive correlation (Fig. 4). Humic acid carbon (HA-C), fulvic acid carbon (FA-C), and humin carbon (HU-C) were negatively correlated with soil pH (Fig. 4). HA-C was positively correlated with Ca^{2+} but negatively correlated with Mg^{2+}, AK, AP, soil pH, TN, SOC, H^+, TP, and Al^{3+}, while soil pH, Al^{3+}, Mg^{2+}, H^+, and Ca^{2+} exhibited positive correlations (Fig. 9). HA-C and HU-C also exhibited positive relationship with exchangeable Al^{3+}, while FA-C showed negative relationship with Al^{3+} and aluminum oxide (Al_2O_3) in granite soil (Fig. 5). In Quaternary red soil, HA-C showed positive relationship with Al^{3+}, whereas FA-C and HU-C exhibited negative relationships with Al^{3+} (Fig. 5). In purple sandy shale soil, HU-C and FA-C showed positive relationship with Al^{3+}, while HA-C exhibited negative relationships with both Al^{3+} and Al_2O_3 (Fig. 5). Moreover, crop yields in granite soil were significantly higher, with sweet potato (*Ipomoea batatas* 'Beauregard') yield reaching 25,000 kg ha^{-1} under NPK-R treatment and 22,136 kg ha^{-1} under OM-R treatment (Fig. 6). Sweet potato (*Ipomoea batatas* 'Beauregard') yield showed a significant positive correlation ($P < 0.01$) with available potassium (AK), while broad bean (*Vicia faba 'Aquadulce* Claudia') yield was positively correlated with total potassium (TK) and soil pH (Figs.7 and 10). In Quaternary red soil, NPK-R and OM-R treatments recorded the highest sweet potato (*Ipomoea batatas* 'Beauregard') yield of 24,012 kg ha^{-1} and 22,226 kg ha^{-1}, respectively (Fig. 6). Significant correlations were observed between sweet potato (*Ipomoea batatas* 'Beauregard') yield SOC, TN, AK, SWC, and TK (Fig.7), while broad bean (*Vicia faba* 'Aquadulce Claudia') yield was positively correlated with AK, BD, SWC, and soil pH (Fig.7). Humus carbon fractions (HA-C, FA-C, HU-C) showed strong correlations with both crop yields (Fig.7). In purple sandy shale soil, NPK-R (632.8 kg ha^{-1}) and NPK-T (475.2 kg ha^{-1}) treatments recorded the highest broad bean (*Vicia faba* 'Aquadulce Claudia') yield, with AP, SWC, SOC, BD, AK, and TN showing positive correlations with the yield (Figs.7 and 10).

3.3 Contributions of Fertility Indicators in The Three Soils Under Long-term Fertilization

The random forest model analysis identified key soil fertility indicators based on their relative importance scores (Fig. 8). In granite soil, calcium (25%), magnesium (21.43%), exchangeable aluminum (17.86%), and total

Table 1. Basic chemical and physical properties of the three soils at start of the experiment in 1982

Soil type	Total nutrient (g kg^{-1})					Available nutrient (mg/kg)			Field capacity	Soil texture
	pH	OM	TN	TP	TK	AN	AP	AK	%	
Granite soil	6.84	2.8	0.12	0.13	46.6	2.8	104.8	39.1	17.6	Sandy clay loam
Quatenary red soil	5.65	5.6	0.50	0.27	15.7	3.3	81.4	46.6	20.6	Clay
Purple sandy shale soil	8·86	3.9	0.38	0.53	28.9	5.5	97.7	25.6	16.7	Sandy loam

Table 2. The long-term fertilization treatments designed for the three parent material soils

Treatment	$(NH_4)_2SO_4$ kg/hm^2	$Ca(H_2PO_4)_2$ kg/hm^2	KCL g/hm^2	Organic fertilizer kg/hm^2	Rice straw
CK-T	0	0	0	0	0
CK- R	0	0	0	0	Return
NPK-T	75	75	125	0	0
NPK-R	75	75	125	0	Return
OM-T	0	0	0	1250	0
OM-R	0	0	0	1250	Return

Table 3. Soil humus composition in 0-20 cm layer of the three soils under different fertilization treatments

Soil type and Treatment	HA-C g kg^{-1}	FA-C g kg^{-1}	HU-C g kg^{-1}	HE-C g kg^{-1}	HA:FA	Soil texture
Granite Soil						
CK-T	3.00 ± 0.20c	1.10 ± 0.17e	0.25 ± 0.08d	7.22 ± 0.37d	1.44 ± 0.11	
CK-R	5.58 ± 0.91c	3.66 ± 0.87d	0.33 ± 0.04c	9.24 ±1.78c	1.52 ± 0.44	
NPK-T	5.88 ± 0.15b	4.04 ± 0.04c	0.41 ± 0.05b	9.92 ± 0.19c	1.46 ± 0.04	Clay loam
NPK-R	7.37 ± 0.48a	5.98 ± 0.54a	0.67 ± 0.06a	13.35 ± 0.72a	1.23 ± 0.14	
OM-T	5.97 ± 0.15b	4.59 ± 0.02c	0.41 ± 0.05b	10.56 ±0.15b	1.30 ± 0.03	
OM-R	6.54 ± 0.44a	4.84 ± 0.21ab	0.44 ± 0.02a	11.38 ±0.49b	1.35 ± 0.11	
Quaternary red soil						
CK-T	4.00 ± 0.51d	1.00 ± 0.14d	0.44 ± 0.01b	7.36 ±0.53d	1.81 ± 0.22	
CK-R	5.96 ± 0.55b	4.30 ± 0.43a	0.45 ± 0.05b	10.26±0.70b	1.39 ± 0.19	
NPK-T	5.47 ± 0.41b	4.15 ± 0.30ab	0.52 ± 0.01a	9.62 ±0.51c	1.32 ± 0.14	Clay
NPK-R	6.35 ± 0.97a	4.43 ± 0.69a	0.49 ± 0.04a	10.78 ± 1.19a	1.43 ± 0.31	
OM-T	6.17 ± 0.65ab	3.41 ± 0.57c	0.49 ± 0.02a	9.58 ± 0.86c	1.81 ± 0.36	
OM-R	5.11 ± 0.70c	4.36 ± 0.58a	0.48 ± 0.05a	9.47 ± 0.91b	1.17 ± 0.22	
Purple sandy shale						
CK-T	2.05 ± 0.09d	1.00 ± 0.06d	1.40 ± 0.01c	4.65 ± 0.11d	2.18 ±0.11	
CK-R	4.44 ± 0.40c	2.35 ± 0.25c	1.52 ± 0.02a	6.79 ± 0.47 b	1.89 ±0.26	
NPK-T	4.21 ± 0.16c	3.60 ± 0.33b	1.45 ± 0.03b	7.81 ± 0.37b	1.17 ± 0.12	Sandy loam

Soil type and Treatment	HA-C g kg^{-1}	FA-C g kg^{-1}	HU-C g kg^{-1}	HE-C g kg^{-1}	HA:FA	Soil texture
NPK-R	5.44 ± 0.41ab	5.72 ± 0.40a	1.49 ± 0.05b	11.16 ± 0.57ab	0.95 ± 0.10	
OM-T	4.30 ± 0.18c	2.58 ± 0.38c	1.48 ± 0.04b	6.88 ± 0.42a	1.67 ± 0.26	
OM-R	5.49 ± 0.23a	4.70 ± 0.24ab	1.53 ± 0.03a	10.19 ± 0.33b	1.17 ± 0.08	

Mean values ± standard errors of three replicates are presented. Values in a column followed by the same letter are not significantly different at $P < 0.05$. Humic acid carbon (HA-C), fulvic acid carbon (FA-C) humin carbon (HU-C). CK-T (control with straw take away), CK-R (control with straw return), NPK-T (NPK with straw take away), NPK-R (NPK with straw return), OM-T (straw take away), OM-R (straw return).

