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Evaluating the effects of formulated nano-NPK slow release fertilizer composite on the performance and yield of maize, kale and capsicum

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ABSTRACT

Effect of formulated slow release NPK fertilizer [cellulose-*graft*-poly(acrylamide)/nanohydroxyapatite/soluble fertilizer] composite (SRF) on the performance and yield of maize, kale and capsicum was evaluated in a greenhouse experiment. No significant difference in growth parameters was observed between SRF and commercial fertilizer (CF) treatments. SRF recorded higher dry matter and yields relative to CF with similar application rates, though statistically insignificant. P deficiency was observed in maize at lowest SRF application rate of 45-57-17. N deficiency in CF was observed at the 8th week, but not in SRF with similar application rates during the same period. Kale showed both N and P deficiencies in the 7th week, while capsicum alone showed N deficiency in the 14th week in SRF at low application rates. NPK content in both maize and kale tissues, was significant between the amendments and control. Capsicum tissues had significantly ($p \leq 0.05$) higher N content both in SRF and CF higher application rates of 125-159-45 & 100-100-100, respectively, compared to control. At final harvest, soil samples planted with maize and amended with the highest SRF rate showed significantly ($p \leq 0.05$) higher P content, compared to lower rates and the control. The agronomic optimal rate of SRF determined by quadratic function were found to be higher than that of CF. SRF was found to enhance growth and yields of crops just like CF and could potentially have greater benefits such as improving soil health and resilience.

1. Introduction

Agriculture is the key driver to economic growth and the main source of livelihood in rural areas, approximately 80% of Kenyan population (Shoals, 2012; Kenya Economic Report, 2017). Maize (*Zea mays*), kale (*Brassica oleracea* var. *sabellica*) and capsicum (*Capsicum annuum*) are among important crops grown in Kenya by smallholder farmers due to their strong impact on food security and farm income. Maize accounts for 40% of cultivated area and > 51% of staple food produced. More than 75% of maize production is by smallholder farmers who produce > 65% of maize consumed in the country (Abate et al., 2015). Kale locally known as *sukuma wiki* is grown by 90% of smallholder farmers and locally consumed by households. It plays a significant role in nutritional balance and provides employment mostly to women and youth who are involved in its production (http://www.nafis.go.ke/vegetables/kales/, 25th March 2019). Capsicum also called bell pepper or sweet pepper is cultivated as a subsidiary crop, but it has a high export potential. Its local consumption has been increasing due to demand by urban consumers and many farmers have developed interest for the crop (Edgar et al., 2017).

Soil fertility decline however, has contributed to low crop yields in Kenya due to lack of nutrient resources, imbalanced nutrient mining, reduced fallow periods, fewer crop rotations and soil erosion, among other factors (Mucheru-Muna et al., 2013). Among the most limiting nutrients are; nitrogen (N), phosphorus (P) and potassium (K) and also the most sought after to boost yields. A major constraint to fertilizer use and profitable farming has been high production cost, a function of a number of variables such as high transport cost, fertilizer unavailability, lack of credit and markets, devaluation of domestic currencies, weak extension services and skewed agricultural policies that favor industrialists but not the farmers (Muthoni et al., 2013; Karuku et al., 2017).

Sustainable agriculture implies maximizing the net benefits a farmer receives from agricultural production. This can be achieved by increasing crop yields, through increased nutrient and water use efficiency, improved soil health/quality among others (Wang et al., 2013). Farmers mainly use mineral fertilizers such as di-ammonium phosphate (DAP), urea and NPK to increase and sustain crop yields. The nutrients

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in these fertilizers are poorly utilized due to environmental and soil related factors such as P-fixation, leaching and volatilization of NO_3 and N_2O, respectively. The low nutrient use efficiency (NUE) and hence high losses are challenges that not only influence crop production, but also the safety of the agricultural environment and groundwater (Wang et al., 2013; Puntel et al., 2016). To improve NUE, “smart” fertilizers have been developed, among them slow release fertilizers (SRF) (Zeroual and Kossir, 2012). Use of SRF in crop production is considered beneficial due to reduced risk of environmental nutrient loss (Guertal, 2009; Li et al., 2017).

Nevertheless, the adoption of SRFs for agronomic use is currently hindered by higher production cost as compared to conventional fertilizers (Liu et al., 2014). Currently, intensive research is directed towards formulating low cost eco-friendly SRFs and evaluating their efficacy on growth and yield of crops. Lui and Lal (2014) assessed carboxymethyl cellulose stabilized nano-HA (nano-hydroxyapatite) fertilizer suspension and observed improved growth and yield of soybeans, higher than those of $CaHPO_4$ treatment. Montalvo et al. (2015) investigated P uptake by wheat (*Triticum aestivum*) derived from nano-HA (20 nm), bulk HA (600 nm) and triple superphosphate (TSP) in a strong P-sorbing Andosols and Oxisols group of soils. The % P in the plant derived from the fertilizers followed the order; TSP > nano-HA > bulk HA. Li et al. (2017) evaluated combined effects of polymer-coated urea (PCU) and carbon-based urea (CU), on the performance of tomato. The yield in CU treatment was better than those of PCU and urea treatments. These SRFs fertilizer formulations demonstrate enhanced NUE; hence, they can minimize economic losses and potential negative effects such as water pollution associated with conventional fertilizer use.

Due to high cost of fertilizers, amounts supplied to the crops should be sufficient and efficient to increase the yields and returns without environmental degradation. This can be achieved by establishing optimal fertilizer application rate, as defined in both agronomic and economic perspective (Hartinee et al., 2010; Puntel et al., 2016). Agronomically, it is the rate of fertilizer application beyond which extra addition produces no change in crop yield, and economically, it is the minimum rate of fertilizer application required to maximize returns (Luce et al., 2015). The effect of fertilizer on crop yield can be evaluated using fertilizer response functions that are usually fitted to the data from fertilizer rate trials through regression analysis (Bachmaier and Gandorfer, 2012) and also in forecasting. Curve fitting techniques have been used to estimate optimal application rates (Hartinee et al., 2010; Bachmaier and Gandorfer, 2012; Wang et al., 2014; Puntel et al., 2016). The current study evaluated the response of maize, kale and capsicum to a formulated slow release NPK fertilizer [cellulose-*graft*-poly(acrylamide)/nano-hydroxyapatite/soluble fertilizer] composite to establish their agronomic optimal application rates in a nitisol soil group in Kabete, Kiambu county, Kenya.

2. Materials and methods

2.1. Study site

The study was carried out in a greenhouse at the College of Agriculture and Veterinary Science, University of Nairobi, located in Kiambu County, coordinates 1° 15′ S and 36° 44′ E. The site is representative, in terms of soils and climate, of large areas of the central Kenya highlands. The geology of the area is composed of the Nairobi Trachyte of the Tertiary age. The soils in the area which were used in the greenhouse are very deep (> 180 m), well-drained, dark-red to dark-reddish-brown, friable clays with moderate to high inherent fertility (Gachene, 1989; Karuku et al., 2012; Mucheru-Muna et al., 2013) and are classified as humic nitisols (WRB, 2015).

