The influence of organic and inorganic nutrient inputs on soil organic carbon functional groups content and maize yields

M. Ndung'u,*, L.W. Ngatia, R.N. Onwonga, M.W. Mucheru-Muna, R. Fu, D.N. Moriasi, K.F. Ngetich

University of Nairobi, College of Agriculture and Veterinary Sciences, Department of Land Resource Management & Agricultural Technology, PO Box 29053 Nairobi 00625 Kenya
Florida A&M University, College of Agriculture & Food Sciences, Tallahassee, FL 32307, USA
Kenyatta University, Department of Environmental Studies, PO Box 43844-00100, Nairobi, Kenya
National High Magnetic Field Laboratory, Florida State University, 1800 E. Paul Dirac Drive, Tallahassee, FL 32310 USA
USDA-ARS Grazinglands Research Laboratory, 7207 W. Cheyenne Street EL Reno, OK 73036 USA
Jaramogi Oginga Odinga University of Science and Technology (JOOUST), School of Agricultural and Food Sciences, PO Box 210 - 40601 Bondo, Kenya

ABSTRACT

Locally available organic inputs to soil, solely or in combination with inorganic fertilizers, are used to reverse declining soil fertility and improve soil organic matter content (SOM) in smallholder farms of most Sub-Saharan Africa (SSA) countries. Soil organic matter characterization can indicate soil organic input, carbon (C) sequestration potential, or even an authentication tool for soil C dynamics in C stocks accounting. This study determined the effects of the long-term application of selected integrated soil fertility management (ISFM) technologies on SOM functional group composition and maize yields. The study was carried out on an ongoing long-term soil fertility field experiment established in 2004 in Mbeere South sub-county, the drier part of upper Eastern Kenya. The experimental design was a randomized complete block design. The ISFM treatments were 60 kg ha\(^{-1}\) nitrogen (N) from goat manure (GM60); 30 kg ha\(^{-1}\) inorganic N fertilizer (IF30); 60 kg ha\(^{-1}\) inorganic N fertilizer (IF60); GM30 + IF30; 90 kg ha\(^{-1}\) inorganic N fertilizer (IF90); 60 kg ha\(^{-1}\) N from lantana (Lantana camara) (LC60); LC30 + IF30; 60 kg ha\(^{-1}\) N from mucuna beans (Mucuna pruriens) (MP60); MP30 + IF30; 60 kg ha\(^{-1}\) N from Mexican sunflower (Tithonia diversifolia) (TD60); TD30 + IF30, and a control with no inputs. The C compositions of ground soil samples and organic amendments were analyzed using \(^{13}\)C solid-state NMR. The GM60, GM30 + IF30, LC60, and TD60 treatments had much higher Alkyl and O-Alkyl C SOM functional groups than the control and other treatments. The average soil C for the control was 7.47 mg kg\(^{-1}\) and ranged from 5.03 to 7.37, 9.57 to 18.77, and 7.03–14.50 mg kg\(^{-1}\) for inorganic fertilizers, organic fertilizers, and organic + inorganic fertilizers, respectively. The mean grain yield for the control was 0.56 Mg ha\(^{-1}\) and ranged from 1.51 to 1.99, 1.94 to 4.16, and 2.98–4.60 Mg ha\(^{-1}\) for inorganic fertilizers, organic fertilizers, and organic + inorganic fertilizers, respectively. The results showed that a long-term application of sole organic fertilizers or combined with inorganic fertilizers increases maize yield and soil C sequestration potential. The increase was attributed to high Alkyl and O-Alkyl C SOM functional groups. Hence, knowing the C fraction content of organic inputs is vital in determining the best-fit management technologies for ameliorating soil fertility and sustaining and/or improving crop yields.

ARTICLE INFO

Keywords:
Grain yield
Carbon sequestration
Organic amendments
Soil carbon fractions
Soil fertility

1. Introduction

Maintenance of soil fertility is critical to sustaining food security under the prevailing climate variability and increasing population. Conversely, deteriorating soil fertility reduces crop yields and increases the threat to food insecurity. Continuous cultivation and low soil replenishment are the leading causes of declining soil fertility (Shisanya et al., 2009). The result being the development of integrated soil fertility management (ISFM) technologies that employ a judicious application of organic and inorganic nutrients to ameliorate soil fertility and boost or sustain crop productivity. In most semiarid environments and Sub-Saharan Africa’s (SSA) smallholder farming systems, where soil
fertility is declining together with soil organic matter (Badalucco et al., 2010), locally accessible organic inputs have been used to ameliorate soil fertility and boost soil organic matter content (SOM) (Kiboi et al., 2018).

Improving SOM content and raising soil nutrients’ bioavailability for improved soil quality requires good management of applied organic inputs (Kiboi et al., 2019). Maintaining a high SOM status is desirable in the long term due to its multiple beneficial effects attributable to its structure, such as soil physical and water holding capacity and good biological properties (von Lützow et al., 2002; Laudicina et al., 2012). Besides its dependence on edaphic and environmental factors, the quantity and quality of SOM in agricultural soils can vary due to agriculture-related management practices such as application of organic inputs (Martyniuk et al., 2019). Therefore, depending on chemical composition of SOM (Li et al., 2015), biomass input levels, micro- and bioclimatic change (Zomer et al., 2017), and management, soils can act as both C sources and sinks.

