Original Research Article

Long-term organic and inorganic fertilization affect soil pH, humus carbon fractions, and crop yield in three soils

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.

Method: A field experiment was conducted in 2023 based on a long-term study established in 1982. 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 (HA-C, FA-C, HU-C) in the three soils. NPK-R increased SOC and SMBC in granite soil than in Quaternary red and purple sandy shale soils. Average humic acid to fulvic acid ratio (HA:FA) across all six treatments was 1.46, with purple sandy shale soil exhibiting the highest humification degree (HA:FA 1.51), surpassing Quaternary red (1.49) and granite soils (1.38).NPK-R produced the highest sweet potato yields in granite (25,000 kg ha^{-1}) and Quaternary red soils (24,012 kg ha^{-1}) and the highest broad bean 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, while NPK fertilizer reduces it. 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 soils.

Keywords: Long-term fertilization, Humus carbon fractions, soil pH, SOC, crop yield

Highlights

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

1. INTRODUCTION

Soil acidification and humus carbon depletion pose significant challenges to agricultural 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. Humus is a form of soil 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 et al., (2015);Powlson et al., (2012), whichinfluences 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 inorganicfertilization, there are still gaps in our understanding of the underlining mechanisms through which they impact soilproperties 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 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).Conversely, 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 or 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 soil 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, southern 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 8m^2 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.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

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).

2.4. 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 across the treatments and soils. The OM-R treatment stabilized pH in all three soils, while NPK-T caused the greatest reductions, with pH decreases of -2.5 units in granite and -3.0 units in Quaternary red soils (Fig. 1, Table 4). NPK-R also reduced the pH, but to a lesser extent than NPK-T. The pH was more stable in purple sandy shale soil than the Quaternary red and granite soils under all treatments (Fig. 1, Table 4). Meanwhile, granite soil accumulated the highest humus carbon content (HA-C 48.64%, FA-C 37.97%, HU-C 2.73%) and soil organic carbon (SOC 15.9 g kg^{-1}) under the NPK-R treatment (Table 3 and Table 4). In Quaternary red soil, HA-C, FA-C, and HU-C accounted for 48%, 21.35%, and 11.60%, respectively, with an SOC of 12 g kg^{-1}. In purple sandy shale soil, humic acid carbon was 45%, fulvic acid carbon was 33%, and HU-C reached 16.81%, with SOC of 8.2 g kg^{-1} under the NPK 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 and Table 4).Additionally, OM-R and NPK-R treatments 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), soil water content (SWC), and bulk density (BD) across the three soils compared to the other treatments (Table 4).

3.2.Relationships among soil properties,humuscarbon 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 correlations (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+} exhibitedpositive correlations (Fig. 9). HA-C and HU-C were also positively correlated with exchangeable Al^{3+}, while FA-C negatively correlated with Al^{3+} and aluminum oxide (Al_2O_3) in granite soil (Fig.5). In Quaternary red soil, HA-C was positively correlated with Al^{3+}, whereas FA-C and HU-C were negatively correlated with Al^{3+} (Fig. 5). In purple sandy shale soil, HU-C and FA-C were positively correlated with Al^{3+}, while HA-C exhibited negative correlations 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 and 22,136 kg ha^{-1} under OM-R (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, 10).In Quaternary red soil, NPK-R and OM-R 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. Humus carbon fractions (HA-C, FA-C, HU-C) also correlated with 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 positively correlating with the yield (Figs. 7, 10).