2.2. Soil sampling for characterization and greenhouse experiment

A field measuring 5 × 5 m was identified and cleaned of trash and plant debris. Soil samples were collected at a depth of 0–40 cm with 600 cm^3 soil auger, bulked to form a composite and sub-samples taken for selected physico-chemical characterization. Sub-soil sample was air-dried in the laboratory and crushed to pass through < 1 mm sieve. Total N was determined by micro-Kjedahl method (Bremner, 1996) and available P by Mehlich 1 method (Mehlich, 1953). Exchangeable cations (Ca, K and Mg) were extracted with 1 M NH_4OAc; Ca and Mg contents were then determined in the leachate using atomic absorption spectrophotometer (AA500, PG Instruments) and K with flame photometer (Corning 410). Organic carbon (OC) was determined by wet oxidation method (Nelson and Sommers, 1996) and organic matter (OM) calculated by multiplying the % OC by 1.724. Soil texture was by hydrometer method (Glendon and Doni, 2002). Soil pH-H_2O was determined with pH meter (Metrohm 632, with glass electrodes) at a 1:2.5 soil to water ratio, while electrical conductivity (ECe) was measured at a 1:2.5 (soil to water ratio) extract using conductivity meter (HANNA, HI 9812). Cation exchange capacity (CEC) was determined by leaching the soil with NH_4OAc at pH 7 and the NH_4^+ concentration in the leachate determined through steam distillation by micro-Kjeldahl method (Bremner, 1996). Extra soil was collected for the potted greenhouse experiment.

2.3. Greenhouse experiment

4 kg of soil were put into experimental pots, water added to field capacity (30% w/w) and amended with SRF 17:22:6 which composed of 57% cellulose-g-poly(acrylamide), 14.3% nano-HA, 8.6% $(NH_4)_2HPO_4$, 14.3% urea and 5.7% K_2SO_4 (w/w) previously formulated by Rop et al. (2018). Alongside SRF treatments, the soil was amended with CF in the rates shown in Table 1. Maize, kale and capsicum were planted as test crops where in the first set of pots, 2 maize seeds (var.

Table 1
Fertilizer application rates at planting.

Treatment	Maize (106, 667 plants/ha)		Kale (74, 074 plants/ha)		Capsicum (59, 259 plants/ha)	
	Appl. rates (kg ha^{-1})	$N:P_2O_5:K_2O$ (kg ha^{-1})	Appl. rates (kg ha^{-1})	$N:P_2O_5:K_2O$ (kg ha^{-1})	Appl. rates (kg ha^{-1})	$N:P_2O_5:K_2O$ (kg ha^{-1})
Control	0	0:0:0	0	0:0:0	0	0:0:0
S1	266	45:57:17	185	31:40:11	148	25:32:9
S2	532	89:114:33	370	62:79:23	296	50:64:18
S3	798	134:171:50	556	93:119:34	444	75:95:27
S4	1064	178:228:66	741	124:159:46	592	100:127:36
S5	1333	223:285:83	926	155:199:57	740	125:159:45
CF1	532	90:90:90	370	63:63:63	296	50:50:50
CF2	1064	180:180:180	741	126:126:126	592	100:100:100

S1–S5 are SRF treatments, CF1 and CF2 are commercial fertilizer treatments, N - Nitrogen; P_2O_5 – Phosphorous; K_2O - Potassium.

Table 2
Physico-chemical characteristics of soil.

Parameter	Units	Value	Rating (Landon, 1991)
Sand	%	24	–
Silt	%	38	–
Clay	%	38	–
Textural class	–	Clay-loam	–
pH (soil: H_2O, 1: 2.5)	–	5.98	Moderate
Electrical conductivity (ECe)	dSm^{-1}	0.20	Salt free
CEC	Cmol(+) kg^{-1}	14.5	Moderate
Organic carbon	%	1.40	Very low
Organic matter (OM)	%	2.41	Low
Total N	%	0.04	Very low
Available P (Melich I)	mg/kg	5.50	Very low
Exchangeable K	Cmol(+) kg^{-1}	0.82	High
Exchangeable Ca	Cmol(+) kg^{-1}	5.10	Moderate
Exchangeable Mg	Cmol(+) kg^{-1}	1.65	Moderate

H513) were sown at a depth of 4 cm. In the other two sets, 2, 4 weeks-old seedlings of kale and capsicum were transplanted. The experiment was laid out in completely randomized design (CRD) consisting of 7 treatments and the control, replicated thrice. The plants were sprinkled with water every 3 days and thinned to one, 3 weeks (wks) after planting. Weeds were uprooted whenever they emerged, pests managed with application of Imidacloprid twice, every 10 days at 1 mL/2 L of water and diseases controlled with Metalaxy-m + Mancozeb, every 10 days at 5 g/2 L of water.

2.4. Data collection

Plant performance was monitored from the 4th week after planting. It involved counting the number of leaves and measuring plant; height, stem thickness, as well as length and maximum width of the leaves. The plant girth was determined from stem diameter measured at half the plant height using Vernier caliper, while the plant height, leaf length and maximum width were measured with a tape measure. The leaf area of harvested kale was measured using a millimeter graph paper (Pandey and Singh, 2011). The leaf was spread over a millimeter graph paper, outline drawn and the area covered by the outline cut and weighed. A 1 cm^2 of the graph paper was also cut and weighed, and the leaf area calculated using Eq. (1).

$$Leaf\,area\ (cm^2) = a/b \tag{1}$$

where, a is the weight of the graph paper covered by the leaf outline and b is the weight of the 1 cm^2 graph paper.

For maize and capsicum, the length and maximum width of all the leaves were measured in a growing plant and the leaf area estimated using the Eq. (2).

$$Area\ (cm^2) = b \times length \times max.width \tag{2}$$

where, b is a coefficient found to be 0.602 for capsicum (Ray and Singh, 1989) and 0.75 for maize according to Montgomery (1911) and adopted by Maddonni and Martínez-Bercovich (2014).

Kale leaves were harvested bi-weekly from the 7th wk after transplanting on 4 occasions and mature capsicum fruits harvested continuously from the 12th wk for a period of 6 wks. The fresh weights measured in the day of harvest were each used to determine cumulative yields. Maize was harvested on the 20th wk after emergence, grains were air-dried to adjust the moisture content to the recommended 13% and then weighed. For dry matter, above ground biomass of maize and capsicum was cut at final harvest and oven dried to constant weight at 60 °C. For kale, cumulative dry weight of harvested leaves was summed up with that of the stem at final harvest. A sub-sample was taken from dry matter, pulverized and NPK extracted by wet oxidation method (Anderson and Ingram, 1993). N content was then determined using micro-Kjedahl method (Bremner, 1996), P with molybdenum blue method (Murphy and Riley, 1962) and K by flame photometry.

2.5. Estimation of optimal fertilizer application rates

The yield response quadratic function was used to determine the optimal fertilizer application rates (Eq. (3)). For a quadratic function, the yield increases to a maximum with increase in the amount of fertilizer and then declines in a mirror image of the increments (Hartinee et al., 2010). The agronomic optimal fertilizer application rate (x_{agr} kg ha^{-1}) was determined using Eq. (4) (Wang et al., 2014; Luce et al., 2015; Puntel et al., 2016).

$$y_{fer} = y - y_0 = a + bx + cx^2 \tag{3}$$

$$x_{agr} = -\frac{b}{2 \bullet c} \tag{4}$$

where, y_{fer} is the increase in crop yield response with the addition of fertilizer (fertilizer-derived yield, Mg/ha), y and y_0 are the crop yields (Mg ha^{-1}) with and without fertilizer application, respectively, x is the fertilizer application rate (kg ha^{-1}), a is the intercept, b and c are linear and quadratic coefficients, respectively.