The physico-chemical environment of the soil and the chemical structure of its organic C controls the biological stability of SOM (Schöning et al., 2005). It, in turn, influences the organic nutrients mineralization of (into plant-available forms) and sequestered soil C amounts. Chemical recyclaritance can explain the formation of passive or long-residence-time-of SOM fractions in the soil (Eusterhues et al., 2003). Soil organic carbon (SOC), a measureable component of SOM, is composed of inorganic and organic components (Wang et al., 2012; Were et al., 2015) and is controlled by organic C and degradation rates. Its dynamics can denote the balance between C input and C output (Breulmann et al., 2010) and influence crop productivity. In light of predicted climate change, the ability of soil to retain C and thus to act as a sink or a source for increasing anthropogenic CO2 concentrations remains largely unknown (Trumbore, 2009; Solomon et al., 2012). Therefore, SOM characterization can indicate soil organic input, carbon (C) sequestration potential, or even an authentication tool for soil C dynamics in C stocks accounting (Leifeld and Ko, 2005; Laudicina et al., 2015), for different agricultural production systems.

The 13C cross-polarization magic angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectroscopy can be applied in structural characterization of SOM for the interpretation of changes induced by the different management practices (Bems and Conte, 2011; Knicker, 2011; Panettieri et al., 2013). This is because most SOM-constituting compounds have poor solubility, making NMR spectroscopy an appropriate option for an in-depth description.

The NMR spectroscopy operation principle is based on the application of a magnetic field to nuclei and determining the amount of energy required to put the nuclei in resonance (Freitas et al., 2012). The NMR spectrum provides peaks/signal that help determine the structure of C fractions in soil samples (Martinez-Richa and Silvestri, 2017). The number of peaks in the spectrum equals the number/type of hydrogen or other atoms in a molecule (Freitas et al., 2016). The 13C NMR spectra of soil samples are assigned to dominant C forms, including carboxyl, aromatic, o-alkyl, alkyl C, phenolic, and methoxyl C. Solid-state CPMAS 13C NMR can offer an in-depth understanding of C composition (Normand et al., 2017). Based on chemical peak shifts, it detects the carbon functional groups with varying molecular composition and microbial utilization in SOM (Knicker, 2011). Hence, 13C NMR spectroscopy can be applied in soil C pools changes and trajectories evaluation at various stages of soil fertility and landuse management changes.

This study aimed to quantify SOM's composition and stability dynamics as influenced by organic and inorganic soil inputs. Specifically, SOM composition was determined using solid-state 13C cross-polarization magic angle spinning (CPMAS) NMR spectroscopy, including CP/MAS 13C NMR spectroscopy. The chemical shifts in the 13C NMR spectra of soil samples were assigned according to the literature. The NMR spectra were collected using a 600 MHz Varian spectrometer fitted with a 14 mm HX probe equipped with a 13C cross-polarization (CP) magic angle spinning (MAS) device. The NMR instrument was equipped with a 13C cross-polarization (CP) magic angle spinning (MAS) device. The NMR instrument was equipped with a 13C cross-polarization (CP) magic angle spinning (MAS) device. The NMR instrument was equipped with a 13C cross-polarization (CP) magic angle spinning (MAS) device.

Table 1. Experimental treatments and amounts of N supplied by the different treatments.

| Treatments | Abbreviation | N from biomass (kg N ha⁻¹) | N from inorganic fertilizer (kg N ha⁻¹) |
|------------|-------------|--------------------------|-------------------------------------|
| Control    | Ctrl        | 0                        | 0                                   |
| Goat Manure| GM60        | 60                       | 0                                   |
| Inorganic fertilizer | IF30 | 0                      | 30                                  |
| Inorganic fertilizer | IF60 | 0                      | 60                                  |
| Goat Manure + Fertilizer | GM+IF30 | 30                     | 30                                  |
| Inorganic fertilizer | IF90 | 0                      | 90                                  |
| Lantana camara | LC60 | 60                     | 0                                   |
| Lantana camara + Inorganic Fertilizer (30 kg ha⁻¹ N) | LC30+IF30 | 30                 | 30                                  |
| Mucuna pruriens | MP60 | 60                     | 0                                   |
| Mucuna pruriens + Inorganic Fertilizer (30 kg ha⁻¹ N) | MP30+IF30 | 30                 | 30                                  |
| Tithonia diversifolia | TD60 | 60                     | 0                                   |
| Tithonia diversifolia + Inorganic Fertilizer (30 kg ha⁻¹ N) | TD30+IF30 | 30                 | 30                                  |
were Lantana camara (LC), Mucuna pruriens (MP), Tithonia diversifolia (TD) and Goat Manure (GM). Table 1 shows the details of the treatments. The test crop was maize (Zea mays L., var. DH04), and it was planted at a spacing of 0.9 m between the rows and 0.6 m within the rows. During sowing, three maize seeds were planted per hill. Immediately after emergence, the third seedling was thinned out to remain with two seedlings per hill. Both organic and inorganic fertilizer application rates were based on the recommended 60 kg N ha⁻¹ (FURP, 1987). The nutrient content of both fertilizers were from laboratory analyses of the input samples (Table 2). The organic materials (TD and LC) were harvested from the established nearby bulking plots (biomass transfer).

