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Nitrogen and sulphur release dynamics and kinetics in soils incubated with sulphur-augmented nitrogen sources

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ABSTRACT

The study investigated N and S release dynamics and kinetics in soils incubated with sole and sulphur-augmented N fertilizer sources to evaluate their release patterns, potentially releasable quantities, and release rate constants. 50g of soil samples (from Ibadan and Ogbomoso, Nigeria) were measured into incubation cups and treated with Cattle Manure (CM) at 90 kg Nha^{-1}, CM at 90 kg Nha^{-1}+sulphur powder (SP) at 30 kg Sha^{-1}, Cocoa Pod Powder (CPP) at 90 kg Nha^{-1}, CPP at 90 kg Nha^{-1}+SP at 30 kg Sha^{-1}, NPK 20-10-10 at 90 kg Nha^{-1}, NPK 20-10-10 at 90 kg Nha^{-1}+SP at 30 kg Sha^{-1} and No Fertilizer Treatment (NFT). The incubated soils were moistened with distilled water at 60% field capacity thrice per week throughout a 105-day incubation period under ambient laboratory conditions and were analysed for N and S contents at 21, 42, 63, 84, and 105 days. The experiment was a completely randomized design with three replicates. Data on N and S release were evaluated, and fitted into zero, first- and second order kinetics equations. Release dynamics of N followed the order; NPK+SP/NPK/CPP+SP/CPP>CM+SP/CM>NFT in soils of both locations, while orders of S release were CPP+SP/CPP>CM+SP>CM/NPK+SP>NPK>NFT and CPP+S/CPP/CM+SP>CM>NPK+SP>NPK>NFT in soils of Ibadan and Ogbomoso, respectively. The release of N and S conformed to zero, first, and second order kinetics with coefficients of determination (R^2), ranging from 0.20 to 0.99. Therefore, soil incorporation of sole and sulphur-augmented CM and CPP could be substituted for sole and sulphur-augmented NPK 21 days before planting of N and S-demanding crops.

Contribution/ Originality: Augmentation of fertilizer materials such as cattle manure and cocoa pod powder with sulphur powder and their comparison with sole and S-augmented NPK for nitrogen and sulphur release dynamics and kinetics studies have not been researched.

1. INTRODUCTION

Nitrogen (N) is an indispensable element and usually becomes the first to be limiting as crop cultivation intensifies. It is the most dynamic of all nutrients [1]. Its functions in plants are numerous. It is a constituent of chlorophyll, amino acids, nucleic acids, enzymes, and proteins [2]. It is responsible for leaf and root expansion, as well as general growth and development of crops. Nitrogen deficiency causes many biochemical and physiological disturbances leading to the reduction in cell division rates and disruption in photosynthetic process. Roggatz, et al. [3]. Akanbi, et al. [4] reported that increased N levels led to an increase in photosynthetic rate and leaf area. In enhancing soil productivity, N application is crucial [5]. It plays an important role in synthesis of growth hormones such as auxin and takes part in regulation of metabolic activities [6]. Nitrogen, being a great determinant of crop's yield, needs to be carefully managed amidst astronomically rising cost of inorganic sources of the element, which is prone to leaching and volatilization.

Sulphur plays a key role in oil, protein, and chlorophyll syntheses. Higher oil content of seed crops due to sulphur application has been attributed to the influence of sulphur in rapid conversion of nitrogen to crude protein and finally to oil as brought about by acetic thiolinase, a sulphur-based enzyme in the presence of S, which converts acetyl Coenzyme-A to melonyl Coenzyme-A, rapidly resulting in higher oil content Krishnamurthy and Mathan [7]. Cecotti [8] reported that S plays an important role in plant metabolism as a component of proteins, glucosinolates, and other compounds that relate to several parameters determining the nutritive quality of plants. High yield and quality of oilseed crops are possible when crops have access to the optimum amount of sulphur [9]. Sulphur is a prominent component of various plant proteins and plays a critical role in root growth and seed production.

It is the component of several amino acids (Cystine cysteine and methionine), which are the basic structural units of protein molecules and responsible for the development of taste and flavour in oilseed crops [10].

Therefore, this study was carried out to evaluate (i) N and S release dynamics in soils incubated with sole and S-augmented N fertilizer sources and (ii) N and S kinetics of soils incubated with sole and S-augmented N fertilizer sources using kinetic equation models as bases for estimating their release potentials and rate constants.