2.6. Statistical analysis

The data was subjected to ANOVA using IBM SPSS Statistics Version 20. Tukey honest significant difference (HSD) post hoc test was used to compare and assess the significance of the mean values at $P \leq 0.05$.

3. Results and discussion

3.1. Soil characteristics before the onset of the experiment

Physico-chemical characteristics of soil for the greenhouse experiment are presented in Table 2. The soil is clay-loam according to soil textural triangle and slightly acidic due to moderate leaching of Ca and Mg ions ascribed to humid conditions in the study area. It had low electrical conductivity (ECe) indicating salt free soils and hence good permeability. ECe in sub-humid tropics has been reported to be < 4 dSm^{-1} (Lelago et al., 2016) due to sufficient rainfall flashing out base forming cations. Thus, absorption of water in such soil is not a problem to the plants due to low osmotic effect of dissolved salts. CEC was moderate hence satisfactory for crops provided adequate fertilizers are supplied (Landon, 1991). Low organic carbon and organic matter was attributed to low organic materials added to the soil as crop residues are completely removed at harvest. Total N was low, an observation attributed to low external inputs such as plant residues and manure, as well as losses of NO_3-N through leaching. The low available P may be attributed to intensive cropping system, mining, imbalanced use of fertilizer and fixation by the kaolinitic clay minerals inherent in this soil. Nitisols have high P fixation capacity (WRB, 2015). High exchangeable K was attributed to predominance of K rich minerals such as mica (Lelago et al., 2016), though its availability and depletion may influence crop yields (Kapkiyai et al., 1999). Exchangeable Ca and Mg were moderate and attributed to the nature of the parent material. These cations can be depleted through continuous cultivation and subsequent removal by crops and use of acidifying fertilizers (Chimdessa, 2016).

3.2. Growth and yield response of maize

Growth parameters and yield of maize are given in Table 3. The number of leaves, leave area and girth increased from the 4th to the 8th wk after planting, with some decrease observed in the 12th wk in SRF treatments S1–S5 probably due to senescence (Fig. 2c & d); a phenomenon attributable to heat stress, age related development and N

Table 3
Maize growth parameters and yield.

Treatment	No. of leaves			Total leaf area (cm^2)			Height (cm)			Girth (cm)			Grain yield (Mg/ha)	Biomass (Mg/ha)
	4 w	8 w	12 w	4 w	8 w	12 w	4 w	8 w	12 w	4 w	8 w	12 w		
Cntrl	4.0^{a}	5.0^{a}	7.0^{a}	204^{a}	637^{a}	1082^{a}	14^{a}	33^{a}	77^{a}	2.1^{a}	2.3^{a}	2.6^{a}	0.00^{a}	2.08^{a}
S1	6.3^{b}	7.7^{ab}	7.0^{a}	775^{b}	2948^{b}	2217^{b}	23^{bc}	75^{b}	226^{b}	3.9^{b}	5.2^{b}	4.4^{b}	2.07^{b}	8.53^{b}
S2	5.6^{ab}	9.0^{bc}	7.6^{ab}	719^{b}	4416^{c}	2988^{b}	25^{bc}	94^{c}	254^{bc}	3.5^{b}	6.3^{bc}	5.3^{bc}	4.10^{c}	12.27^{bc}
S3	6.3^{b}	10.0^{bc}	8.3^{ab}	821^{b}	4650^{c}	3539^{cd}	21^{bc}	98^{c}	268^{bc}	3.8^{b}	6.9^{c}	6.0^{cd}	5.30^{d}	12.41^{bc}
S4	6.0^{ab}	9.3^{bc}	8.6^{abc}	809^{b}	4649^{c}	4141^{cd}	27^{c}	102^{c}	255^{bc}	3.6^{b}	7.0^{c}	6.0^{cd}	5.40^{de}	13.30^{bc}
S5	6.0^{ab}	9.7^{bc}	9.0^{abc}	734^{b}	4593^{c}	4361^{d}	24^{bc}	95^{c}	254^{bc}	3.8^{b}	7.3^{c}	6.6^{d}	6.80^{e}	14.73^{c}
CF1	6.5^{b}	9.5^{bc}	10.0^{bc}	529^{ab}	3892^{bc}	3930^{cd}	24^{bc}	95^{c}	255^{bc}	3.9^{b}	6.3^{bc}	5.3^{bc}	3.97^{c}	12.74^{bc}
CF2	6.0^{b}	11.0^{c}	11.0^{c}	709^{b}	4715^{c}	4543^{cd}	22^{bc}	92^{c}	254^{bc}	4.1^{b}	6.6^{bc}	6.2^{cd}	6.03^{d}	12.59^{bc}

Different letters in the same column are significantly different ($P \leq 0.05$ level).
Cntrl = 0:0:0, S1 = 45:57:17, S2 = 89:114:33, S3 = 134:171:50, S4 = 178:288:66, S5 = 223:285:83, CF1 = 90:90:90, CF2 = 180:180:180.

limitation at plant's maturity stage. Senescence is an oxidative process involving degradation of cellular and sub-cellular structures and macromolecules such as chlorophyll, and mobilization of degradation products such as thylakoid proteo-lipids to other parts of the plant, resulting in decline in photosynthetic rate and subsequent death (Woo et al., 2013). No significant difference in the number of leaves was observed in the 4th and 8th wk among the treatments. In the 12th wk, CF2 recorded the highest number of leaves, though insignificant compared to SRF of similar application rate, S4. Plant height, leaf area and girth increased generally with fertilizer application rates, though not significant among the amendments in the 4th wk. In the 8th wk, the control and had significantly ($p \leq 0.05$) lower values compared to S2, S3, S4, S5 and CF2 while in the 12th wk, highest leaf area and girth was observed in CF2 and S5, respectively, though statistically insignificant compared to S3 and S4. Data on growth parameters indicated that the response of maize to SRF (e.g. S4) compared well to that of CF treatment of similar application rate, CF2.

Grain yield increased significantly ($p \leq 0.05$) with increased application rate from S1 to S3 where the highest value was recorded at S5 though not statistically different from S4. The control recorded zero yields due to inadequate amounts of N and P in the soil (Table 2), suggesting exclusive dependence of maize performance on supplied fertilizer sources. SRF treatments had insignificantly higher grain yields compared to CF treatments with similar application rates such as S2 & CF1. No statistical significance was observed in biomass yield between SRFs (S2, S3, S4, S5) and CFs (CF1 & CF2), implying that, the quantities of nutrients supplied at these rates were sufficient to produce similar biomass. The data thus indicated that SRF improved maize grain yield in the study; though not significant in the cases of growth parameters and dry matter yield (DMY). Hatfield and Parkin (2014) made similar observation when evaluating the effect of enhanced efficiency fertilizers (EEFs) relative to their non-EEF forms on grain yield and biomass of corn. They observed no significant effect of EEFs on the biomass or leaf area indices but, a higher grain yield was recorded in EEFs than non-EEF treatments, an observation related to increased leaf chlorophyll index that increased the ability of corn canopy to capture photosynthetic active radiation (PAR) thus converting it into higher yields. Unlike the current study, Cahill et al. (2010) did not observe increased grain yield in SRF treated corn and wheat, better than that of aqueous urea ammonium nitrate treatment.