At the onset of each season, the organic inputs were collected (from the hedgerows and those planted on the soil conservation structures/terraces). They were then dried under a shade, chopped, and required amounts per plot weighed. During land preparation, the organic inputs were spread and incorporated into the soil to a depth of 15 cm. Calcium ammonium nitrate (CAN), the source of inorganic N, was split-applied as a top-dresser at the rate of a third (of the target inorganic N amount as per Table 1) four weeks after planting and two-thirds six weeks after planting. Due to the low P content of organic inputs, triple superphosphate (TSP) fertilizer was blanket applied in all plots, taking into account a top-dresser at the rate of a third (of the target inorganic P amount as per Table 1). The average residual soil available P, to attain 60 kg P ha⁻¹ of phosphate (TSP) fertilizer was blanket applied in all plots, taking into account a top-dresser at the rate of a third (of the target inorganic P amount as per Table 1) four weeks after planting and two-thirds six weeks after planting. Calcium and other soil organic inputs, GM had the lowest carboxyl C and phenolic C fractions did not vary much across the organic inputs. Compared to the control, significantly the highest content of grain yields against soil N or soil C was evaluated by subjecting the total C of MP, GM, LC and TD were 40.53 g kg⁻¹, 40.13 g kg⁻¹, 39.8 g kg⁻¹, 36.52 g kg⁻¹, respectively (Figure 1). The O-alkyl C fraction was comparatively the highest across the organic inputs, ranging from 19.14 g kg⁻¹ in TD to 25.83 g kg⁻¹ in LC. It was evident that alkyl was the second-highest fraction. The Alkyl C fraction was highest in GM (10.35 g kg⁻¹) and lowest in MP (5.03 g kg⁻¹). Aromatic C and methoxyl C fractions did not vary much across the organic inputs. Compared to the other soil organic inputs, GM had the lowest carboxyl C and phenolic C content (0.71 g kg⁻¹ and 0.46 g kg⁻¹, respectively) compared to the other inputs. The test crop was maize (Zea mays L., var. DH04), and it was planted at a spacing of 0.9 m between the rows and 0.6 m within the rows. During sowing, three maize seeds were planted per hill. Immediately after emergence, the third seedling was thinned out to remain with two seedlings per hill. Both organic and inorganic fertilizer application rates were based on the recommended 60 kg N ha⁻¹ (FURP, 1987). The nutrient content of both fertilizers were from laboratory analyses of the input samples (Table 2). The organic materials (TD and LC) were harvested from the established nearby bulking plots (biomass transfer).

At the onset of each season, the organic inputs were collected (from the hedgerows and those planted on the soil conservation structures/terraces). They were then dried under a shade, chopped, and required amounts per plot weighed. During land preparation, the organic inputs were spread and incorporated into the soil to a depth of 15 cm. Calcium ammonium nitrate (CAN), the source of inorganic N, was split-applied as a top-dresser at the rate of a third (of the target inorganic N amount as per Table 1) four weeks after planting and two-thirds six weeks after planting. Due to the low P content of organic inputs, triple superphosphate (TSP) fertilizer was blanket applied in all plots, taking into account a top-dresser at the rate of a third (of the target inorganic P amount as per Table 1) four weeks after planting and two-thirds six weeks after planting. Calcium and other soil organic inputs, GM had the lowest carboxyl C and phenolic C fractions did not vary much across the organic inputs. Compared to the control, significantly the highest content of grain yields against soil N or soil C was evaluated by subjecting the total C of MP, GM, LC and TD were 40.53 g kg⁻¹, 40.13 g kg⁻¹, 39.8 g kg⁻¹, 36.52 g kg⁻¹, respectively (Figure 1). The O-alkyl C fraction was comparatively the highest across the organic inputs, ranging from 19.14 g kg⁻¹ in TD to 25.83 g kg⁻¹ in LC. It was evident that alkyl was the second-highest fraction. The Alkyl C fraction was highest in GM (10.35 g kg⁻¹) and lowest in MP (5.03 g kg⁻¹). Aromatic C and methoxyl C fractions did not vary much across the organic inputs. Compared to the other soil organic inputs, GM had the lowest carboxyl C and phenolic C content (0.71 g kg⁻¹ and 0.46 g kg⁻¹, respectively) compared to the other inputs.

2.4. Statistical analysis

Data were analyzed using SAS 9.4 (SAS Institute, 2004). Soil carbon, Nitrogen, and grain yields were subjected to analysis of variance to establish the effects across the treatments. The mean separation was done using the least significant difference (LSD) at p = 0.05. The relationship of grain yields against soil N or soil C was evaluated by subjecting the data to bivariate Pearson Correlation to produce a correlation coefficient.

3. Results and discussion

3.1. Carbon fractions of the organic inputs

The total C of MP, GM, LC and TD were 40.53 g kg⁻¹, 40.13 g kg⁻¹, 39.8 g kg⁻¹, 36.52 g kg⁻¹, respectively (Figure 1). The O-alkyl C fraction was comparatively the highest across the organic inputs, ranging from 19.14 g kg⁻¹ in TD to 25.83 g kg⁻¹ in LC. It was evident that alkyl was the second-highest fraction. The Alkyl C fraction was highest in GM (10.35 g kg⁻¹) and lowest in MP (5.03 g kg⁻¹). Aromatic C and methoxyl C fractions did not vary much across the organic inputs. Compared to the other soil organic inputs, GM had the lowest carboxyl C and phenolic C content (0.71 g kg⁻¹ and 0.46 g kg⁻¹, respectively) compared to the other inputs.

3.2. Soil organic carbon fractions

With respect to the relative abundance of C functional groups, based on ¹³C NMR spectra of the different soil input treatments, a declining trend was observed from soils treated with only organic amendments, followed by soils with organic + inorganic amendments, and then soils with only inorganic amendments (Figure 2). The reported high C content under organic amendments was consistent with Goyal et al. (1999) Carbon functional groups of the soil treated with sole organic inputs was in the order of O-alkyl C > alkyl C > methoxyl > carboxyl > aromatic C content, with GM treatment having the highest of these fractions. The C fractions in the inorganic fertilizer-based treatments were closely identical to the control (Figure 2).

3.2.1. O-alkyl C

O-alkyl C was the dominant C fraction among the different functional groups under different treatments (Figure 2). Compared to the control, GM60 treatment had significantly (p < 0.001) the highest content (231%) followed by GM30+IF30 (159%), then sole LC60 (142%) followed by TD60 (129%) (Figure 3). Compared to the control, slight differences were observed in the remaining treatments ranging from -44% in IF30 to 21% in LC30+IF30. The O-alkyl C content in the sole inorganic...
fertilizer treatments, were generally low, with IF30 and IF90 having significantly (p < 0.001) lower O-alkyl C (about -44% and -33%, respectively) than that of the control. IF60, LC30+IF30, MP30+IF30, TD30+IF30 and MP60 treatments were not significantly different from the control.