2. MATERIALS AND METHODS

Soil samples were taken at 0-15 cm depth from two locations, namely Ibadan (7°22′N; 3°55′E) and Ogbomoso (8°07′N; 4°14′E) in southwestern Nigeria. Prior to incubation, soils were analysed. The pH (H_2O) was determined with the aid of a pH meter buffered between pH 4 and 7. Total N was determined by macro-kjeldahl method as described by Bremner [11].

Available P was determined by Bray-1 P method [12]. Exchangeable bases (Ca, Mg, K, and Na) were determined according to Jackson [13] using a 1M neutral ammonium acetate (1M NH_4OAc pH 7.0) solution. Available sulphur was determined by turbimetric method [14]. Organic carbon was determined by wet dichromate method [15]. Texture was determined by Bouyoucos hydrometer method [16]. The computed textural components (% sand, % silt, and % clay) were finally input on texture check menu of Soil Kit App for confirmation of the textural class, thereby eliminating the rigour of tracing the textural class on textural triangle. Cattle manure (CM) was collected from Institute of Agricultural Research and Training, Ibadan, while cacao pod husk (CPH) was collected from fermentatory unit of Cocoa Research Institute of Nigeria (CRIN), Ibadan. The CPH was spread in windrow chamber of composting section of the screenhouse at the back of the Agronomy Building, University of Ibadan, Nigeria to air-dry for four weeks and was later ground into powder to form Cocoa Pod Powder (CPP). Analysis for nutrient contents (N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu) was done using prescribed procedures of Association of Official Analytical Chemist (A. O. A. C.) [17].

In the incubation study, 50g of soil sample was measured into incubation cups (4 cm diameter x 6.5 cm height) and treated with Cattle Manure (CM) at 90 kg N ha^{-1}, CM at 90 kg N ha^{-1} + sulphur powder (SP) at 30 kg S ha^{-1}, Cocoa Pod Powder (CPP) at 90 kg N ha^{-1}, CPP at 90 kg N ha^{-1} + SP at 30 kg S ha^{-1}, NPK 20-10-10 at 90 kg Nha^{-1}, Nitrogen-phosphorus-potassium (NPK) fertilizer grade 20-10-10 at 90 kg N ha^{-1} + SP at 30 kg S ha^{-1} and No Fertilizer Treatment (NFT). The incubated soils were moistened with distilled water at 60% field capacity thrice per week throughout a 105-day incubation period under ambient laboratory conditions (temperature; 22-28^{0}C, relative humidity; 82- 89%). The experiment was completely randomized design with three replicates (five incubation cups per replicate to cater for five-time incubation periods of 21, 42, 63, 84, and 105 days). Two hundred and ten incubation cups (7 fertilizer treatments x 3 replicates x 5 incubation periods x 2 location soils) were used. Total N and available S contents of incubated soils were determined at 21, 42, 63, 84 and 105 days of incubation (DOI) to ascertain the extent of their release dynamics.

Furthermore, nitrogen and sulphur release patterns were subjected to kinetics study by fitting their release data into zero-, first- and second- order kinetics using the relationship denoted by the equations [18, 19] stated below:

$$Zero - order: q_t = q_0 - k_0 t \qquad (1)$$

$$First - order: ln(q_t) = ln\,(q_0) - k_1 t \text{ or } log_e\, q_t = log_e\, q_o - k_1 t \text{ or } q_1 = q_0 e{-}^{k1t} \qquad (2)$$

$$Second - order: 1/q_t = 1/q_0 - k_2 t \qquad (3)$$

Where q_0 is the estimated quantity or releasable potential of nutrient initially present in the incubated soil at day 1, q_t is the amount present after a specific time of incubation, and t is time of incubation (21, 42, 63, 84, 105), while k_0, k_1 and k_2 are zero, first- and second- order kinetics constants, respectively. The essence of the kinetics study of N and S is to determine whether the release of each of the nutrients is independent of its initial entire concentration (zero-order) or dependent on its initial concentration with constant proportion of release (first-order) or dependent on concentration of one nutrient and the other (second-order) if they interact. Therefore, a mathematical description of N and S release could provide useful indices for estimating their release potentials and rates in soils.