Table 4. Soil properties of Granite, Quaternary and Purple sandy shale soils under different long-term fertilization treatments

Soil type & Treatment	Soil pH	SOC g kg^{-1}	TN gkg^{-1}	TP g kg^{-1}	TK g kg^{-1}	AP mg kg^{-1}	AK mg kg^{-1}	C:N Ratio	Ca^{2+} $\text{Cmol}_+\text{kg}^{-1}$	Mg^{2+} Cmol_+ kg^{-1}	Al^{3+} Cmol_+ kg^{-1}	H^+ Cmol_+ kg-1	SWC (%)	BD g cm^3	CEC Cmol_+ kg^{-1}
Granite soil															
CK-T	5.1c	4.1c	0.9c	0.18c	46abc	3.28d	40d	3.6c	8.5b	0.8c	1.5b	0.13b	19b	1.4a	8a
CK-R	5.3bc	5.1c	1c	0.47b	47abc	4.37c	65cd	5.1a	7.7b	0.8c	1.4b	0.13b	20b	1.4a	8.7a
NPK-T	3.9d	13.6a	2.4a	0.82b	44c	55b	97bc	4.5b	7.7b	0.7cd	3.3a	0.54a	24ab	1.3bc	9.7a
NPK-R	4.3d	15.9a	2.9a	1.49ab	45bc	64a	121ab	5.7a	6.6c	0.7d	2.8a	0.44a	25a	1.2c	8.4a
OM-T	5.4b	7.1bc	1.4bc	0.18c	48ab	4.92c	140a	4.7b	8.3b	0.9b	0.3c	0.06b	22ab	1.4ab	9.6a
OM-R	5.8a	8.2b	1.8b	0.27c	50a	5.22c	128ab	5.3a	9.6a	1.0a	0.07c	0.02b	22ab	1.3abc	9.3a
LSD (0.05)	0.2	2.1	0.3	0.5	2.7	1.0	2.9	0.4	0.05	0.05	0.4	0.05	3	0.1	ns
Quaternary red soil															
CK-T	5.0c	6d	1.8d	0.3b	16a	3.40c	92d	3.3c	9ab	0.76b	2.7b	0.28b	23c	1.29a	8.4a
CK-R	5.1bc	8cd	2.1cd	0.3b	16a	4.78c	124cd	3.8c	8.5ab	0.77b	2.7b	0.22b	25bc	1.19ab	9.5a
NPK-T	3.8d	11ab	2.6b	1.6a	15a	48b	156bc	4.2b	6.8b	0.71b	6.1a	0.6a	26ab	1.15b	9.1a
NPK-R	3.9d	12a	3a	1.4a	14a	60a	197ab	5.2a	6.8b	0.7b	5.8a	0.67a	27a	1.2ab	9.5a
OM-T	5.3ab	9bc	2.3bc	0.4b	15a	5.5c	153bc	3.9c	11.6a	1.02a	0.8c	0.18b	23c	1.28a	9.3a
OM-R	5.4a	10abc	2.6b	0.3b	16a	3.85c	224a	4.9b	9.7ab	0.91ab	1.2c	0.15b	24bc	1.26a	8.7a
LSD (0.05)	0.1	0.8	0.2	0.1	ns	2.2	3.6	0.2	2.2	0.1	0.8	0.1	0.6	0.1	ns
Purple sandy shale soil															
CK-T	8.5bc	3.5c	1.6d	0.6b	31a	2.87c	56d	2.2b	54ab	0.91b	-	-	18ab	1.5a	8a
CK-R	8.5abc	4.2bc	1.8cd	0.5b	31a	4.95c	60d	2.3b	56a	0.94ab	-	-	18ab	1.4ab	9.1a
NPK-T	8.3d	7.6ab	2.4ab	1.4a	34a	29b	161b	3.2a	46b	0.92b	-	-	20ab	1.3bc	8.1a
NPK-R	8.4cd	8.2a	2.7a	1.8a	32a	38a	225a	3.4a	49ab	0.93ab	-	-	21a	1.3c	8.9a
OM-T	8.5ab	3.9c	1.8cd	0.4b	33a	3d	104c	2.2b	52ab	0.95ab	-	-	18b	1.5ab	8.4a
OM-R	8.6a	6.6abc	2.2bc	0.5b	33a	7c	122bc	3.0a	51ab	0.98a	-	-	19ab	1.4ab	8.8a
LSD (0.05)	0.1	2.3	0.3	0.6	ns	3	2.6	0.3	6	0.3	-	-	1.8	0.1	ns

SOC (Soil Organic Carbon), TN (Total Nitrogen), TP (Total Phosphrus), TK (Total Potassium), AP (Available Phosphrus)AK (Available Potassium) C:N (Carbon-to-Nitrogen ratio) Ca^{2+} (Calcium) Mg^{2+} (Magnesium) Al^{3+} (Exchangeable Aluminium) H^+ (Hydrogen ions) SWC (Soil Water Content) BD (Bulk Density) and CEC (Cation Exchange Capacity). CK-T (control with starw take away), CK-R (control with rice straw), NPK-T (NPK with starw take away), NPK-R (NPK with starw return), OM-T (starw take away), OM-R (straw return). LSD 0.05 values indicate least significant differences at the 5% level to discern impact of treatments in the three soils. There are no values for the Al^{3+} and H^+ in the puurple sandy shale soil due to the higher soil pH.

phosphorus (14.29%) were the most influential factors (Fig. 8). In Quaternary red soil, bulk density (22.22%) had the highest importance, followed by available phosphorus (16.67%), calcium (9.44%), soil water content (3.89%), and available potassium (2.76%). For purple sandy shale soil, available potassium (25%) was the most important indicator, followed by soil water content (21.43%), total nitrogen (17.86%), and available phosphorus (14.29%) (Fig. 8).