O-alkyl C is composed of methoxyl C (lignin) and carbohydrate C (cellulose and hemicellulose) components (Wang et al., 2013; Yu et al., 2015; Li et al., 2017; He et al., 2018; Guan et al., 2018). Based on the C fraction composition of the organic inputs (Table 1), it is evident that the amounts of O-alkyl C across the four organic inputs were almost equal. Contrariwise, the soil residual O-alkyl C at the end of the season showed significant variation across the sole organic inputs and their combinations with the inorganic inputs. GM60 treatment showed strikingly high amounts of O-alkyl C, depicting a potential for high contribution to SOM. The high decrease of the O-alkyl in the three plant-based residues suggests that a larger portion of the constituent is the cellulose and hemicellulose, which are easily biodegraded by microorganisms (Schöning et al., 2005; Solomon et al., 2010).

Organic + inorganic inputs applied to the soil that showed no relative difference of O-alkyl C content relative to the untreated control could be due to the positive effect on the organic input mineralization rated of the N from the inorganic fertilizers. It can indicate that the integration of inorganic and organic inputs facilitates a faster decomposition of the original inputs throughout the season (Gram et al., 2020).

3.2.2. Alkyl C

The GM60 treatment had significantly (p < 0.001) the highest Alkyl C content (58%) followed by GM+IF30 (48%) treatment, then LC30+IF30 (20%) and TD60 (19%), compared to the control (Figure 4). Except for MP60, all the other treatments (LC60, IF60, IF90, MP30+IF30, TD30+IF30, IF30) had significantly lower Alkyl C content compared to the control.
Figure 3. Total amount of O-alkyl C fraction in each treatment. Ctrl is the Control; GM60 is Goat Manure (60 kg ha\(^{-1}\) N), IF30 is Inorganic fertilizer (30 kg ha\(^{-1}\) N), IF60 is Inorganic fertilizer (60 kg ha\(^{-1}\) N); GM30+IF30 is the Goat Manure + Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each); IF90 is Inorganic fertilizer (90 kg ha\(^{-1}\) N); LC60 is Lantana camara (60 kg ha\(^{-1}\) N); LC30+IF30 is Lantana camara + Inorganic Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each); MP60 is Mucuna pruriens (60 kg ha\(^{-1}\) N); MP30+IF30 is the Mucuna pruriens + Inorganic Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each); TD60 is Tithonia diversifolia; and TD30+IF30 is Tithonia diversifolia + Inorganic Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each).

Figure 4. Total amount of Alkyl C fraction in each treatment. Ctrl is the Control; GM60 is Goat Manure (60 kg ha\(^{-1}\) N), IF30 is Inorganic fertilizer (30 kg ha\(^{-1}\) N), IF60 is Inorganic fertilizer (60 kg ha\(^{-1}\) N); GM30+IF30 is the Goat Manure + Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each); IF90 is Inorganic fertilizer (90 kg ha\(^{-1}\) N); LC60 is Lantana camara (60 kg ha\(^{-1}\) N); LC30+IF30 is Lantana camara + Inorganic Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each); MP60 is Mucuna pruriens (60 kg ha\(^{-1}\) N); MP30+IF30 is the Mucuna pruriens + Inorganic Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each); TD60 is Tithonia diversifolia; and TD30+IF30 is Tithonia diversifolia + Inorganic Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each).

Figure 5. Total amount of Aromatic C fraction in each treatment. Ctrl is the Control; GM60 is Goat Manure (60 kg ha\(^{-1}\) N), IF30 is Inorganic fertilizer (30 kg ha\(^{-1}\) N), IF60 is Inorganic fertilizer (60 kg ha\(^{-1}\) N); GM30+IF30 is the Goat Manure + Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each); IF90 is Inorganic fertilizer (90 kg ha\(^{-1}\) N); LC60 is Lantana camara (60 kg ha\(^{-1}\) N); LC30+IF30 is Lantana camara + Inorganic Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each); MP60 is Mucuna pruriens (60 kg ha\(^{-1}\) N); MP30+IF30 is the Mucuna pruriens + Inorganic Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each); TD60 is Tithonia diversifolia; and TD30+IF30 is Tithonia diversifolia + Inorganic Fertilizer (at a rate of 30 kg ha\(^{-1}\) N each).
Alkyl C is a recalcitrant C; that is, it is more stable, hydrophobic (Carrington et al., 2012; Chen et al., 2013; Habte et al., 2013; Yu et al., 2015), and an aliphatic hydrocarbon with strong chemical structure bonds that are more resistant to degradation (Zhang et al., 2019). Singh and Rengel (2007) associate high recalcitrant organic C content in the soil with alkyl C. The accumulation of alkyl C content, derived from lignin and polyphenol components of the plant residues, occurs at the onset of decomposition of the plants. In the case of this study, the organic amendments supplied lesser proportions of alkyl C, relative to O-alkyl C, suggesting that during decomposition of the plant residues, the stable alkyl C is left intact while the carbohydrate C (O-alkyl C) undergoes decomposition. In addition, degradation of labile O-alkyl results in accumulation of alkyl C and aromatic C (Quideau et al., 2001). However, the presence of oxygen enhances degradation of aromatic C (Fuchs et al., 2011). The findings of Kögel-Knabner (2002) corroborates this and further underscores that the lignin component minimizes the decomposition of the plant residues and increases the likelihood of the organic inputs to contribute to soil C stocks.

### 3.2.3. Aromatic C

Compared with control, GM60, LC60, GM30+IF30, LC30+IF30, TD60, and TD30+IF30 treatments had significantly (p < 0.001) higher aromatic C contents (Figure 5). The aromatic C content in soils treated with MP60, IF60, and MP30+IF30 treatments were not significantly (p < 0.001) different from the control while those of IF30 (by -22%) and IF90 (by -23%) treatments were significantly lower.