The growth and development of maize at early stages is shown in Fig. 1. Maize growth was more vigorous in fertilizer amended soil compared to the control (Fig. 1a). P deficiency was observed as at the 5th week in the control and S1 treated pots, manifesting itself as purplish color in the stalk (Fig. 1b). This was also observed in CF1 and CF2 (Fig. 1c) treated pots, but was less severe compared to the control and S1. The deficiency observed in S1 may be attributed to inadequate supply of P, whereas for CF1 and CF2, P fixation by clays may have occurred due to direct and prolonged interaction of soluble P with soil particles. The nitisol in the Kenya highlands are dominated by kaolinitic clay (Karuku, 2011; Karuku et al., 2012) with high P sorption capacity (WRB, 2015). The kaolinite is a 1:1 type clay mineral with the chemical composition $Al_2Si_2O_5(OH)_4$ (Wei et al., 2014). The surface sites of kaolinite contain aluminol groups (≡Al-OH) located at the edges and the OH-terminated planes of the clay lamellae. This type of clay is often present in the soil alongside Fe oxides, where they tend to associate by forming oxide coatings on the surface of clay mineral (Karuku, 2011; Wei et al., 2014). The Al (and Fe) hydrous oxides have the capacity to adsorb large quantities of P added to the soil through; (i) ligand exchange where P anions replace the –OH groups at the surface of Al (and Fe) oxides and hydrous oxides, (ii) precipitation of Al and Fe phosphates at low pH (< 4.5–5.0), or the formation of insoluble calcium phosphates at high pH (> 6.0) (Haynes and Mokolobate, 2001).

SRFs amendments with higher rates S3, S4 and S5 were not manifested with P deficiency an observation attributed to sustained release of sufficient quantities of soluble P from DAP as well as solubilization of nano-HA through the action of microbes by secreting organic acids such as oxalic, formic, citric and acetic acids to chelate mineral ions or lower the pH (Alori et al., 2017). Plant roots also modify the physico-chemical environment of the rhizosphere through exudation of organic acids and release of proton [H^+] due to the activity of proton pump ATPases located at the root plasmalemma (Houmani et al., 2015). The rhizosphere is the zone in soil where plant roots influence microbial activity (Karuku, 2019). Active interaction occurring among the plant roots, soil and microbes within this zone results in increased N mineralization which subsequently, increases the net plant N assimilation (Karuku, 2019).

Plant nutrition is thought to largely influence the release of H^+ and generally, addition of NH_4^+ leads to acidification of rhizosphere due to excess uptake of cations over anions (Wang and Tang, 2018). This acidity within the rhizosphere initiates the dissolution of nano-HA according to Scheme 1. The increased concentration of H^+, continuous removal of the reaction products i.e., $H_2PO_4^-$ and Ca^{2+} through crops' uptake (Arcand and Schneider, 2006) and neutralization of OH^- by the acidic soil, favor the equilibrium shift to the right, making it a self-propagating process. Microbial degradation of polyacrylamide to polyacrylic acid could also create an acidic environment within the copolymer thus enabling dissolution of P. This formulated slow release NPK is therefore a smart fertilizer since the chances of P fixation are reduced due to less duration of its interaction with soil particles.

The images of maize at mid and advanced growing stages are shown in Fig. 2. N deficiency manifested as yellowing of leaves in CF1 and CF2 is observed in the 8th wk (Fig. 2a). However, this manifestation was not observed in SRF treatments with similar or higher application rates in the same period (Fig. 2b). This is an indication of low availability of N in CF treatments, attributed to microbial immobilization, leaching losses and/or binding by the soil due to early interaction with the soil particles. Conversely, the N in SRF was physically shielded, thus delaying its interaction with soil particles due to initial slow release of soluble N and later release of mineralized amide-N. This is

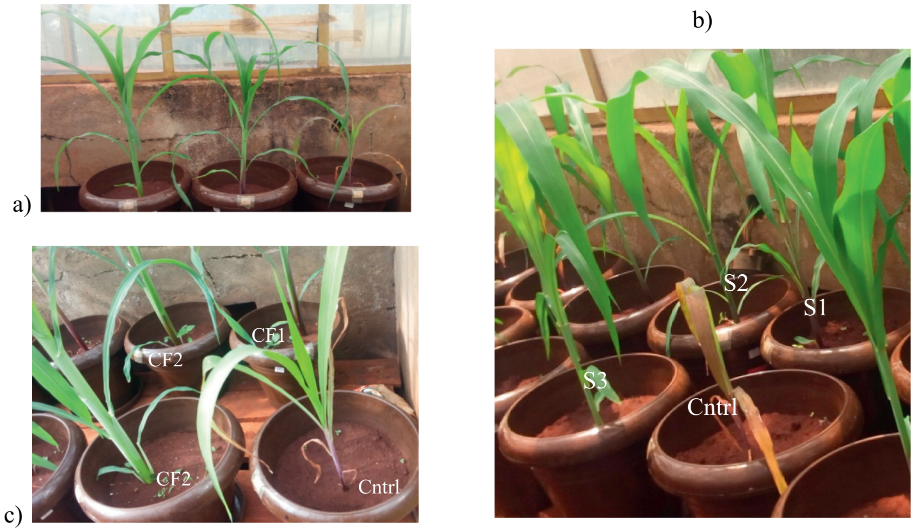


Fig. 1. Photographs of maize after; a) 3 weeks in SRF treatments; from right to left is the control, S1, S2, b) 5 weeks in SRF treatment, c) 5 weeks in CF treatments. Key: control = 0:0:0, S1 = 45:57:17, S2 = 89:114:33, S3 = 134:171:50, CF1 = 90:90:90, CF2 = 180:180:180.

advantageous because N requirement by maize is low at establishment, high at development and reproductive phases, and declines at maturity. This release synchronizes with plant N requirement, reduces losses thus increasing NUE. Khan et al. (2015) in a similar study observed that delayed hydrolysis of urea in Super urea and Agrotain, synchronize N availability with crop's requirement.

Nonetheless, leaf senescence was observed in the 12th wk both in SRF (Fig. 2c) and CF treatments (Fig. 2d), progressing from the lower leaf upwards and more pronounced at low application rates. Senescence enables the degradation of nutrients produced during the growing stages of the leaf and their redistribution to developing seeds and other plant parts (Woo et al., 2013). Leaf senescence in the study occurred earlier than expected towards the end of maturity in maize. Possibly, the amount of N assimilated by plants during development stage may not have been sufficient to build up reserves for utilization in the reproduction stage. N being mobile both in soil and plants, tends to relocate from older to younger leaves, a phenomenon observed by Schildhauer et al. (2008) in *Hordeum vulgare* and *Arabidopsis thaliana* deprived of N, a situation later alleviated when these plants were resupplied with N. Senescence has also been linked to growth conditions such as high temperatures (Hatfield and Prueger, 2015), that induce formation of reactive oxygen species (ROS) such as H_2O_2, $\dot{O}_2^-$ and $\dot{O}H^-$ radicals (De la Haba et al., 2014). Low ROS levels trigger stress defense responses, though they may at times increase to toxic levels, injuring cellular membranes and other cellular components due to oxidative stress and eventually cell death (Wang et al., 2013). ROS play a key role in the degradation of lipids and proteins, inactivation of enzymes, pigment bleaching and disruption of DNA strands during senescence (Woo et al., 2013; De la Haba et al., 2014).