3.3. Contributions of fertility indicatorsin thethree soils underlong-term fertilization

The random forest model analysis identified key soil fertility indicators based on their relative importance scores. In granite soil, calcium (25%), magnesium (21.43%), exchangeable aluminum (17.86%), and total 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 varied fertilization practices, the contrasting responses of the three soils showed that inherent soil properties could also influence soil health under different agricultural management practices. The minimal pH decline observed in the granite and purple sandy shale soils, despite prolonged chemical fertilization, could also be attributed to their inherent buffering capacities. 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 enhance resistance to acidification compared to the Quaternary red soil (Fig. 1). The significant increases in SOC and humus content in treatments with straw contributed to improvements in soil structure, nutrient retention, and microbial activity (Lal, 2020; Meena et al., 2020).This improvement, coupled 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 better buffering capacity against pH reduction under straw application, they are not immune to the cumulative acidifying effects of the chemical fertilizers over time.The Quaternary red soil showed the most pH decline under NPK-T treatment (chemical fertilizer straw take away), (Table 4). This indicates the soil's heightened susceptibility to acidification, likely due to its lower buffering capacity compared to granite and purple sandy shale soils, which showed better responses to the mitigating effects of straw application. The continuous application of chemical fertilizers without straw return accelerated acidification by depleting base cations such as calcium and magnesium and increasing the accumulation of exchangeable aluminum. These changes not only reduced pH but also created a less favorable environment for soil microbial activity and nutrient availability. A study by Wang et al. (2024) reported the vulnerability of the Quaternary soil type to long-term chemical fertilization and highlighted the role of organic amendments in mitigating soil acidification.The low pH in the Quaternary red soil created unfavorable conditions that negatively affected crop performance, resulting in the lowest broad bean (*Vicia faba* 'Aquadulce Claudia') yield observed in this soil (Fig.6). Despite the challenges posed by the low pH in the Quaternary soil, sweet potato (*Ipomoea batatas* 'Beauregard') yield was higher in this soil compared to the alkaline purple sandy shale soil (Fig 6). Sweet potato has demonstrated 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 ('Beauregard') can tolerate a soil pH as low as 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 content in the Quaternary red soil, despite the declining pH, could also be attributed to the soil initial organic carbon content, supported by the straw return, contributing to sustain carbon buildup rather than carbon lossin the soil (Figure 2). 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 higherresilience against pH decline compared to the Quaternary red and granite soils (Table 4). The geological composition of purple sandy shale soil, characterized by sandstone and shale, contributes to 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, indicating a natural buffering capacity against acidification. Furthermore, the balanced distribution of humic acid, fulvic acid, and humin fractions in this soil enhances cation exchange capacity (CEC) and improves the soil structure.

Humic substances, including humic and fulvic acids, are known to improve soil structure, water-holding capacity, and CEC, thereby supporting stable nutrient cycling processes. Additionally, humins function as a cation exchange system that aids in soil structure improvement and stability for water holding capacity. These properties collectively contribute to the soil's resilience against acidification and its ability 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 inorganic NPK fertilizer enhanced the nutrient availability in the three soils for crop productivity.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 the 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 are 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 straw take away treatments (Table 4 and Fig. 6)

(Farooqi et al., 2023; Mushtaq et al., 2021). The soils' humus carbon content was higher in treatments with straw return than the straw take away treatments (Table3). This consistent with the findings of Guggenberger, (2005); Jindo et al. (2011),who reported that organic materials such as straw return to the soil can stimulate microbial activity, which in turn increase the formation of humic 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 pools (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) stronglycorrelated 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 correlation with soil pH and positive correlated with these soil with nutrient indicate that humification is improved in environments where organic matter decomposition drives nutrient 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, thereby reducing direct mineralization (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, followed by Quaternary and purple sandy shale soils (Fig. 3). This contributed to improvement in organic matter stability and total and available nutrients, such as TN, TK, AK, AP and the organic carbon in these soils (Table 4) (Heijboer et al., 2016; Luo et al.,2023; Lian et al.,2022). The NPK-R and OM-R treatments significantly increased the carbon to nitrogen ratio (C/N) (Table 4), suggesting improvement in organic matter decomposition and nutrient cycling (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 synergistic benefits of straw and chemical fertilizers in improving the soil and crop performance (Chen et al., 2020; Zhang et al., 2021).The application of manure and continuous straw return, combined with mineral fertilizers, can enhance soil pH and fertility in Quaternary red and granite soils, thereby supporting the sustainable cultivation of nutrient-demanding crops like sweet potato (*Ipomoea batatas*) and broad bean (*Vicia faba* 'Aquadulce Claudia'). Integrating organic amendments with mineral fertilizers has been shown to improve soil quality and crop performance (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 maintaining resilience against pH decline and ensuring 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 strategies 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 unique properties of each soil type to achieve sustainable production.

4.2. Relationship between soil properties and crop yieldunder long-term fertilization

In granite soil, sweet potato (*Ipomoea batatas* 'Beauregard') yield was notably higher than in Quaternary red and purple sandy shale soils (Fig 6). The yield improvement was strongly linked to the positive correlation between total nitrogen (TN), soil organic carbon (SOC), and the soil 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 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 exchangeable aluminum concentration and caused nutrient imbalances (Table 4), which adversely affected root development and nutrient uptake in the broad bean crop(Hartemink & Barrow, 2023).Aluminum toxicity in acidic soils is known to inhibit root growth and function, thereby reducing crop yields. Additionally, low pH can decrease the availability of essential nutrients such as phosphorus, further limiting 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 significant fluctuations in crop yield(Chaudhury et al. 2005; Liu et al. 2021; Zhaoet al. 2013).