As regards zero-order kinetics, q_t values were plotted against days of incubation (DOI) values for determining their coefficients of determination (R^2) and equations on regression curves, q_0 was estimated from the equation of the curve at first day, k_0 was derived from the gradient of the curve by dividing the estimated q_0 with mean interval of DOI. For first-order, ln q_t values were plotted against t values with R^2 values and equations determined from the curve as well; the ln q_0 was determined from the equation of the curve for the first day and converted to q_0 value as e^{lnq0}, while k_1 was determined by dividing the slope with mean interval of DOI.

For second-order kinetics, $1/q_t$ values were plotted against t (DOI) values with their R^2 values and equations displayed by regression curve; $1/q_0$ was determined from the equation of the curve and converted to q_0 value as inverse of $1/q_0$. The second-order constant (k_2) was determined by dividing the slope with mean interval of DOI as well. The release dynamics and kinetics studies are useful for the purpose of determining periodic release level, initial releasable potential, and kinetics rate constant prior to growing a crop at the field locations from where such soils are collected.

3. RESULTS AND DISCUSSION

3.1. Pre-Incubation Soil Properties

The pH (H_2O) was 6.1 (slightly acidic) in soil of Ibadan, whereas it was 5.9 (moderately acidic) in soil of Ogbomoso (Table 1). The soil of Ibadan had higher organic carbon (12.2 g/kg) than that of Ogbomoso, which was valued of 11.7 g/kg. The available phosphorus was above critical level of 10.0 mg/kg stated by Akinrinde and Obigbesan [20]. The total N values of soils from the two locations were low (1.3, 1.2) considering the critical values of 1.5g/kg [20, 21]. The soils of Ibadan and Ogbomoso had exchangeable potassium of 0.2 cmol/kg, which was above critical level of 0.15 cmol/kg according to Akinrinde and Obigbesan [20] and Chude, et al. [21]. Available sulphur of soil from Ibadan and Ogbomoso had lower values of 6.1 and 5.6 mg/kg, respectively, than 10 mg/kg critical level stated by Oseni, et al. [22]. The soils were sandy loam and loamy sand for Ibadan and Ogbomoso, respectively.

Table 1. Pre-incubation soil properties of Ibadan and Ogbomoso locations.

Parameter	Ibadan	Ogbomoso
pH (H_2O)	6.1	5.9
Organic C (g/kg)	12.2	11.7
Total N (g/kg)	1.3	1.2
Available nutrients (mg/kg)		
P	12.0	13.0
S	6.1	5.6
Exchangeable cations (cmol/kg)		
Ca^{2+}	1.6	1.4
Mg^{2+}	1.4	1.2
K^+	0.2	0.2
Na^+	0.2	0.1
Exchangeable acidity (cmol/kg)	0.1	0.2
ECEC (cmol/kg)	3.5	3.1
Extractable micronutrients (mg/kg)		
Cu	1.5	3.1
Fe	21.0	22.0
Mn	3.5	3.0
Zn	48.2	50.1
Particle size analysis (g/kg)		
Sand	673	768
Silt	131	122
Clay	196	110
Textural class	Sandy loam	Loamy sand

Table 2. Nutrient contents of cattle manure, cocoa pod powder and NPK.

Nutrient	Cattle manure	Cocoa pod powder	NPK
g/kg			
N	5.0	4.0	200.0
P_2O_5	2.0	5.0	100.0
K_2O	4.0	7.0	100.0
Ca	1.3	1.6	0.0
Mg	6.0	8.0	0.0
mg/kg			
S	3.0	7.0	0.0
Zn	46.0	58.0	0.0
Cu	22.0	36.0	0.0
Fe	11.0	7.0	0.0
Mn	36.0	31.0	0.0

Note: NPK- nitrogen-phosphorus-potassium fertilizer grade 20-10-10.

3.3. Influence of Nitrogen and Sulphur Application on Total Nitrogen Across Incubation Periods

In soils of Ibadan location, all fertilizers improved total N status of the soil across incubation periods, as shown in Table 3. Cow dung manure-CM increased total N from 1.75 g/kg at 21 DOI to 2.63 g/kg at 105 DOI (34.6-102.3%) over initial value of 1.30 g/kg prior to incubation. Soil treated with CM + SP had total N increase of 34.6-105.4% (1.75–2.67 g/kg). Increments of 52.3–126.1% (1.98–3.07 g/kg) and 40.7–141.5% (1.83–3.14 g/kg) were observed in soil treated with CPP and CPP + SP, respectively (Table 3). On the other hand, NPK and NPK + SP fertilizers increased total N with percentage values of 66.9–140.8% (2.17–3.13 g/kg) and 63.1–142.3% (2.12–3.15 g/kg). In soils with NFT, total N was raised from 1.61 g/kg at 21 DOI to 1.90 g/kg at 105 DOI (23.8–53.8%). Up to 63 DOI, NPK and NPK + SP treated soils outperformed others. However, as of 84 DOI, NPK and NPK + SP were no longer superior to CPP and CPP + SP in terms of N release but to CM and CM + SP, which were better than NFT.