3.3. Growth and yield response of capsicum

Growth parameters, DMY and fruit yields of capsicum are shown in Table 4. The highest number of leaves was recorded in S5, while control pots had the lowest. No significant difference in leaf number was observed in the 4th and 12th wk between S1, S2, S3, S4, S5, CF1 and CF2, treated pots. In the 8th wk, S5 had the highest number of leaves though not significantly different compared to S3 and S4 treated pots. The leaf area, plant height and girth all increased with fertilizer application rates but were not significant among the amendments (S1-S5, CF1 & CF2). The number of fruits, DMY and fruit yields obtained in treatment with the lowest application rate (S1) relative to the control was however significant ($p \leq 0.05$), implying that the amounts of fertilizer applied influenced the performance of capsicum. The highest number of fruits per plant was also recorded in S5 treated pots, though insignificant compared to S3, S4 and CF2 treated pots after mean separation. The fruit and DMY were found to increase significantly ($p \leq 0.05$) with increased amount of SRF from S1 to S4, above which significance between S4 and S5 treated pots ceased. Higher fruit and DMY were recorded in SRF S4, relative to CF of similar application rate CF2, though not significant. Reyes et al. (2008) made similar observation where capsicum in SRF performed better compared to $CaNO_3$ treatment due to improved availability of N. In a similar experiment, Stagnari and Pisante (2012) observed that urea and $Ca(NO_3)_2$ amendments recorded statistically higher capsicum DMY and fruit yields compared to SRF amendment due to delayed N release contrary to this study. However, the two workers observed that ryegrass DMY was higher in SRF due to later release of N after the removal of capsicum from the field. The authors did not observe any advantage of SRF over CF in capsicum nutrition. Conversely, the current study indicated an improved capsicum DM and fruit yield with SRF over CF amendments though insignificant variation in growth parameters.

SRF treated capsicum at the 8th and 14th wk after transplanting is shown in Fig. 3. No deficiency symptoms were observed all through the 4th, 8th to the 12th wk (Fig. 3a). However, a pale-greenish color was noted in the 14th wk in leaves of SRF treated pots receiving low application rates, S1 and S2 (Fig. 3b). This suggested insufficient N supply during growth and hence the exhaustion of N reserves at reproduction stage. Plants with application rates higher than S2 (i.e., S3, S4, S5 and CF2) showed no N deficiency symptoms probably due to higher availability and uptake of N leading to high biomass and fruit yields. The leaf color change could also be attributed to senescence at the end of growing period (Woo et al., 2013). Control pots with stunted crop growth at the end of the study period could be attributed to limited N & P as indicated in the initial soil chemical characterization (Table 2).

3.4. Performances parameters and yield response of kale

The performance parameters and the yield of kale are shown in Table 5. The plant height generally increased with increased fertilizer

$$Ca_{10}(PO_4)_6(OH)_2 + 12H^+ \rightleftharpoons 10Ca^{2+} + 6H_2PO_4^- + 2OH^-$$

Scheme 1. Neutralization reaction expressing the dissolution of nano-HA.

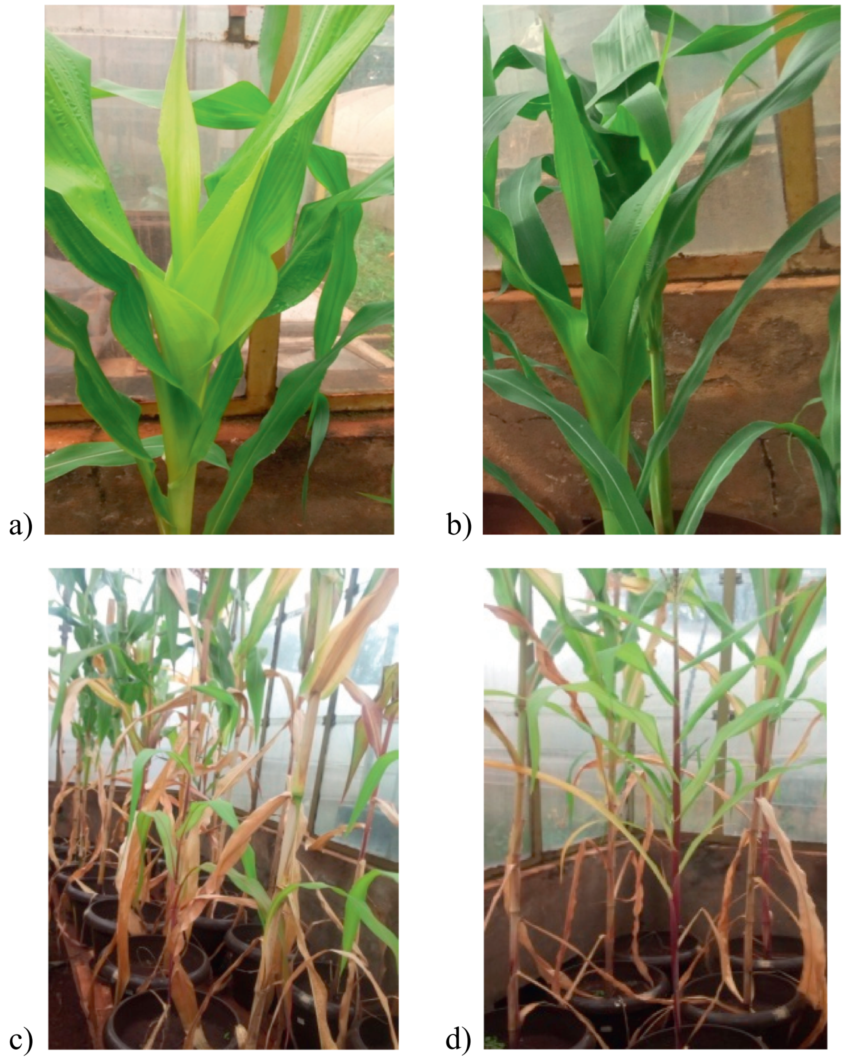


Fig. 2. Photographs of maize after, a) 8 weeks in CF treatment CF1, b) 8 weeks in SRF treatments S2, c) 12 weeks in SRF treatments, d) 12 weeks in CF treatments. Key: CF1 = 90:90:90, S2 = 89:114:33.

application rates, though statistically insignificant among the treatments. No significant difference was observed in the girth as well at the 4th wk since transplanting among the fertilizer treatments S1 to S5, CF1 and CF2. The highest girth size was recorded in S5 treatment in the 8th wk, though not significant compared to S2 to S4, CF1 and CF2. In the 12th wk after planting, S5 treatment had significantly the highest girth ($P \leq 0.05$) compared to all other treatments. The cumulative number of leaves was however not significant among all the amendments (S1 to S5, CF1 & CF2). The cumulative leave area increased significantly ($P \leq 0.05$) with increased fertilizer application rate, with S5 treatment having the highest value recorded. However, this S5 value was not significantly different compared to S3 and S4. Generally, the effect of SRF on growth parameters was not statistically significant from that of CF treatments; hence, either can substitute the other with SRF being more beneficial as it improves soil health and resilience over time.

The cumulative kale fresh weight also increased significantly

Table 4
Mean growth parameters, biomass and fruit yield of capsicum.