4. DISCUSSION

4.1 Changes in Physicochemical and Biological Properties of Three Soils Under Long-Term Fertilization

After 41 years of different fertilization practices, the contrasting responses of the three soils demonstrate that inherent soil properties can influence soil health under various agricultural management practices. The minimal pH decline observed in the granite and purple sandy shale soils, despite prolonged chemical fertilization, could be attributed to their inherent buffering capacity. In granite soil, higher levels of soil organic carbon (SOC) and humus, particularly humic acid carbon (HA-C), may have interacted with its mineral composition to improve the soil pH compared with the Quaternary red soil (Fig.1). The significant increases in the soil organic carbon (SOC) and humus carbon content in the treatments with straw return contributed to improvements in soil structure, nutrient retention, and microbial activity (Lal, 2020; Meena et al., 2020). This improvement, along with the interplay between the organic straw amendments and the soil mineralogy also help to stabilize the soil pH (Jiang et al., 2023; Wang et al., (2024). The pH results of the purple sandy shale and granite soils showed that despite their stronger pH buffering ability under straw return, they are not immune to the cumulative acidifying effects of chemical fertilizers. Quaternary red soil showed the most pH decline under chemical fertilizers with straw take away (NPK-T) treatment (Table 4). This indicates the soil's heightened susceptibility to acidification, likely due to its lower soil pH buffering compared with the granite and purple sandy shale soils, which showed better responses to the mitigating effects of straw application (Table 4). Continuous application of the chemical fertilizer without straw (NPK-T) increased the acidification by depleting base cations such as calcium and magnesium, thereby increasing the concentration of exchangeable aluminum ($Al3^+$) (Table 4). These interactions not only reduced the soil pH but also created a less favorable environment for soil microbial activity (Fig.3). A study by Wang et al., (2024) reported vulnerability of the Quaternary red soil to long-term chemical fertilization and highlighted the role of organic amendments, like straw in mitigating acidification in this soil. The low pH in the Quaternary red soil created unfavorable conditions that negatively impacted crop yield, leading to the lowest broad bean (*Vicia faba* 'Aquadulce Claudia') yield observed in this soil compared with the purple sandy shale soil (Fig. 6). Despite the low pH in the Quaternary red soil, sweet potato (*Ipomoea batatas* 'Beauregard') yield was higher in this soil than in the alkaline-purple sandy shale soil (Fig. 6). Sweet potato has shown adaptability to acidic conditions, making it a viable crop for acid-prone soils. Studies by Dong, (2021); Tedesco et al., (2023) showed that sweet potato (*Ipomoea batatas* 'Beauregard') can tolerate a soil pH at 5.0, with optimal growth occurring in slightly acidic soils with a pH range of 5.5 to 6.5. This adaptability is likely attributed to the plant's efficient nutrient uptake mechanisms and its ability to thrive in well-drained, loamy soils, which are often present in acidic environment. The higher SOC and humus carbon content in the Quaternary red soil, despite declining pH, is also attributed to the soil initial organic carbon content, supported by the straw return, contributing to sustain carbon buildup rather than carbon loss in this soil (Fig. 2) (Galantini & Rosell, 2006). This observation is consistent with Liu et al., (2021), who reported that straw inputs in the soil can provide buffer against acidification. Under the straw return treatments, the purple sandy shale soil exhibited the higher resilience against soil pH decline compared to the Quaternary red and granite soils (Fig.1 and Table 4). The geological composition of purple sandy shale soil, characterized by sandstone and shale, can support its resistance to acidification, even under long-term chemical fertilization. A study by (Zhao et al., 2019) showed that soils derived from purple shale parent materials tend to maintain neutral pH levels, ranging from 7.41 to 8.00, with strong natural buffering against acidification. Furthermore, the balanced distribution of humic acid, fulvic acid, and humin carbon fractions in this soil improved the cation exchange capacity (CEC) (Table 4). Soil humus carbon fractions have known to improve soil structure, soil water-holding capacity, and soil cation exchange capacity (CEC), thereby supporting stable nutrient cycling processes in the soil (Zhang et al., 2024). Additionally, humin function as a cation exchange system that aids in soil structure improvement and stability for water holding capacity. Soil humus can contribute to soil resilience against acidification and help to sustain productive agricultural systems over extended periods (Wang et al., 2024). The rice straw return in this study contributed to the improvement in soil pH and microbial activity, and its combination with the mineral fertilizers (NPK) increased nutrient availability for crop production in the three soils (Table 4 and Fig.6). Studies done by Wang et al.,(2023); Yan et al.,(2023); Luo et al., (2023); Rahman et al., (2016) also showed that long-term straw return with NPK fertilizers improved soil nutrient concentrations, contributing to higher crop yield. Organic acid formation during straw decomposition temporarily reduce soil pH but in the long term, organic matter accumulation in the soil can buffer this effect and stabilize soil pH over time Liu et al., (2023), whereas acidification under chemical fertilizers could be attributed to nitrification processes, where ammonium converts to nitrate, releasing hydrogen ions (H^+), thereby elevating soil acidity (Ni et al., 2023). Straw with chemical fertilizers (NPK-R) significantly increased the soils nutrient concentrations with higher improvement in crop yield compared to the single straw return (OM-R) and the straw take away treatments (Table 4 and Fig. 6) (Farooqi et al., 2023; Mushtaq et al., 2021). Soil humus carbon content was higher in treatments with straw return than treatments without straw (Table 3) (Kaur et al., 2008). This is consistent with the findings of Guggenberger, (2005); and Jindo et al., (2011), who reported that organic material, such as straw return to the soil can stimulate microbial activity, which in turn increase the formation of humus substances. Additionally, the highest humic acid to fulvic acid ratio (HA:FA) was recorded in the purple sandy shale soil, which indicates improved humification and organic matter stability, compared to the Quaternary and granite soils (Table 3). Higher HA:FA ratio reflects greater humification and are indicative of more stable soil organic matter (DOU et al., 2020; Zhang et al., 2017).

Meanwhile, the soil humus carbon fractions, humic acid carbon (HA-C), fulvic acid carbon (FA-C), and humin carbon (HU-C) strongly correlated with soil pH, soil organic carbon (SOC), available potassium (AK), available phosphorus (AP), total nitrogen (TN), and total phosphorus (TP). The incorporation of rice straw and NPK fertilizers increased humus formation and higher soil humification can contribute to soil organic matter stability and improve nutrient availability (Xu et al., (2017); Zhang et al., 2018). The negative correlations between the soil humus carbon fractions and soil pH, while positively correlating with the soil nutrient concentrations suggest that humification is improved in environments where organic matter decomposition drives soil nutrients release and stabilization (Khaled et., 2011; Xu et al., 2020).The application of rice straw, a carbon-rich substrate, replenished humus carbon while also serving as an external carbon source for microbial activity (Dhamak et al., 2020; Fan et al., 2022; Piccolo et al., 2004; Yu et al., 2022). Under straw return with mineral fertilizers treatment (NPK-R), soil microbial biomass carbon (SMBC) and soil microbial biomass nitrogen (SMBN) were higher in granite soil compared with Quaternary and purple sandy shale soils (Fig. 3). This contributed to improvement in organic matter stability and the soil total and available nutrients, such as TN, TK, AK, AP and the organic carbon content in these soils (Table 4) (Heijboer et al., 2016; Luo et al., 2023; Lian et al., 2022). The NPK-R and OM-R treatments increased the carbon to nitrogen ratio (C/N) compared to other treatments (Table 4). This likely contributed to improvement in organic matter decomposition and nutrient cycling in the soil (Zech et al., 1997). The higher CEC values reflect the soil ability to retain essential nutrients and buffer against leaching, a key factor for sustainable soil management (Oorts et al., 2007; Walker et al., 2006). These results highlight the benefits of straw return with chemical fertilizers in improving the soil and crop productivity (Chen et al., 2020; Zhang et al., 2021).

The application of manure and continuous straw return, along with mineral fertilizers, can improve the pH and fertility in the Quaternary red and granite soils. This can support the sustainable cultivation of nutrient-demanding crops like sweet potato (*Ipomoea batatas* 'Beauregard') and broad bean (*Vicia faba* 'Aquadulce Claudia'). Integrating organic amendments with mineral fertilizers has shown to improve soil quality and crop yield (Zhang et al., 2024). In purple sandy shale soil, the consistent application of straw and other organic amendments, alongside balanced mineral fertilizers, is crucial for sustaining the soil pH for long-term productivity. Organic soil amendments, such as compost and manure, improve soil structure, nutrient availability, and microbial activity, which are essential for sustaining soil health and crop yields (Chen et al., 2020). These soil-specific management approaches are vital for optimizing fertilization benefits, especially as global agriculture faces challenges from soil degradation and climate change. The variability in these soils responses to similar fertilization treatments underscores the necessity for precision soil management practices that consider the characteristics of each soil type to achieve sustainable production.