However, long-term organic amendments such as straw input can improve soil nutrients 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) contributed to the higher crop yield (Fig. 6) observed in these two soils compared to purple sandy shale soil (Fig. 6). C/N ratio is a crucial indicator of soil health and crop yield potential, which influences both nutrient availability and microbial processes under different fertilization systems 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 crop performance was strongly influenced by the soil properties, particularly pH, organic carbon content and the microbial activity. Sweet potato adaptability to the lower pH and nutrient variability in Quaternary red and Granite soils makes it a suitable crop for such acidic environments, while broad bean suits the purple sandy shale soil (Fig. 6). These differences in crop yield responses indicatethe importance of crop selection in relation to soil characteristics and long-term sustainability of fertilization practices. These results reinforce the necessity for precision fertilization strategies that account for specific interactions between soil properties and crop needs. Integrated nutrient management practices, which involve organic amendments like straw and NPK mineral fertilizers, are essential for maintaining soil health and long-term crop productivity.This can also promote agricultural sustainability and reduce environmental impact from 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 to the purple sandy shale soil. The NPK fertilizer with straw (NPK-R) treatment significantly increased nutrient concentrations and crop yield compared to the sole straw return (OM-R) in all three soils. Although mineral fertilizers provided immediate nutrients for crop productivity, their application without straw led to a decline in soil pH. Combining straw return with mineral fertilizers proved the most effective approach for enhancing these soils quality and crop yield. Adding lime to the chemical fertilizer with straw take away treatment (NPK-T) could mitigate pH decline in Quaternary red and granite soils, while incorporating leguminous cover crops in purple sandy shale soil could boost the soil organic matter for long-term productivity.

Data availability

Data will be available upon request.

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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	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

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
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
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+} $Cmol_+$ 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	122b	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 due to high (pH 8.5).