Treatment	No. of leaves			Leaf area (cm^2)			Height (cm)			Girth (cm)			No. of fruits/plant	Fruit yield (Mg/ha)	Biomass (Mg/ha)
	4 w	8 w	12 w	4 w	8 w	12 w	4 w	8 w	12 w	4 w	8 w	12 w			
Cntrl	5.4^{a}	8.0^{a}	11.2^{a}	48^{a}	74^{a}	211^{a}	6.9^{a}	9.6^{a}	16.8^{a}	0.96^{a}	1.07^{a}	1.38^{a}	0.8^{a}	0.45^{a}	0.11a
S1	8.6^{ab}	18.3^{ab}	27.0^{ab}	174^{abc}	610^{ab}	1066^{ab}	13.0^{a}	35.6^{b}	52.3^{b}	1.43^{ab}	2.20^{b}	2.62^{b}	3.0^{b}	9.41^{b}	0.57^{b}
S2	8.7^{ab}	20.0^{ab}	32.0^{ab}	150^{abc}	640^{ab}	1357^{bc}	13.0^{a}	35.5^{b}	57.3^{b}	1.60^{b}	2.10^{b}	2.41^{b}	3.6^{b}	18.14^{c}	0.70^{bc}
S3	10.3^{b}	23.0^{c}	35.6^{ab}	225^{bc}	798^{ab}	1435^{bc}	13.3^{a}	34.6^{b}	52.7^{b}	1.40^{ab}	2.25^{b}	2.51^{b}	4.0^{bc}	21.53^{d}	0.83^{bcd}
S4	10.6^{b}	22.7^{c}	36.3^{b}	289^{c}	885^{b}	1679^{bc}	14.3^{a}	39.0^{b}	50.0^{b}	1.60^{b}	2.36^{b}	2.46^{b}	4.3^{bc}	23.37^{de}	1.06^{cde}
S5	11.3^{b}	24.3^{c}	46.0^{b}	300^{c}	986^{b}	2230^{c}	12.0^{a}	32.3^{b}	58.0^{b}	1.63^{b}	2.51^{b}	2.98^{b}	5.6^{c}	25.35^{e}	1.18^{e}
CF1	8.7^{ab}	18.5^{ab}	40.5^{b}	115^{ab}	852^{b}	1809^{bc}	10.5^{a}	36.0^{b}	56.7^{b}	1.47^{ab}	1.51^{b}	2.83^{b}	3.0^{b}	16.66^{c}	0.86^{bcd}
CF2	9.5^{b}	19.5^{ab}	36.0^{b}	140^{abc}	1042^{b}	1859^{bc}	10.0^{a}	35.5^{b}	52.5^{b}	1.63^{b}	2.75^{b}	3.14^{b}	4.0^{bc}	21.80^{d}	0.96^{cde}

Different letters in the same column are significantly different ($P \leq 0.05$ level).
Cntrl = 0:0:0, S1 = 25:32:9, S2 = 50:64:18, S3 = 75:95:27, S4 = 100:127:36, S5 = 125:159:45, CF1 = 50:50:50, CF2 = 100:100:100.

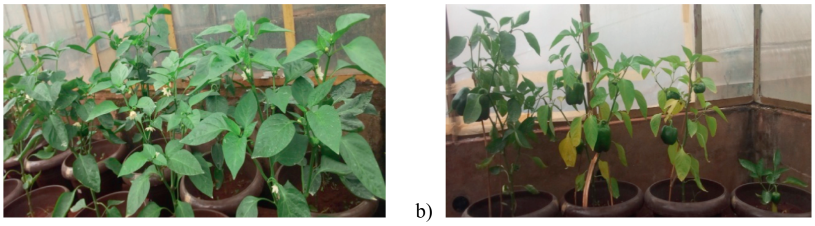
a) b)


Fig. 3. Photographs of SRF treated capsicum after; a) 8 weeks, b) 14 weeks, from right to left is the control, S1, S2 and S3.
Key: Control = 0:0:0, S1 = 25:32:9, S2 = 50:64:18, S3 = 75:95:27.

Table 5
Mean growth parameters and yield of kale.

Treatment	Height (cm)			Girth (cm)			Cum. no. of leaves	Cum. leaf area (cm^2)	Cum. fresh wt (Mg/ha)	Biomass (Mg/ha)
	4 w	8 w	12 w	4 w	8 w	12 w				
Cntrl	6.0^{a}	10.0^{a}	10.8^{a}	1.2^{a}	1.83^{a}	1.57^{a}	9.4^{a}	250^{a}	1.04^{a}	0.18^{a}
S1	10.3^{a}	17.3^{a}	20^{ab}	2.53^{b}	3.24^{b}	3.35^{b}	16.7^{ab}	1482^{b}	7.30^{b}	1.31^{b}
S2	9.70^{a}	18.6^{ab}	22^{ab}	3.31^{b}	4.61^{bc}	4.92^{bc}	19.6^{b}	2316^{c}	12.47^{c}	2.35^{cd}
S3	15.0^{a}	31.0^{ab}	35^{ab}	3.06^{b}	4.29^{bc}	4.82^{bc}	22.3^{b}	3531^{de}	16.15^{bc}	3.05^{d}
S4	11.0^{a}	23.7^{ab}	25^{ab}	3.33^{b}	4.92^{c}	5.23^{c}	20.0^{b}	3912^{ef}	18.66^{cd}	2.96^{d}
S5	10.7^{a}	24.7^{ab}	35^{ab}	2.35^{b}	5.13^{c}	7.01^{d}	22.0^{b}	4596^{e}	22.40^{d}	3.06^{d}
CF1	6.6^{a}	14.0^{ab}	17^{ab}	2.91^{b}	4.40^{bc}	4.24^{bc}	19.0^{ab}	2705^{c}	14.67^{bc}	1.71^{bc}
CF2	7.5^{a}	15.5^{ab}	24^{ab}	3.31^{b}	4.40^{bc}	5.50^{bc}	22.5^{b}	2909^{cd}	18.23^{bc}	1.86^{bc}

Different letters in the same column are significantly different (P ≤ 0.05 level).
Cntrl = 0:0:0, S1 = 31:40:11, S2 = 62:79:23, S3 = 93:119:34, S4 = 124:159:46, S5 = 155:199:57, CF1 = 63:63:63, CF2 = 126:126:126.

a) b) c)


Fig. 4. Photographs of SRF treated kale, a) 7 weeks old, from right to left is the control, S1 and S2, b) 8 weeks, S1 and c) leave with signs of nutrient deficiency.
Key: Control = 0:0:0, S1 = 31:40:11, S2 = 62:79:23.

(P ≤ 0.05) with increased application rates with the highest value again recorded in S5, though insignificant compared to S4. No significant difference in the cumulative fresh weight was observed between SRF and CF treated pots with similar application rates. However, significantly higher biomass (P ≤ 0.05) was observed in SRF treatments S2 and S4, compared to CF treatments with similar rates; CF1 and CF2. This was attributed to higher P content in SRF shipments (S2 & S4) compared to CF (CF1 & CF2) (Table 1). This invariably increased the availability and assimilation of P, with a greater portion coming from nano-HA. Further, the copolymer fraction of SRF composite may have conditioned the soil through increased water holding capacity, providing favorable microbial conditions that enhanced N mineralization and assimilation by kale. In similar studies, Li et al. (2013) obtained insignificantly higher biomass yield in zeolite SRF compared to CF treatment with the same nutrient content and attributed it to enhanced NUE and reduced nutrient loss.