The presence of Aromatic C is indicative of the dominance of the stable and recalcitrant C fraction in the organic inputs (Fuchs et al., 2011). The results indicate an increase in aromatic C under the treatments composed of organic inputs and showed a positive relationship with the high O-alkyl C trends. Panetteri et al. (2014) reported similar results, attributing the high aromatic C content to the incorporation of the high O-alkyl C trends.

### 3.2.5. Carboxyl C

Carboxyl C content was significantly (p < 0.001) higher in GM60 and LC60 treatments by 106% and 74%, respectively, compared to control (Figure 7). Carboxyl C content LC30+IF30, MP60, TD60, IF60 and TD30+IF30 treatments were not significantly (p < 0.001) different from the control. On the other hand, carboxyl C content in GM30+IF30, IF30, MP30+IF30 an IF90 treatments were significantly lower compared to the control.

Carboxyl C, an aliphatic acid of plant and microbial origins (Yu et al., 2015), was relatively abundant under the GM60, although they were very low in the input characterization (Figure 1). Carboxyl C is an organic input constituent, and it is also microbially generated. Carboxyl-rich compounds are oxidation products of plant-derived biomolecules, such as lignin and associated phenolic substances (Kramer et al., 2012). Although highly oxidized lignin polyphenols, tannins, and other recalcitrant plant-derived compounds are partly solubilized and mobilized by peroxidase and ligninase enzymes in the soil, the resulting carboxyl-rich compounds are generally less stable than the original lignin and polyphenol molecules.
ring structures are more resistant to microbial biodegradation (Kalbitz et al., 2006). Carboxyl C is considered an important pathway for DOM production and potential for organic matter accumulation in soil (Kramer et al., 2012). The high amounts of carboxyl C under the GM60 treatment indicate the high potential of the GM60 treatment to contribute significantly towards SOM enrichment over time, hence soil C sequestration. Besides the SOM enrichment, Carboxyl C is responsible for the negative charge of soil organic matter (Anda et al., 2013), which relates to in cation exchange capacity (CEC) of soil (Schnitzer and Desjardins, 1965), hence soil fertility potential. Although the carboxyl C for the other three treatments was also high, it is worth noting that, compared to the amounts of carboxyl C in the organic characterization, the observed results show a general decline in the amounts, unlike in the GM60 treatment. In contrast, treatments with organic + inorganic inputs and sole inorganic inputs led to decreased carboxyl C content, which might be detrimental to soil C stocks.

3.2.6. Phenolic C

The GM60 treatment had significantly highest Phenolic C contents followed GM30+IF30, LC20+IF30, LC60, TD60 and MP60 treatments compared to control (Figure 8). Phenolic C contents in the TD30+IF30 MP30+IF30 IF30 and IF90 treatments were not any different (p < 0.001) relative to control. However, phenolic C contents, IF60 was significantly (p < 0.001) lower from the control.

Phenolic C is a less humified organic material in SOM, as it contains an abundance of diester P and amide N (Wissing et al., 2013). Generally, phenolic C was significantly the lowest C fraction in the soil, indicating, but then, based on Table 1, the difference between the phenolic C in the inputs and the residual at the end of the season was small. Phenols originate from recalcitrant plant litter compounds (Rumpel et al., 2004); hence its degradation is slower than the degradation of other C fractions (Min et al., 2015). Therefore, the observed high phenolic contents in the GM60 treatment indicate its high potential to contribute to SOM. This observation is supported by Yu et al. (2015), who observed that as a result of lignin recalcitrance of organic inputs, there was an accumulation of phenolic C in the soil. Pane et al. (2013) also reported that high phenolic C content reflects the lack of microbial degradation due to the recalcitrant characteristic of the organic inputs. Further, according to Ng et al. (2014), phenolic compounds correlate with the antioxidant capacity of soils that neutralize free radicals and protect organic matter from oxidation.

3.3. The effects of treatments on soil nitrogen, soil carbon, and grain yields

The average grain yield ranged from 0.56 Mg ha$^{-1}$ in the control to 4.60 Mg ha$^{-1}$ in the MP30+IF30 treatment (Table 3). The IF30, IF60, IF90, and LC60 treatments had low grain yields within the range of the control treatment. The LC30–IF30 and LC60 treatments had an average effect on the grain yields. At the same time, the combination of organic and inorganic amendments, i.e., fertilizer LC30+IF30, TD30+IF30, GM30+IF30, and MP30+IF30 (2.98 Mg ha$^{-1}$, 3.30 Mg ha$^{-1}$, 3.36 Mg ha$^{-1}$, and 4.6 Mg ha$^{-1}$, respectively) and sole application of MP60 and GM60 (4.63 Mg ha$^{-1}$ and 4.16 Mg ha$^{-1}$) produced higher grain yield compared with control.