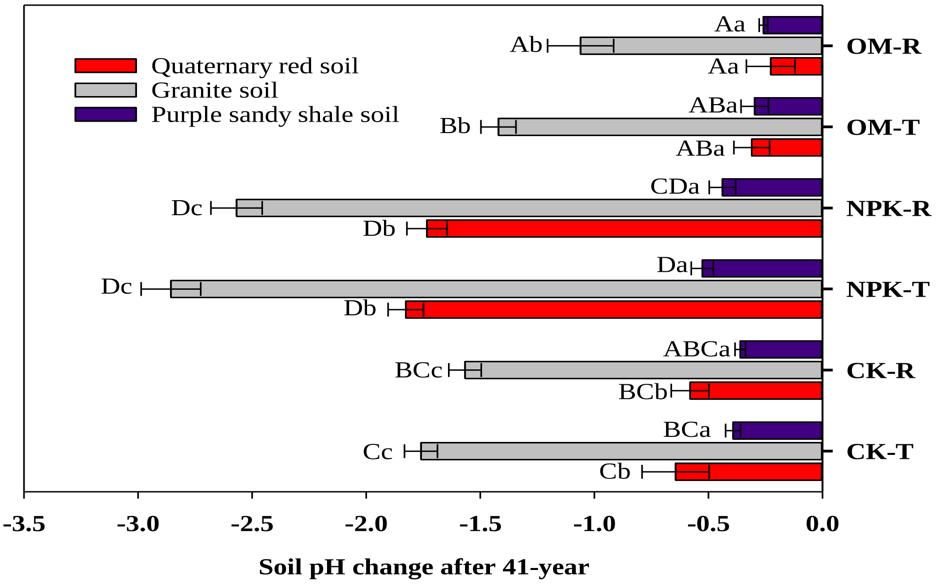

Fig. 1. Changes in soil pH under different fertilization treatments in granite, Quaternary red and purple sandy shale and soils. Each soil type pH change is represented by different color bar, with treatments on the vertical axis and changes in pH units on the horizontal axis, scaled negatively, reduction in pH levels (an increase in soil acidity). Uppercase letters compared different soil types within the same treatments, while the lowercase letters compared treatments within the same soil. Bars with both uppercase and lowercase letters mean statistical significant (*P* < *0.05*) differences in pH change, between soil types and treatments.

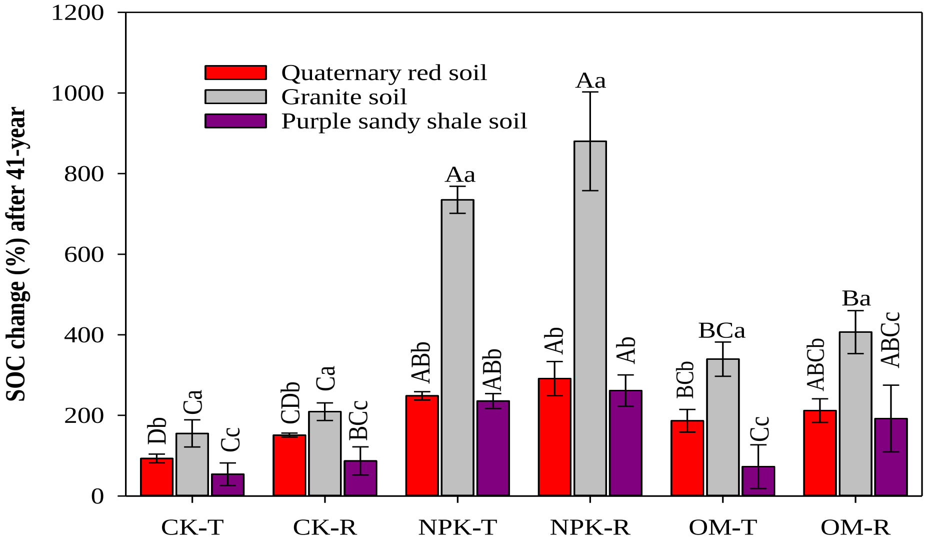

Fig. 2. Change of soil organic carbon (SOC) under different long-term fertilization in granite, Quaternary red and purple sandy shale soils after 41 years. Letters above the bars represent statistical *(P< 0.05)* groupings, while those with the same letters are not statistically significant. Uppercase letters compared between soil types within a single treatment, while lowercase letters compared between treatments within a single soil type.

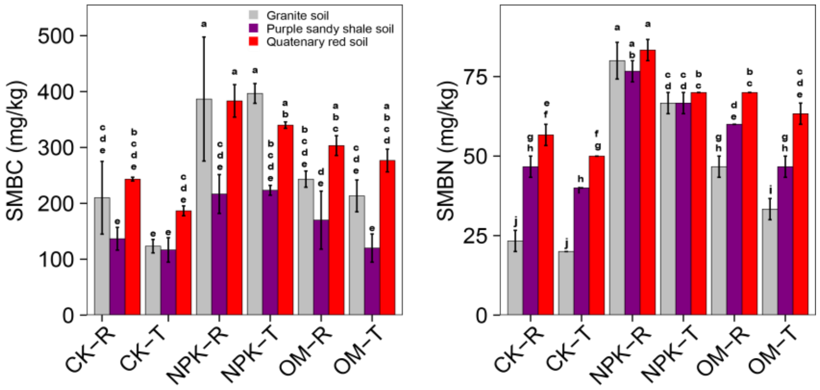

Fig. 3. Mean standard deviation and count of SMBC (Soil Microbial Biomass Carbon) and SMBN (Soil Microbial Biomass Nitrogen) under different fertilization treatments in the granite, Quaternary red and purple sandy shale soils. Lowercase letters denote statistical significance *(P< 0.05)* with bars having the same letter within a soil type not differing significantly from each other. Each colored bar represents the level of SMBC and SMBN for a particular treatment in a given soil type, while the error bars indicate variability of the treatment effects

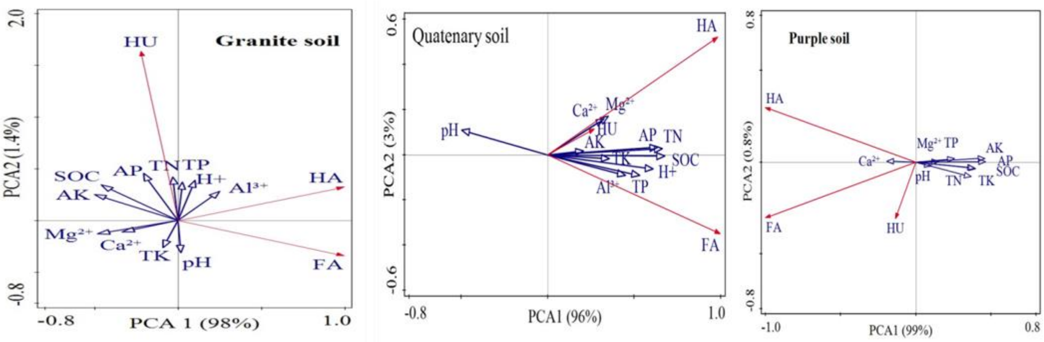

Fig. 4. Principal component analysis of soil properties and humus carbon fractions in granite and Quaternary and purple sandy shale soils, employed to examine patterns and relationships of humus carbon fractions and the soil properties. HA-C (humic acid carbon), FA-C (fulvic acids carbon), and HU-C, (humin carbon)