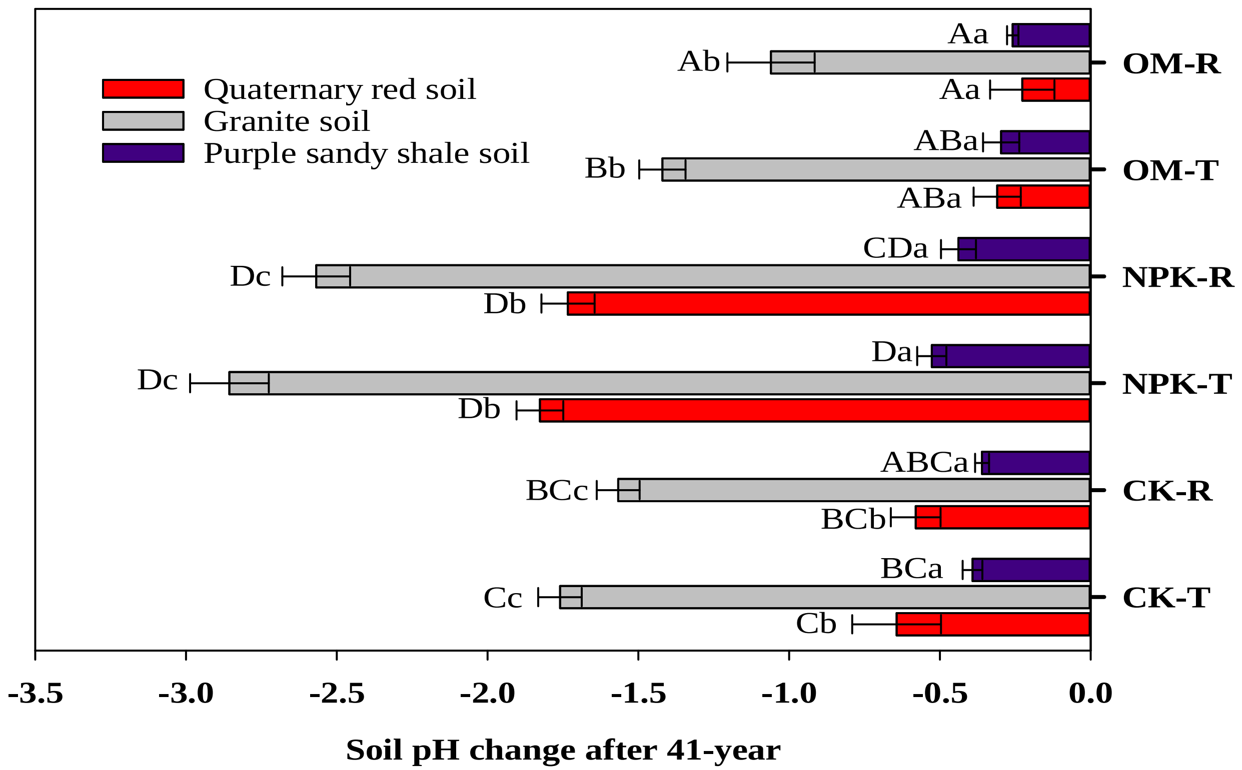

Figure 1. Changes in soil pH under different fertilization treatments in granite, purple sandy shale and Quaternary red soils. Each soil type pH change is represented by different color bar, with treatments on the vertical axis and changes in pH units on the horizontal axis, scaled negatively, reduction 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.

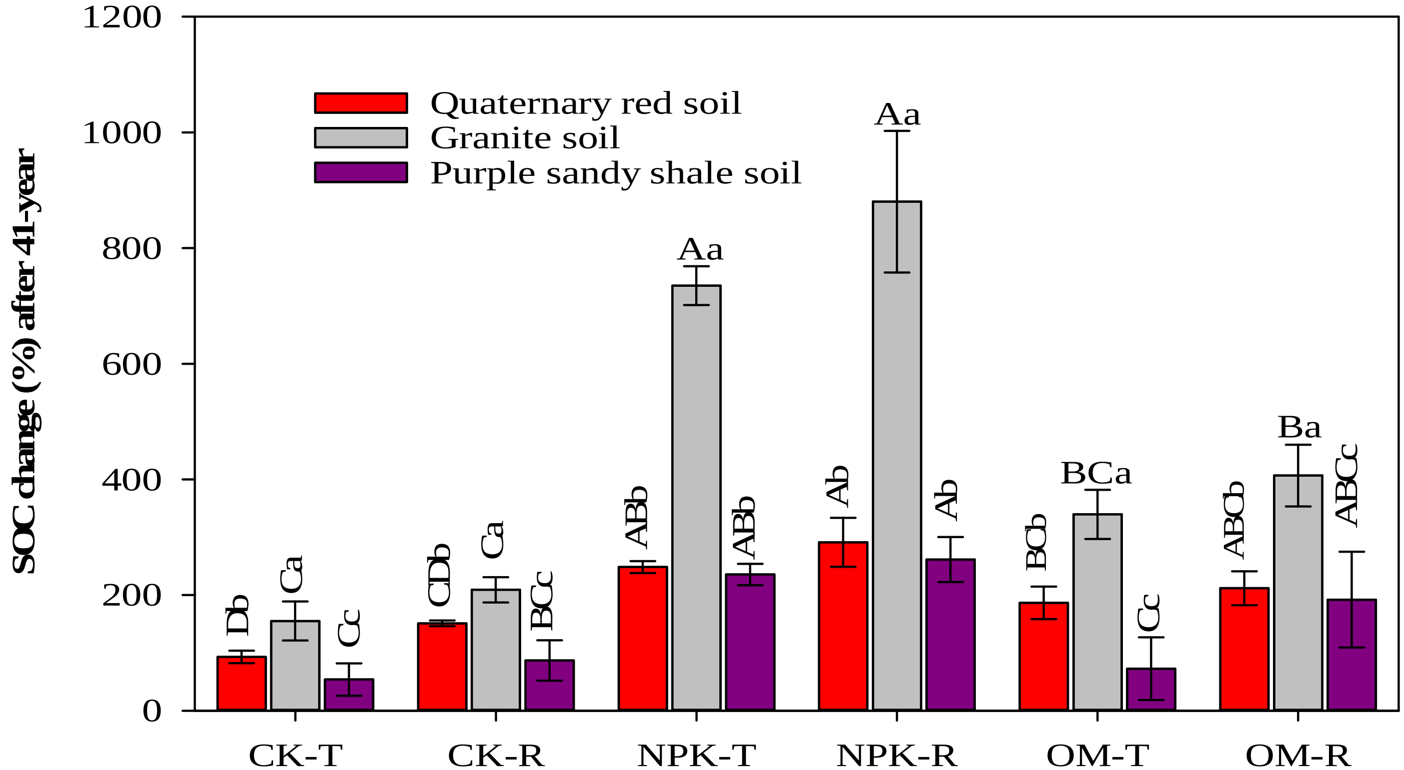

Figure 2. Change of soil organic carbon (SOC) under different long-term fertilization in granite and Quaternary red and purple sandy shale soils after 41 years. Letters above the bars represent statistical *($P< 0.05$)* groupings, while those with the same letters are not statistically significant. Uppercase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