| Treatment | Nitrogen (g kg$^{-1}$) | Carbon (g kg$^{-1}$) | Grain Yield (Mg ha$^{-1}$) |
|-----------|----------------------|----------------------|---------------------------|
| Control   | 0.73 ± 0.03$^{ab}$   | 7.47 ± 0.50$^{ab}$   | 0.56 ± 0.045$^{ab}$       |
| IF30      | 0.53 ± 0.12$^{cd}$   | 5.03 ± 1.14$^{cd}$   | 1.89 ± 0.33$^{cd}$        |
| IF60      | 0.80 ± 0.06$^{def}$  | 7.27 ± 0.61$^{de}$   | 1.51 ± 0.17$^{de}$        |
| IF90      | 0.50 ± 0.06$^{de}$   | 5.27 ± 0.63$^{de}$   | 1.99 ± 0.45$^{de}$        |
| LC30+IF30 | 1.37 ± 0.07$^{bc}$   | 13.37 ± 0.71$^{bc}$  | 1.94 ± 0.09$^{bc}$        |
| LC60      | 1.18 ± 0.03$^{ab}$   | 9.23 ± 0.38$^{de}$   | 2.98 ± 0.36$^{bd}$        |
| GC30      | 0.85 ± 0.12$^{ab}$   | 18.77 ± 1.11$^{a}$   | 4.16 ± 0.20$^{ab}$        |
| GM30+IF30 | 1.47 ± 0.12$^{bc}$   | 14.50 ± 1.50$^{bc}$  | 3.36 ± 0.19$^{bc}$        |
| MP30+IF30 | 0.97 ± 0.03$^{bc}$   | 9.57 ± 0.41$^{bcde}$ | 4.03 ± 0.51$^{bc}$        |
| TD60      | 1.23 ± 0.09$^{bc}$   | 11.77 ± 1.52$^{bcde}$| 2.23 ± 0.10$^{bcde}$      |
| TD30+IF30 | 0.80 ± 0.06$^{def}$  | 7.77 ± 0.57$^{de}$   | 3.30 ± 0.34$^{bde}$       |

* Mean with same superscript letters indicate no significant difference between treatments. Ctrl is the Control; GM60 is Goat Manure (60 kg ha$^{-1}$ N); IF30 is Inorganic fertilizer (30 kg ha$^{-1}$ N); IF60 is Inorganic fertilizer (60 kg ha$^{-1}$ N); GM30+IF30 is the Goat Manure + Fertilizer (at a rate of 30 kg ha$^{-1}$ N each); IF90 is Inorganic fertilizer (90 kg ha$^{-1}$ N); LC30 is Lantana camara + Inorganic Fertilizer (at a rate of 30 kg ha$^{-1}$ N each); LC60 is Lantana camara (60 kg ha$^{-1}$ N); LC30+IF30 is Lantana camara + Inorganic Fertilizer (at a rate of 30 kg ha$^{-1}$ N each); IF90 is Inorganic fertilizer (90 kg ha$^{-1}$ N); LC60 is Lantana camara (60 kg ha$^{-1}$ N); LC30+IF30 is Lantana camara + Inorganic Fertilizer (at a rate of 30 kg ha$^{-1}$ N each); MP60 is Mucuna pruriens (60 kg ha$^{-1}$ N); MP30+IF30 is the Mucuna pruriens + Inorganic Fertilizer (at a rate of 30 kg ha$^{-1}$ N each); TD60 is Tithonia diversifolia; and TD30+IF30 is Tithonia diversifolia + Inorganic Fertilizer (at a rate of 30 kg ha$^{-1}$ N each).
The GM60 and GM30+IF30 treatments had the highest soil N, while IF30, IF60, IF90, MP30+IF30, and TD30+IF30 treatments had the lowest. The LC60, LC30+IF30, MP60, and TD60 treatments had moderate amounts of soil N (Table 3). There was a positive correlation between grain yields and soil N content (Figure 9). Concerning grain yields, MP60 and MP30+IF30 treatments had the highest grain yields. The high soil N in the GM60 and GM30+IF30 treatments are indicative of the potential of these treatments to build up soil N over time.

The effects of the treatments on the soil C content followed almost the same trend as the soil N with GM60 and GM30+IF30 treatment having, strikingly, the highest soil C levels (Table 3). Except for the sole MP60 treatment, the soil C content increased in organic-based treatments, i.e., TD60, LC60, and GM60, compared to the control. Apart from for GM30+IF30 treatment, combined organic and inorganic inputs resulted in slight changes in soil C contents. The amount of C was much lower for these treatments than the organic inputs when applied solely. Sole inorganic fertilizer-based treatments had the lowest soil C content, close to that of the control.

Based on the observed results, GM60 and GM30+IF30 treatments emerged superior in terms of enhancing grain yields and soil N and C. Coincidentally, the two treatments had high O-alkyl and alkyl C fraction, most likely attributable to the nature of goat manure. This is not only indicative of the potential dual benefits the treatments have both in terms of soil C sequestration and enhancing crop productivity but also the synergetic influence of N and C on crop yields. Also, based on the chemical composition, except for N content, goat manure had superior amounts of P, Ca Mg, and K. Based on the law of the minimum, as applied in soil fertility and plant nutrition, it implies that GM related treatments present a more nutrient balanced soil fertility inputs compared to the other inputs. This agrees with the observation by Awodun et al. (2007) that manure improves soil nutrient availability, nutrient status and enhances crop growth and yields. The SOC storage in agricultural systems is a balance between carbon losses and C additions (from crops residues and organic inputs) (Thelem et al., 2010), resulting in increased soil fertility and high yield linked to improved physical properties of the soil (Sloosnijder, 2009; Nayak et al., 2012). The application of organic amendments is regularly used to improve the SOM levels and increase atmospheric CO2 sequestration potential in soils (Yu et al., 2015).

Besides the goat manure-related treatments, MP30+IF30 registered the highest grain yields. The high grain yield was probably due to a lower C:N ratio compared to other treatments. The additional inorganic N in this treatment created a N (mineralization) surplus, which allowed for decomposition, N uptake, and significantly increased yield (Shang et al., 2014). It points towards the novelty of combining the inorganic and organic amendment, commonly referred to as integrated nutrient management (Schuman et al., 2002). Contrariwise, the treatment effect on soil C content was detrimental, probably due to the observed low Alkyl and O-alkyl fraction present in MP60, making it less recalcitrant and prone to exhaustion within a season of application. The low recalcitrance has a direct implication on the SOC status in that, to sustain SOM, there will be a need for continuous addition of mucuna. Integration of chemical fertilizers into farming systems through a combination of inorganic fertilizer and organics such as farmyard manure or crop residue, or green manure improves the SOC (Kirkby et al., 2011; Nayak et al., 2012; Kirkby et al., 2013).