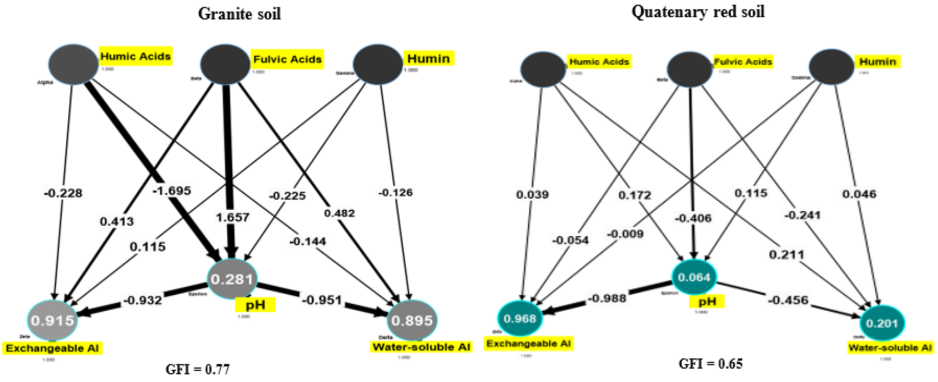

Fig. 5. Partial Least Squares Structural Equation Modeling (PLS-SEM) employed to estimate complex cause-effects of humus carbon fractions on soil pH and aluminum in the acidic granite and Quaternary red soils. Numbers on the arrow are standardized path coefficients, while numbers inside the latent variable circles are the R^2 values. Thickness of the line indicates magnitude of the path coefficient. GFI is goodness-of-fit index

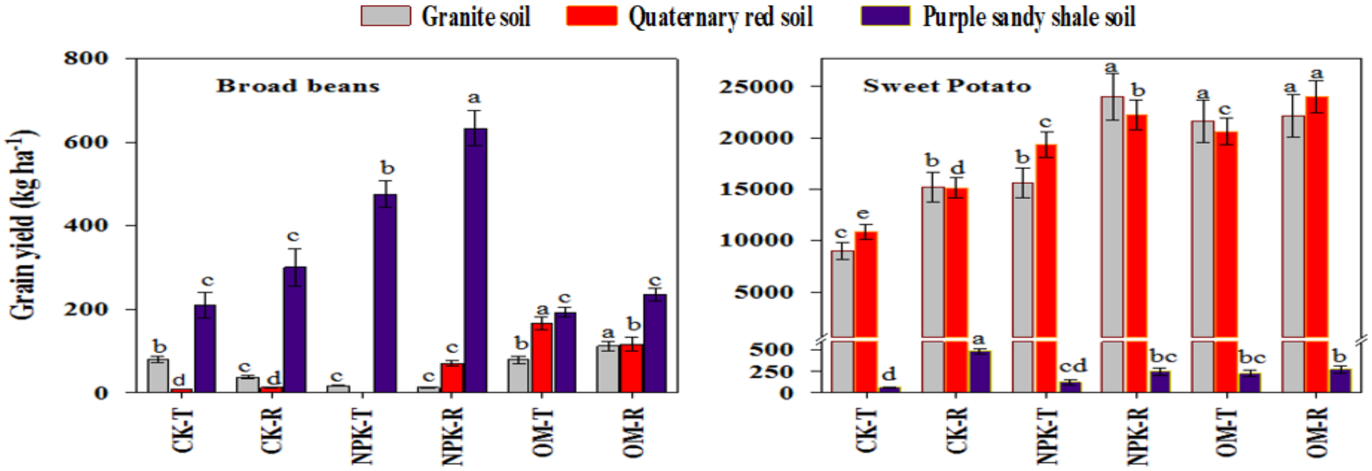

Fig. 6. Sweet potato (*Ipomoea batatas* 'Beauregard') and broad bean (*Vicia faba* 'Aquadulce Claudia') yields under different long-term fertilization treatments in granite, Quatenary red soils and purple sandy shale soil. Lowercase letters indicate statistical significance (*P< 0.05*) where different letters above the bars mean significant differences in yields among soil treatments

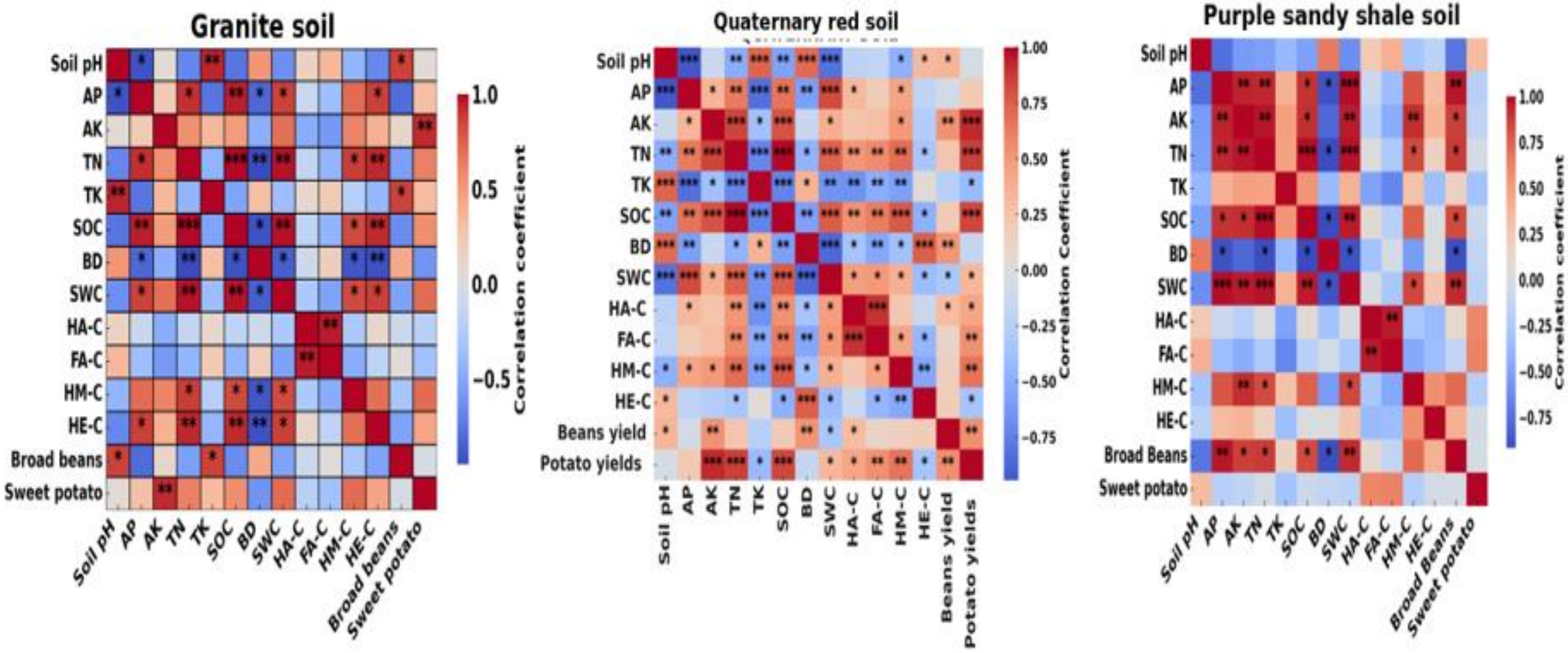

Fig. 7. Correlation Analysis amongst soil properties, sweet potato (*Ipomoea batatas* 'Beauregard') and broad bean (*Vicia faba* 'Aquadulce Claudia') yields and soil humus carbon fractions in granite, Quaternary and purple sandy shale soils. (*) correlation is significant at the *P < 0.05* level, (**) correlation significant at the *P < 0.01* level, (***) correlation significant at the *P < 0.001* level. BD (Bulk density), SWC (Soil water capacity), TN (Total nitrogen), AP (Available phosphorus), AK (Available potassium), TP (Total phosphorus), TK (Total potassium), SOC (Soil organic carbon), HA-C (Humic acids carbon), FA-C (Fulvic acids carbon), and HU-C (Huimin carbon).