Fig. 4 shows kale growth in SRF amended soil at 7th and the 8th wk after transplanting. The vegetative growth of kale was increased in SRF fertilizer amendment, the effect more pronounced with increased application rate, whereas the control was stunted (Fig. 4a). P deficiency was observed in kale (Fig. 4b) plots that received the lowest application rate. The lower leaves had yellowish and purplish coloration, subsequently becoming necrotic, originating from the leaf tip (Fig. 4c). These observations indicated deficiency of N, P and K, respectively.

3.5. Plant tissue and soil nutrient content at harvest of the crops

The plant tissue and soil nutrient contents post-harvest of the three crops are shown in Table 6. Significantly higher (≤0.05) N content in capsicum tissues was observed in both SRF and CF treatments with the highest rates, compared with the control. This implies sufficient N amounts at these application rates. NPK content in plant tissues was not significantly different in most of the amendments (S1-S5, CF1 & CF2) relative to the control, an observation attributable to the utilization of these nutrients in biomass, fruits and grains production. N is an essential constituent of amino acids and proteins; P promotes root development and plays a key role in metabolic processes as the main constituent of energy compounds in nucleic acids and phospholipids, while K is involved in physiological processes such as osmoregulation, assimilate transport and enzyme activation (Wang et al., 2013; Yayeh et al., 2017). The nutrients may have been utilized by plants to improve their general health and yields.

Soil pH, TN and K content had No significant difference between the control and the amendments post-harvest. Significantly higher P (P ≤ 0.05) relative to the control was observed in S4 and S5 where maize was harvested. This observation was attributable to the residual nano-HA. For the soil where capsicum and kale were harvested, the highest P contents were also recorded in S5 whereas the lowest values were observed in the controls, though not significant. Nonetheless, the levels of total N and available P in S5, were quite low to support plant's growth according to Landon (1991).

Fig. 5 shows the residual fertilizer composite after harvest of crops at the end of the experiment. The plant's roots penetrated into the fertilizer composite, suggestive of direct nutrient uptake. The copolymer composite material also lost its hydrophilicity, an indication of microbial degradation of hydrophilic amide group that causes swelling (Laftah and Hashim, 2014). Oven-dried sample transformed from initial strong material, enough to withstand adverse conditions/rough handling, to easily pulverizable material suggestive of degraded copolymer chains.

Table 6
Maize, capsicum and kale tissue, and soil nutrient contents after harvest.

	Plant tissue nutrient content			Soil nutrient content			
Treatment	N (g/kg)	P (g/kg)	K (g/kg)	pH	% N	P (mg/kg)	K (Cmol/kg)
Maize							
Cntrl	2.6[a]	0.75[a]	7.91[abc]	6.27[ab]	0.09[a]	8.67[a]	0.83[a]
S1	2.8[ab]	0.77[a]	7.49[a]	6.40[ab]	0.13[ab]	13.26[ab]	1.40[ab]
S2	5.7[ab]	0.82[a]	7.76[ab]	6.23[ab]	0.13[ab]	12.71[ab]	1.30[ab]
S3	2.7[ab]	0.77[a]	9.53[bcd]	6.27[ab]	0.15[a]	10.57[ab]	1.25[ab]
S4	3.0[ab]	0.74[a]	10.46[cd]	6.14[a]	0.16[ab]	15.63[b]	1.20[ab]
S5	4.3[ab]	0.80[a]	10.36[cd]	6.18[a]	0.11[ab]	23.15[c]	1.41[ab]
CF1	2.0[a]	0.77[a]	9.73[cd]	6.08[a]	0.13[ab]	10.64[ab]	1.15[ab]
CF2	2.7[ab]	0.79[a]	9.74[cd]	6.40[ab]	0.11[ab]	12.85[ab]	1.04[ab]
Capsicum							
Cntrl	3.3[a]	0.81[a]	12.58[a]	6.26[abc]	0.11[ab]	6.72[a]	1.34[a]
S1	4.9[abc]	0.86[a]	15.50[a]	6.51[bc]	0.15[ab]	13.55[ab]	1.55[ab]
S2	5.1[abc]	0.76[a]	14.41[a]	6.66[c]	0.17[b]	10.71[ab]	1.53[ab]
S3	5.4[abc]	0.86[a]	13.96[a]	6.32[abc]	0.11[ab]	11.15[ab]	1.50[ab]
S4	3.7[ab]	0.84[a]	13.91[a]	6.13[ab]	0.10[ab]	14.51[ab]	1.72[ab]
S5	6.0[bc]	0.87[a]	13.90[a]	6.02[a]	0.17[b]	19.14[ab]	1.46[ab]
CF1	5.0[abc]	0.85[a]	12.30[a]	6.16[ab]	0.10[a]	11.15[ab]	1.47[ab]
CF2	6.5[c]	0.90[a]	12.90[a]	6.46[abc]	0.13[ab]	17.95[ab]	1.95[ab]
Kale							
Cntrl	19.2[abc]	2.30[a]	18.77[ab]	6.19[a]	0.10[a]	8.07[a]	0.83[a]
S1	17.3[a]	2.21[a]	19.21[ab]	6.45[a]	0.11[a]	10.43[a]	1.39[ab]
S2	18.5[ab]	2.75[a]	19.27[ab]	6.08[a]	0.13[a]	11.70[a]	1.27[ab]
S3	16.9[a]	2.82[a]	17.61[a]	6.45[a]	0.13[a]	11.70[a]	1.33[ab]
S4	22.3[abc]	3.00[a]	18.67[ab]	6.58[a]	0.11[a]	10.93[a]	1.40[ab]
S5	24.5[bc]	2.66[a]	19.38[ab]	5.97[a]	0.11[a]	14.63[a]	1.21[ab]
CF1	20.7[abc]	2.59[a]	18.71[ab]	6.27[a]	0.11[a]	9.55[a]	1.11[ab]
CF2	25.5[c]	2.50[a]	22.30[ab]	6.13[a]	0.12[a]	11.35[a]	1.51[ab]

Different letters in the same column for each crop, are significantly different ($P \leq 0.05$ level).
Cntrl = 0:0:0, S1 = 25:32:9, S2 = 50:64:18, S3 = 75:95:27, S4 = 100:127:36, S5 = 125:159:45, CF1 = 50:50:50, CF2 = 100:100:100.

Fig. 5. Fertilizer composite in the soil after crop harvest.

Table 7
Nutrient content (n = 9) of the composite material after harvesting the three crops.

Treatment	N (g/kg)	P (g/kg)	K
S1	89[a]	6.48[a]	1.07[a]
S2	95[ab]	6.99[ab]	1.10[a]
S3	100[ab]	6.95[ab]	1.08[a]
S4	106[ab]	7.55[ab]	1.16[a]
S5	100[ab]	8.41[ab]	1.12[a]

Different letters in the same column are significantly different ($P \leq 0.05$ level).
S1 = 25:32:9, S2 = 50:64:18, S3 = 75:95:27, S4 = 100:127:36, S5 = 125:159:45.

The nutrient content of the composite material after harvesting the crops is shown in Table 7. No statistical significance was observed among the SRF treatments after harvesting the crops. N and P contents in SRF composite were not completely exhausted by crops, which may in the long term, improve the soil quality, an added advantage over CF which is susceptible to leaching and fixation. The residual composite could also enhance further degradation of the remaining polymeric portion because the microbes require sufficient amounts of N & P and a carbon (energy) source for maintenance and growth (Karuku, 2019).