The observed negative effects of the sole inorganic related treatments on yields and soil N and C were attributed to the lack of organic inputs. Nitrogen is highly mobile, and with limited SOM, it is prone to losses through leaching, runoff, and volatilization (Wissing et al., 2013). Pre-vious studies that evaluate Fertilizer N management have shown similar results that varying amounts of N fertilizer can produce significantly high levels of soil mineral N, leading to soil degradation (Owens et al., 1994). A significant portion of the applied N is removed during harvest. The remaining N may be stored in soils in the form of organic matter, while some might be lost through different pathways, such as N denitrification, volatilization, and leaching. The lower C content under inorganic inputs compromised the N storage ability of soil. Given the prevailing rainfed conditions, leaching is inevitable. As a result, this creates N deficiency and makes these treatments unsustainable in the long term.

4. Conclusion

The contribution of sole organic, or combined with inorganic fertilizers to SOM and soil fertility, is essential, especially in sub-Saharan Africa’s tropical smallholder farming systems. This study demonstrates the effects of organic and inorganic fertilizers, and their combination on maize yields and soil N and C. High SOM under the GM60 GM60, GM30+IF30, LC60, and TD60 treatments were linked to the high Alkyl and O-alkyl C fractions. This points towards a high C sequestration potential of these treatments, besides having an immediate beneficial impact on crop productivity. Besides the sole organic inputs, the results imply that long-term application of organic inputs combined with inorganic fertilizers can have a dual effect, i.e., improved soil physiochemical properties and crop productivity. This was demonstrated by the GM+IF30, a treatment where significant soil N and C built-up was observed, besides enhanced grain yields. Hence, the conclusion was that: GM60, with its high Alkyl and O-alkyl fractions, can significantly influence SOM and crop productivity; the dominance of alkyl and O-alkyl C fractions in an organic input directly affected its SOC recalcitrance; hence SOM content and built-up potential; goat manure contained adequate amounts of nutrients to meet plant requirements for optimal growth. As a result, the manure retained more N, thus increasing its fertilizing potency; a combination of organic and inorganic inputs can have the desired dual effect of simultaneously improving crop productivity (economic and social benefits) and soil C sequestration (environmental benefit). Finally, the knowledge of the C fraction content of organic soil
inputs is vital in the soil input characterization and development of soil fertility ameliorating technologies.

Declarations

Author contribution statement

Ndung'u, M.: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Ngatia, L.W.: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Onwonga, R.N.: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Moriasi D.N.: Analyzed and interpreted the data.

Additional information

No additional information is available for this paper.

References

Abakumov, E.V., Rodina, O.A., Eskov, A.K., 2018. Humification and humic acid composition of suspended soil in oligotrophic Environments in South Vietnam. Appl. Environ. Soil Sci. 2018.

Anda, M., Shamsuddin, J., Fauzi, C.I., 2013. Increasing negative charge and nutrient contents of a highly weathered soil using basalt and rice husk to promote cocoa growth under field conditions. Soil Tillage Res. 132, 1–11.

Awadon, M.A., Omonjo, L.I., Omoniyi, S.O., 2007. Effect of goat dung and NPK fertilizer on soil and leaf nutrient content, growth and yield of pepper. Int. J. Soil Sci. 2, 142–147.

Badalucco, L., Rao, M., Colombo, C., Palumbo, G., Lauricina, V.A., Gianfreda, L., 2010. The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

Abakumov, E.V., Rodina, O.A., Eskov, A.K., 2018. Humification and humic acid composition of suspended soil in oligotrophic Environments in South Vietnam. Appl. Environ. Soil Sci. 2018.

Anda, M., Shamsuddin, J., Fauzi, C.I., 2013. Increasing negative charge and nutrient contents of a highly weathered soil using basalt and rice husk to promote cocoa growth under field conditions. Soil Tillage Res. 132, 1–11.

Awadon, M.A., Omonjo, L.I., Omoniyi, S.O., 2007. Effect of goat dung and NPK fertilizer on soil and leaf nutrient content, growth and yield of pepper. Int. J. Soil Sci. 2, 142–147.

Badalucco, L., Rao, M., Colombo, C., Palumbo, G., Lauricina, V.A., Gianfreda, L., 2010. The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

Abakumov, E.V., Rodina, O.A., Eskov, A.K., 2018. Humification and humic acid composition of suspended soil in oligotrophic Environments in South Vietnam. Appl. Environ. Soil Sci. 2018.

Anda, M., Shamsuddin, J., Fauzi, C.I., 2013. Increasing negative charge and nutrient contents of a highly weathered soil using basalt and rice husk to promote cocoa growth under field conditions. Soil Tillage Res. 132, 1–11.

Awadon, M.A., Omonjo, L.I., Omoniyi, S.O., 2007. Effect of goat dung and NPK fertilizer on soil and leaf nutrient content, growth and yield of pepper. Int. J. Soil Sci. 2, 142–147.

Badalucco, L., Rao, M., Colombo, C., Palumbo, G., Lauricina, V.A., Gianfreda, L., 2010. The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

Abakumov, E.V., Rodina, O.A., Eskov, A.K., 2018. Humification and humic acid composition of suspended soil in oligotrophic Environments in South Vietnam. Appl. Environ. Soil Sci. 2018.

Anda, M., Shamsuddin, J., Fauzi, C.I., 2013. Increasing negative charge and nutrient contents of a highly weathered soil using basalt and rice husk to promote cocoa growth under field conditions. Soil Tillage Res. 132, 1–11.

Awadon, M.A., Omonjo, L.I., Omoniyi, S.O., 2007. Effect of goat dung and NPK fertilizer on soil and leaf nutrient content, growth and yield of pepper. Int. J. Soil Sci. 2, 142–147.