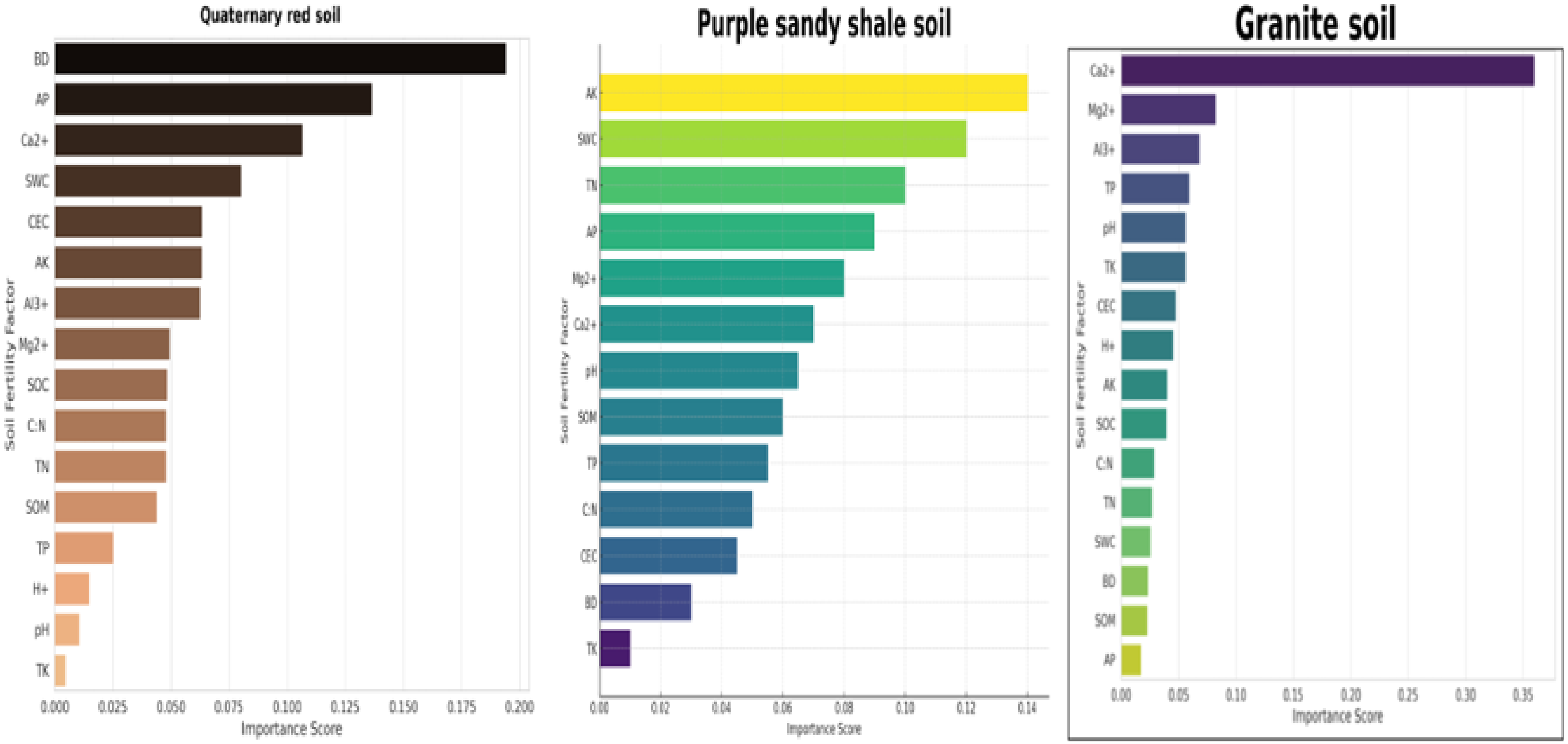

Fig. 8. Relative importance of fertility factors in the granite, Quaternary red and purple sandy shale soils based on random forest model. Relative fertility factors are on the y-axis and corresponding importance scores on the x-axis. Accuracy importance measure was computed for each tree and averaged over the forest (5000 trees). Percentage of increase in MSE (mean squared error) of variables was used to estimate the importance of these predictors, and a higher MSE% value implies more important predictors. Significance levels of each predictor were $P<0.001$ and $P<0.05$.