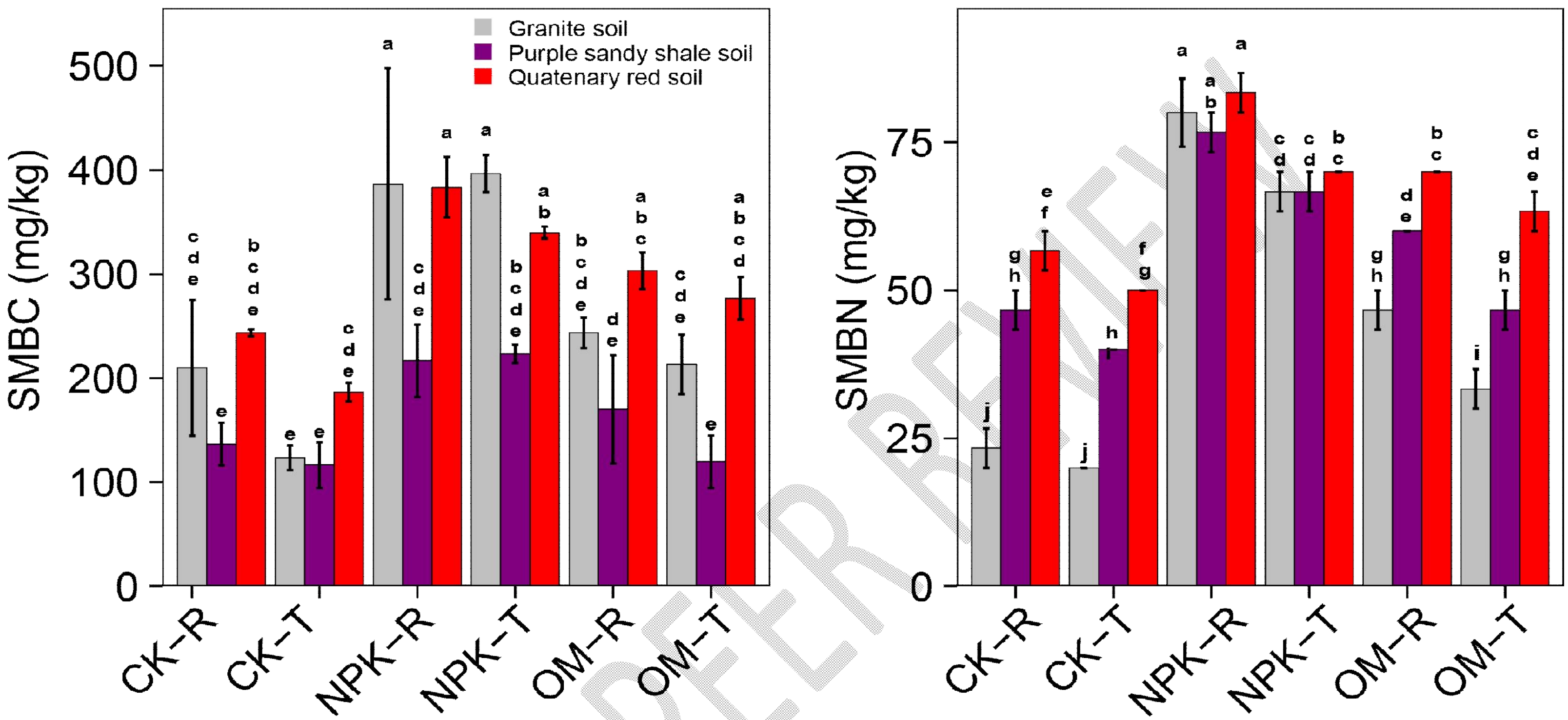

Figure 3. Mean standard deviation and count of SMBC (Soil Microbial Biomass Carbon) and SMBN (Soil Microbial Biomass Nitrogen) under different fertilization treatments in the granite, Quaternary red and purple sandy shale soils.Lowercase letters denote statistical significance *(P< 0.05)* with bars having 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.