3.6. Optimal formulated fertilizer application rates

The yield response regression curves for kale, capsicum and maize are given in Fig. 6. The R^2 value ranged from 0.97 to 0.99 indicating good fit of the experimental data to the quadratic regression model. The crop yields at agronomic optimal application rates (AOAR) are presented in Table 8. The AOARs of SRF were found to be generally higher compared to CF treatments. This implies that the soil may need higher dosage of SRF and plants could utilize the nutrients efficiently, whereas in CF, the nutrients may be lost through leaching or denitrification processes, fixed by the soil particles or bound to soil organic matter into unavailable forms. Further, the associated injury or "burning" of the root hairs of young plants at high application rates is unlikely in SRF due to the slow release nature. The crop yields at AOARs were also found to be higher in SRF compared to CF treatments, an indication of improved NUE. As observed in the regression curves (Fig. 6), untreated soil recorded near zero crop yields due to insufficient supply of N and P (Table 2). The determination of AOAR in similar studies are commonly carried out in the field experiments using conventional fertilizers with focus directed towards a single nutrient such as N. For example, Wang et al. (2014) determined optimal N rate for summer maize in 91 sites in a 2 year field experiment and reported increased grain yield with application rate to an optimum value above which it declined.

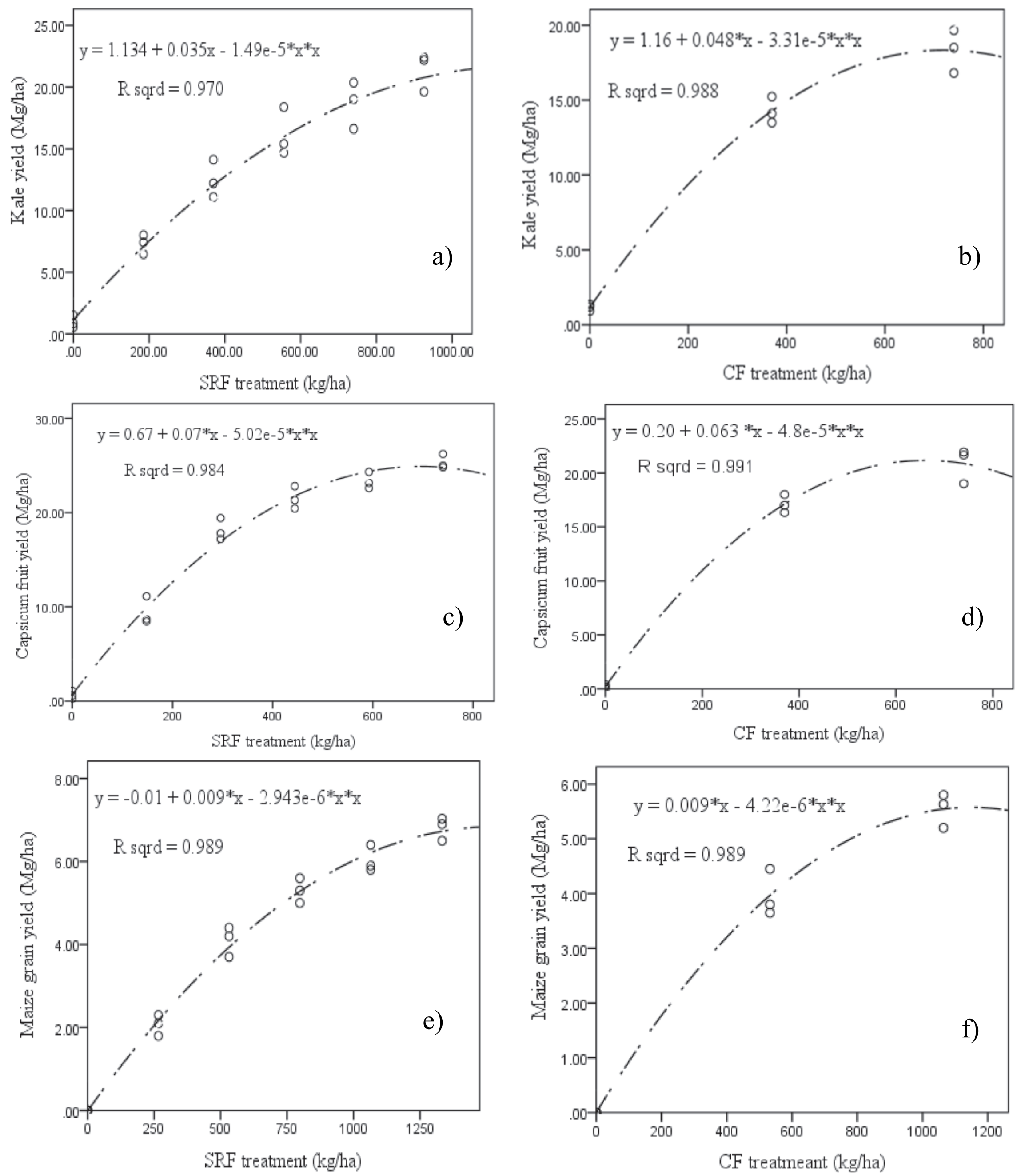


Fig. 6. Yield response regression curves; (a&b) SRF and CF treated kale, (c&d) SRF and CF treated capsicum, (e & f) SRF and CF treated maize, respectively.

Table 8
The crop yields at agronomic optimal application rates.

Treatment	Kales		Maize		Capsicum	
	AOAR (Mg ha^{-1})	Fresh wt. yield (kg ha^{-1})	AOAR (Mg ha^{-1})	Grain yield (kg ha^{-1})	AOAR (Mg ha^{-1})	Fruit yield (kg ha^{-1})
SRF	1175	21.8	1529	7.0	697	25.1
CF	725	18.6	1066	5.4	656	20.9

SRF = slow release fertilizer, CF = commercial fertilizer, AOAR = agronomic optimal application rates.

Poffenbarger et al. (2017) also evaluated crop response to N rate and obtained agronomic optimum of N rates for a continuous maize system and for maize in rotation with soybean. The workers found a mean difference between the yields at agronomic optimal N rate and the yield at zero N rate of 6.6 Mgha^{-1} for maize following maize and 4.8 Mg ha^{-1}for maize following soybean.

4. Conclusion and recommendations

The performance parameters had no significant difference among the SRF and CF treatments with similar application rates. However, SRF showed increased maize grain yield, capsicum fruit numbers and DMY, and increased kale DMY, though none was significantly different from CF treatments. The crops depended mainly on the external supply of nutrients and deficiency was observed in all crops at low application rates. N deficiency was observed in CF treated maize (CF1 &CF2) as at the 8th wk but not in SRFs of similar (S2) or higher rates. This probably suggests synchrony of N release in SRF with crop's requirement. The agronomic optimal application rates of SRF were higher than CF, suggesting enhanced NUE even at higher SRF doses. S5 though the agronomic optimal rate for capsicum, was slightly higher than S5 for both maize and kale. CF2 was the optimal rate for the three test crops and hence, the study objective realized. SRF can therefore replace CF as it is more eco-friendly, easy to synchronize and thus promoting NUE and environmental protection.

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