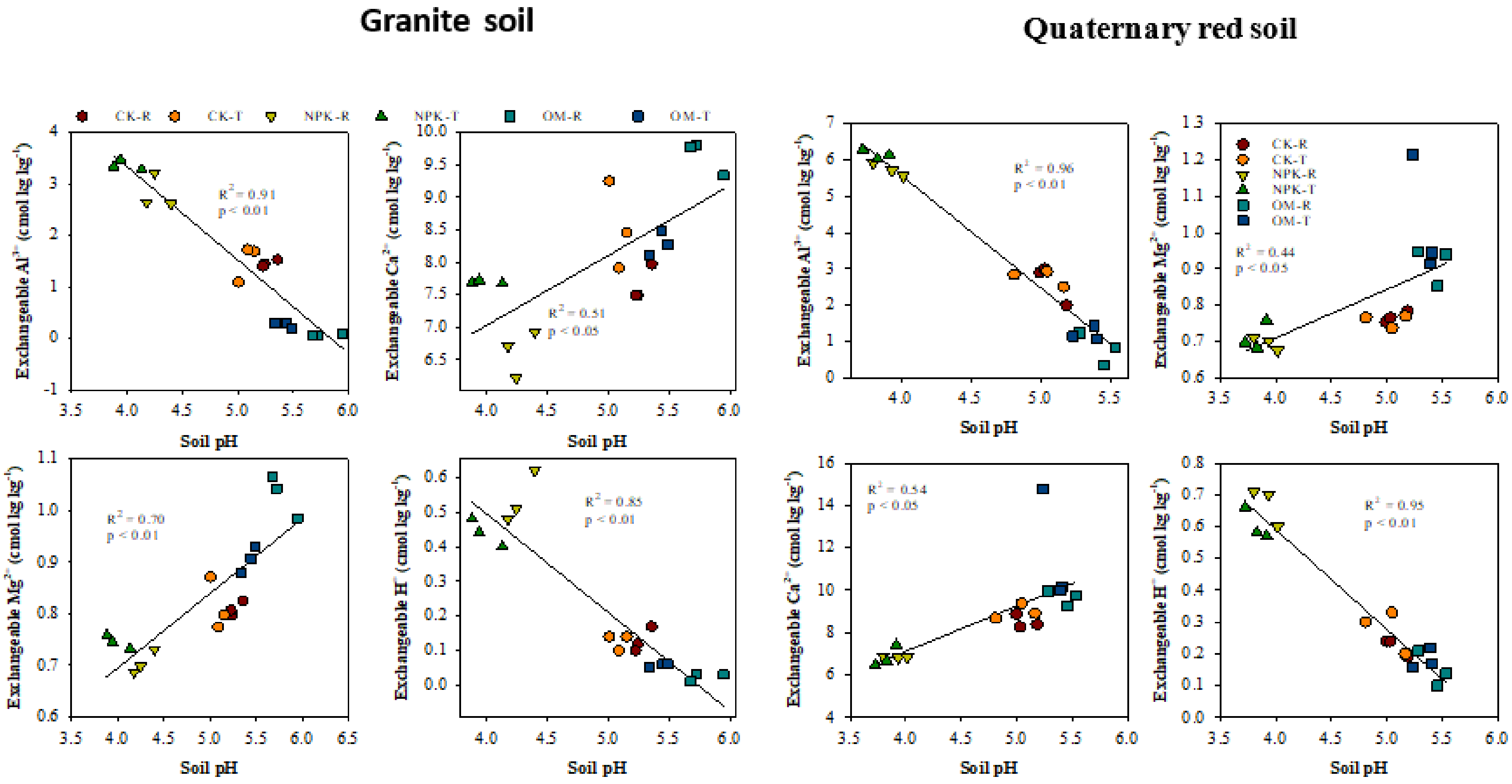

Fig. 9. Regression plots showing the relationship between soil pH, exchangeable magnesium (Mg^{2+}), exchangeable aluminum (Al^{2+}), exchangeable hydrogen (H^+), exchangeable calcium (Ca^{2+}), in granite and Quaternary red soils. Each plot shows a different relationship with corresponding regression lines, R^2 values, and p-values, indicating the strength and significance of the relationships.

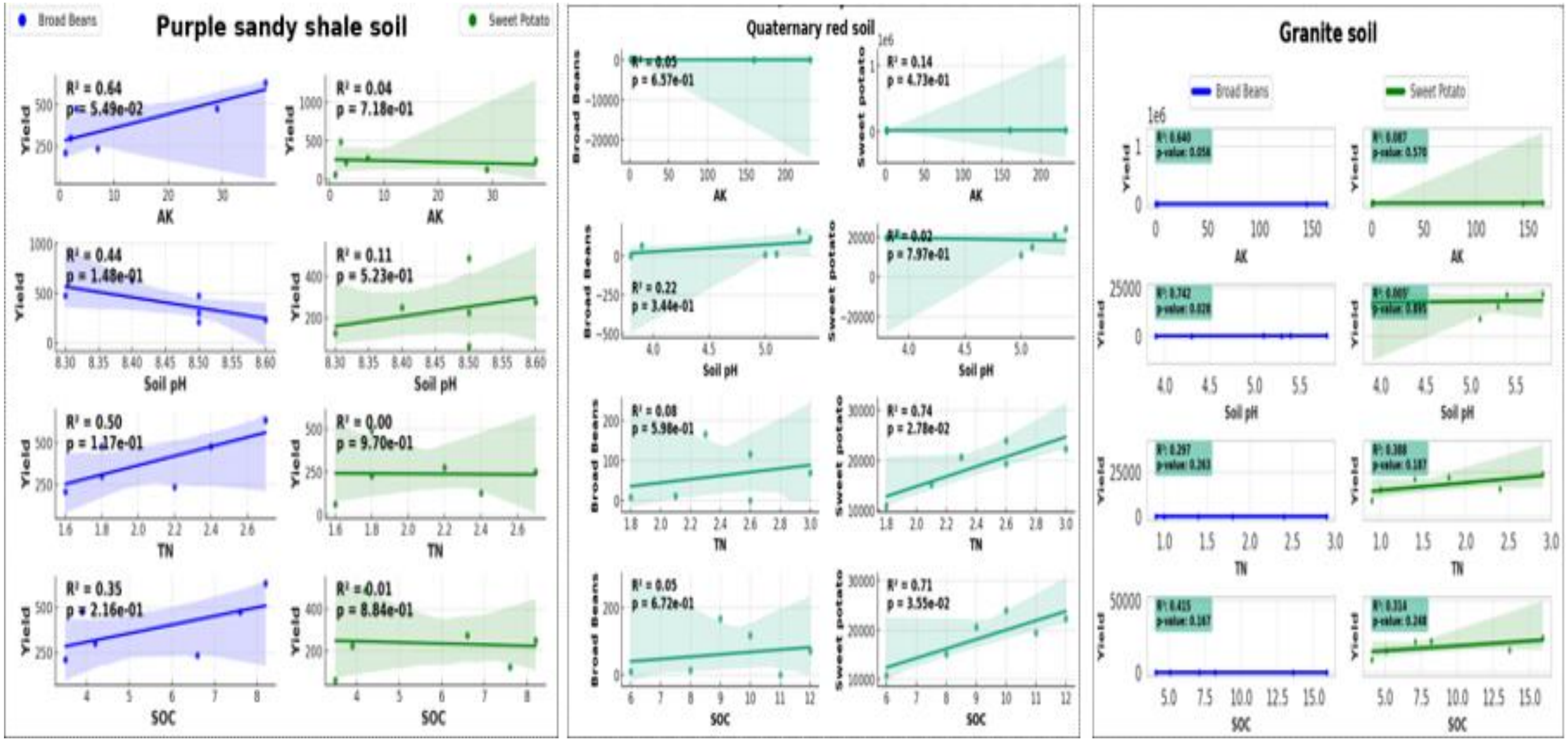

Fig. 10. Linear regression analysis showing relationship between crop yields (sweet potato and broad bean), available potassium (AK), total nitrogen (TN) and soil organic carbon (SOC) and in the granite, Quaternary red and purple sandy shale soils. R² is the coefficient of determination and the indicated p-values, while the shaded areas around the lines indicate the confidence intervals.