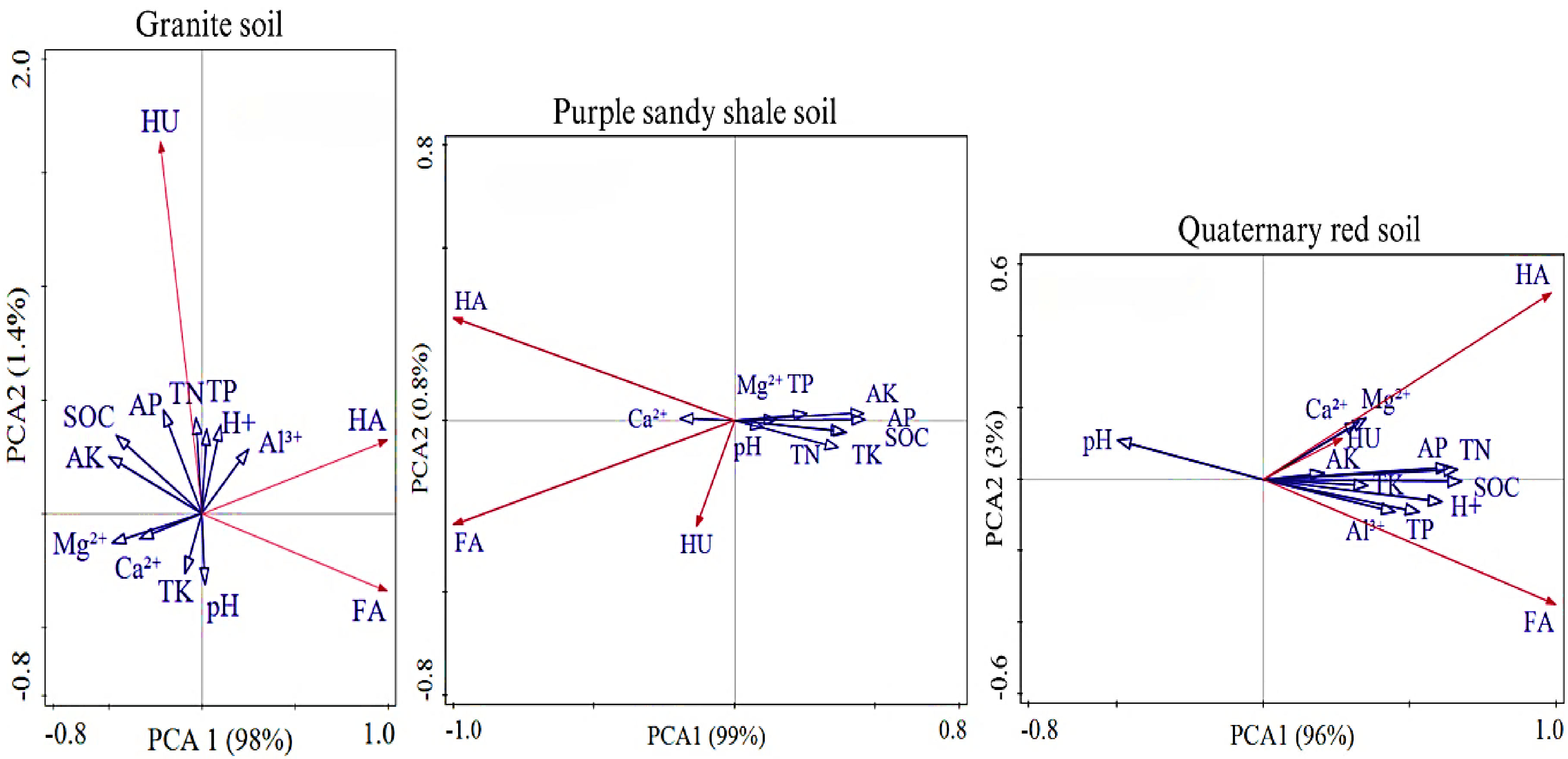

Figure 4. Principal component analysis of soil properties and humus carbon fractions in granite and Quaternary and purple sandy shale soils, employed to examine patterns and relationships of humus carbon fractions and the soil properties. HA-C (humic acid carbon), FA-C (fulvic acids carbon), and HU-C,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

Figure 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.

Figure 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 soils. Lowercase letters indicate statistical significance ($P < 0.05$) where different letters above the bars mean significant differences in yields among soil treatments.

Figure 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).

Figure 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 $P<0.05$.

Figure 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.

Figure 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. R^2 is the coefficient of determination and the indicated p-values, while the shaded areas around the lines indicate the confidence intervals.