Badalucco, L., Rao, M., Colombo, C., Palumbo, G., Lauricina, V.A., Gianfreda, L., 2010. The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

Abakumov, E.V., Rodina, O.A., Eskov, A.K., 2018. Humification and humic acid composition of suspended soil in oligotrophic Environments in South Vietnam. Appl. Environ. Soil Sci. 2018.

Anda, M., Shamsuddin, J., Fauzi, C.I., 2013. Increasing negative charge and nutrient contents of a highly weathered soil using basalt and rice husk to promote cocoa growth under field conditions. Soil Tillage Res. 132, 1–11.

Awadon, M.A., Omonjo, L.I., Omoniyi, S.O., 2007. Effect of goat dung and NPK fertilizer on soil and leaf nutrient content, growth and yield of pepper. Int. J. Soil Sci. 2, 142–147.

Badalucco, L., Rao, M., Colombo, C., Palumbo, G., Lauricina, V.A., Gianfreda, L., 2010. The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

Abakumov, E.V., Rodina, O.A., Eskov, A.K., 2018. Humification and humic acid composition of suspended soil in oligotrophic Environments in South Vietnam. Appl. Environ. Soil Sci. 2018.

Anda, M., Shamsuddin, J., Fauzi, C.I., 2013. Increasing negative charge and nutrient contents of a highly weathered soil using basalt and rice husk to promote cocoa growth under field conditions. Soil Tillage Res. 132, 1–11.

Awadon, M.A., Omonjo, L.I., Omoniyi, S.O., 2007. Effect of goat dung and NPK fertilizer on soil and leaf nutrient content, growth and yield of pepper. Int. J. Soil Sci. 2, 142–147.

Badalucco, L., Rao, M., Colombo, C., Palumbo, G., Lauricina, V.A., Gianfreda, L., 2010. The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

Abakumov, E.V., Rodina, O.A., Eskov, A.K., 2018. Humification and humic acid composition of suspended soil in oligotrophic Environments in South Vietnam. Appl. Environ. Soil Sci. 2018.

Anda, M., Shamsuddin, J., Fauzi, C.I., 2013. Increasing negative charge and nutrient contents of a highly weathered soil using basalt and rice husk to promote cocoa growth under field conditions. Soil Tillage Res. 132, 1–11.

Awadon, M.A., Omonjo, L.I., Omoniyi, S.O., 2007. Effect of goat dung and NPK fertilizer on soil and leaf nutrient content, growth and yield of pepper. Int. J. Soil Sci. 2, 142–147.

Badalucco, L., Rao, M., Colombo, C., Palumbo, G., Lauricina, V.A., Gianfreda, L., 2010. The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

Abakumov, E.V., Rodina, O.A., Eskov, A.K., 2018. Humification and humic acid composition of suspended soil in oligotrophic Environments in South Vietnam. Appl. Environ. Soil Sci. 2018.

Anda, M., Shamsuddin, J., Fauzi, C.I., 2013. Increasing negative charge and nutrient contents of a highly weathered soil using basalt and rice husk to promote cocoa growth under field conditions. Soil Tillage Res. 132, 1–11.

Awadon, M.A., Omonjo, L.I., Omoniyi, S.O., 2007. Effect of goat dung and NPK fertilizer on soil and leaf nutrient content, growth and yield of pepper. Int. J. Soil Sci. 2, 142–147.

Badalucco, L., Rao, M., Colombo, C., Palumbo, G., Lauricina, V.A., Gianfreda, L., 2010. The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.
Min, K., Freeman, C., Kang, H., Choi, S., 2015. The Regulation by Phenolic Compounds of Soil Organic Matter Dynamics under a Changing Environment 2015. Muchen-Muna, M., Pypers, P., Mugendi, D., Kung, J., Mugwe, J., Merckx, R., Vanlauwe, B., 2010. Field Crops Research A staggered maize – legume intercrop arrangement robustly increases crop yields and economic returns in the highlands of Central Kenya. Field Crop. Res. 115, 132–139. Nayak, A.K., Gangwar, B., Shukla, A.K., Manumar, S.P., Kumar, Anjani, Raja, R., Kumar, Anil, Kumar, V., Rai, P.K., Mohan, U., 2012. Long-term effect of different integrated nutrient management on soil organic carbon and its fractions and sustainability of rice-wheat system in Indo Gharatik Plains of India. Field Crop. Res. 127, 129–139.

Ng, E.L., Patti, A.F., Rose, M.T., Schefe, C.R., Wilkinson, K., Smernik, R.J., 2011. Organic soils and their relation to the degree of humification. Can. J. Soil Sci. 91, 181–188.

Ng, E.L., Patti, A.F., Rose, M.T., Schefe, C.R., Wilkinson, K., Smernik, R.J., 2011. Organic soils and their relation to the degree of humification. Can. J. Soil Sci. 91, 181–188.

Panettieri, M., Knicker, H., Murillo, J.M., Madej, C., Piccolo, A., Spaccini, R., Celano, G., Villecco, D., Zaccardelli, M., 2013. Soil and Plant Analysis Laboratory Manual. Jointly published by International Center for Agricultural Research in the Dry Areas (ICARDA) and the National Agricultural Research Centre (NARC), second ed., pp. 46–48 SAS Institute Inc. 2004. SAS/STAT Cary, NC, USA, p. 5121.

Schnitzer, M., Desjardins, J.G., 1965. Carboxyl and phenolic hydroxyl groups in some organic soils and their relation to the degree of humification. Can. J. Soil Sci. 45, 257–264.

Schuman, G.E., Janzen, H.H., Herrick, J.E., 2002. Soil carbon dynamics and potential carbon sequestration by rangelands. Environ. Pollut. 116, 591–596.

Zomer, R.J., Bossio, D.A., Sommer, R., Verchot, L.V., 2017. Global sequestration potential of increased organic carbon in cropland soils. Sci. Rep. 1–8.