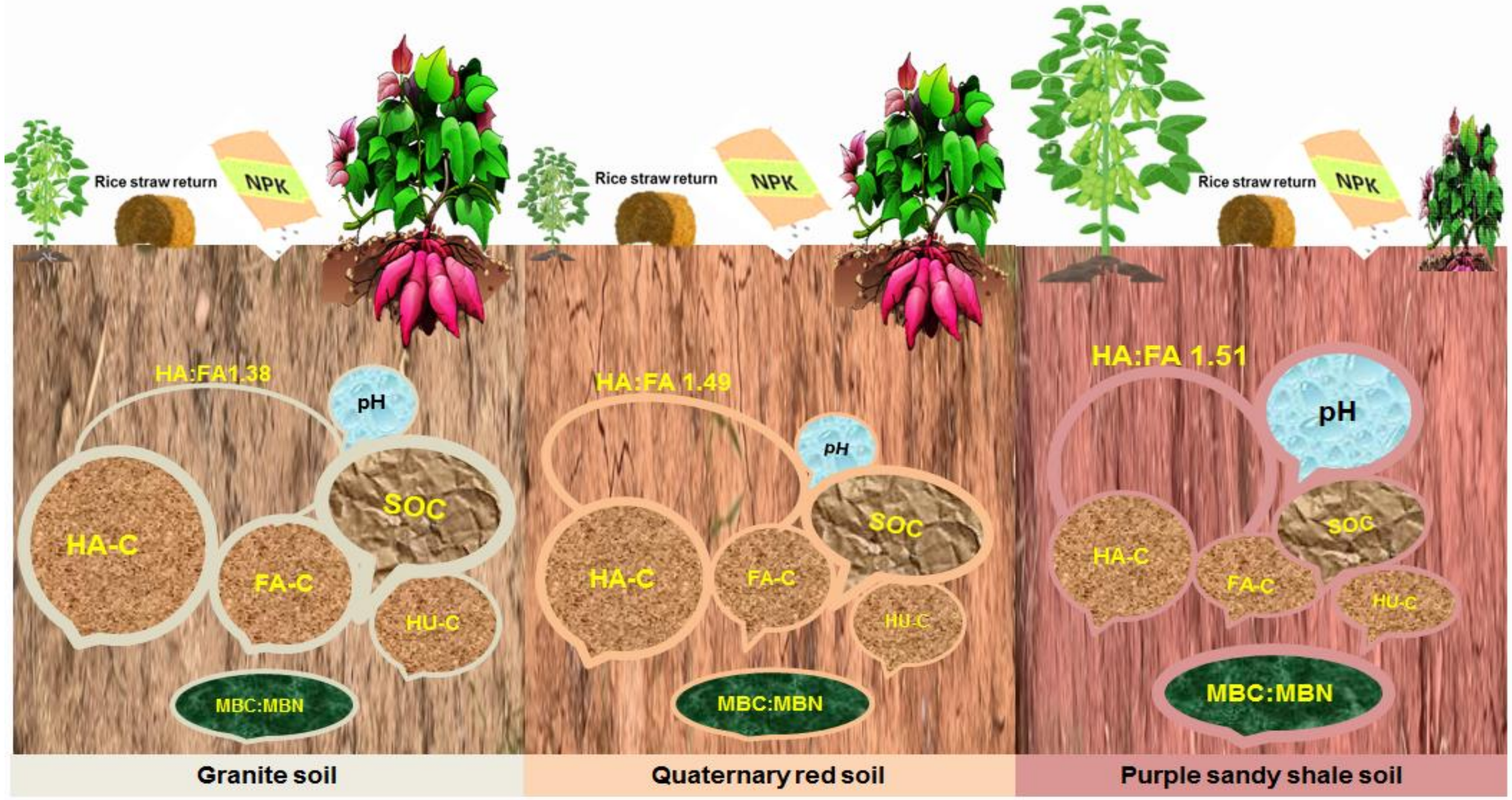

Fig. 11. Conceptual model illustrating the study's key findings, such as soil humus carbon fractions: humic acids carbon (HA-C), fulvic acids carbon (FA-C), and humin carbon (HU-C). Humic acids to fulvic acid ratios (HA:FA), soil organic carbon (SOC), soil pH, soil microbial biomass carbon to soil microbial biomass nitrogen ratios (MBC:MBN), and crop performance (broad bean, Vicia faba 'Aquadulce Claudia' and sweet potato, Ipomoea batatas 'Beauregard') in the granite, Quaternary red, and purple sandy shale soils under rice straw return and NPK fertilization. Variable sizes, text, and line weights indicate the relative magnitudes of concentrations and crop yield performance.

4.2 Relationship Between Soil Properties and Crop Yield Under Long-Term Fertilization

In granite and Quaternary red soils, sweet potato (*Ipomoea batatas* 'Beauregard') yield was notably higher than in the purple sandy shale soil (Fig. 6). The crop yield improvement was strongly linked to the positive correlation between total nitrogen (TN), soil organic carbon (SOC), and humus carbon fractions (Fig.7). These soil nutrients are essential for improvement in soil structure, microbial activity, crop productivity (Lal et al., 2020; Oldfield et al., 2019). In granite and Quaternary red soils, NPK-R and OM-R treatments produced the highest sweet potato yield but broad bean (*Vicia faba* 'Aquadulce Claudia') yield was lower in these two soils compared to sweet potato yield (Fig. 6).

Sweet potato, being more tolerant to lower pH, performed well in both soils, whereas broad bean yield was higher in the purple sandy shale soil, particularly under the NPK-R and NPK-T treatments (Fig. 6). These results highlight the differing adaptability of crops to specific soil types, with sweet potato thriving in the low pH soils, while broad bean requires more stable soil conditions for optimal growth (Nasiroleslami et al., 2021; Jiang et al., 2023; Nasiroleslami et al., 2021). The significant reduction in soil pH under the mineral fertilizer with straw take away treatment (NPK-T) in the Quaternary red soil increased the concentration of exchangeable aluminum (Al^{3+}) (Table 4). This can adversely affect root development and nutrient uptake in the broad bean crop (Hartemink & Barrow, 2023). Additionally, low soil pH can reduce the availability of essential soil nutrient, especially phosphorus, which can limit plant growth. These factors collectively contributed to the observed lack of broad bean yield under the NPK-T treatment in the Quaternary red soil (Barrow & Hartemink, 2023). Although chemical fertilizers can supply a substantial amount of the nutrients needed by crops, the lack of organic components leads to soil degradation, nutrient depletion, and fluctuations in crop yield (Chaudhury et al., 2005; Liu et al., 2021; Zhao et al., 2013). However, long-term organic amendments such as straw input can improve soil nutrients and resilience to mitigate yield fluctuations caused by environmental stressors (Giacometti et al., 2021; Zhang et al., 2015). The higher nutrient concentrations and carbon-to-nitrogen ratio (C/N) in the granite and Quaternary soils (Table 4) also contributed to the higher crop yield observed in these two soils compared to the purple sandy shale soil (Fig. 6). C/N ratio is a crucial indicator of soil health and crop yield potential, which can influence nutrient availability and microbial processes under different fertilization systems in soil (Huang et al., 2017; Liu et al., 2023). Sweet potato yield consistently outperformed broad bean yield in both granite and Quaternary red soils, while the reverse was true for purple sandy shale soil, where broad bean yield was the highest (Fig. 6). These results suggest that the crops performance was strongly influenced by the soil properties, particularly the soil pH and soil organic carbon content. Sweet potato adaptability to the lower pH and the nutrient variability in the Quaternary red and granite soils makes it a suitable crop for these soils, while the broad bean is most suitable for purple sandy shale soil (Fig. 6). These differences in crop yield responses suggest the importance of crop selection in relation to the soil characteristics and sustainability of the fertilization practices. These results reinforce the necessity of precision fertilization strategies that account for the specific interactions between soil properties and crop needs. Integrated nutrient management practices, involving organic amendments such as rice straw and the balanced application of mineral fertilizers (NPK), are essential for maintaining soil health and ensuring long-term crop productivity. This approach could also help reduce the environmental impact of intensive farming systems.

5. CONCLUSION

Straw return improved soil pH and humus carbon, while NPK fertilizer significantly reduced pH in the Quaternary red and granite soils compared with the purple sandy shale soil. The NPK fertilizer with straw (NPK-R) treatment significantly increased nutrient concentrations and crop yield compared to the single straw return (OM-R) treatment in all three soils. Although the mineral fertilizers provided immediate nutrients for crop productivity, their application without straw led to a decline in soil pH. Straw return with mineral fertilizers proved to be the most effective approach for improving soil properties and increasing crop yield. Adding lime to the mineral fertilizers with straw take away (NPK-T) treatment could mitigate pH decline in the Quaternary red and granite soils, while incorporating leguminous cover crops into the purple sandy shale soil could improve the soil organic matter for sustained productivity.

STUDY HIGHLIGHTS

1. Straw return improved soil pH, while NPK fertilizer reduced pH in the three soils.
2. Straw combined with NPK fertilizer increased humus carbon fractions, SMBC, and crop yield.
3. Humus carbon fractions exhibited a negative correlation with soil pH.
4. Crop yield significantly correlated with soil pH, humus carbon fractions, SOC, TN, AK, AP.

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 the writing or editing of this manuscript.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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