Table 3. Effects of fertilizers on total nitrogen (g/kg) at successive incubation periods in soils of Ibadan and Ogbomoso locations

Treatment	Ibadan					Ogbomoso				
	Days of incubation									
	21	42	63	84	105	21	42	63	84	105
CM	1.75d	2.19c	2.58c	2.60d	2.63b	1.64d	2.10c	2.43c	2.49d	2.58b
CM + SP	1.75d	2.17c	2.62c	2.63d	2.67b	1.60d	2.12c	2.49c	2.48d	2.57b
CPP	1.98b	2.62b	2.85b	2.88b	3.07a	1.87b	2.42b	2.67b	2.69b	2.89a
CPP + SP	1.83c	2.65ab	2.87b	2.91ab	3.14a	1.79c	2.46ab	2.69b	2.75ab	2.94a
NPK	2.17a	2.71a	2.96a	2.99a	3.13a	2.11a	2.56a	2.82a	2.89a	3.10a
NPK + SP	2.12a	2.67a	2.99a	3.01a	3.15a	2.03a	2.55a	2.78a	2.93a	3.15a
NFT	1.61e	1.71d	1.82d	1.87e	1.90c	1.52e	1.70d	1.77d	1.82e	1.88c

Note: CM- cattle manure at 90 kg N/ha, CPP- cattle manure at 90 kg N/ha, NPK20-10-10 – nitrogen phosphorus potassium fertilizer grade 20-10-10 at 90 kg N/ha, SP- Sulphur powder at 30 kg S/ha.
Means with similar letter along a column within a group are not significantly different according to Tukey pairwise comparison at 5% level of significance.

In the soils of Ogbomoso experimental location, all fertilizers enhanced total N of the soil across successive incubation periods (3). Treatment CM increased total N from 1.64 g/kg at 21 DOI to 2.58 g/kg at 105 DOI (26.7–115.0%) over initial value of 1.20 g/kg before incubation. Soil treated with CM + SP had total N rise of 33.3-114.2% (1.60–2.57 g/kg). Increases of 55.8 – 140.8% (1.87–2.89 g/kg) and 49.1–145.0% (1.79–2.94 g/kg) were observed in soil treated with CPP and CPP + SP, respectively. Likewise, NPK and NPK + SP fertilizers increased total N by 75.8 – 158.3% (2.11–3.10 g/kg) and 69.2–162.5% (2.03–3.15 g/kg). In NFT soil, total N was raised from 1.52 g/kg at 21 DOI to 1.88 g/kg at 105 DOI (26.6–56.7%). At 21 DOI, NPK and NPK + SP outclassed other fertilizers as regards N release, but as from 42 DOI, CPP, CPP + SP, NPK, and NPK + SP incubated soils were similar in their N release ability till 105 DOI. There was no difference between CM and CM + SP treatments, though higher than NFT.

3.4. Influence of Nitrogen and Sulphur Application on Available Sulphur (S) Across Incubation Periods

In soils of Ibadan location, CM application increased the available S from pre-incubation value of 6.1 mg/kg to 6.89 mg/kg at 21 DOI by 13.0% and continued till 105 DOI when available S value reached 9.66 mg/kg, indicating 58.3% over the pre-incubation value (Table 4). Across incubation periods, similar increment trends were observed for other treatments. Soil treated with CM + SP enhanced S by 25.4–66.4% (7.53–10.41 mg/kg) compared with initial value (6.1 mg/kg) before incubation. Incubation of the soil with CPP increased S from 7.25 mg/kg at 21 DOI to 10.38 mg/kg at 105 DOI representing 18.9–70.1% increment in comparison with value prior to incubation. The fertilizer CPP + SP improved S with range of 23.0–78.3% (7.50–10.88 mg/kg while NPK and NPK + SP fertilizers resulted in rise of available S of 13.0 – 28.0% (6.83 – 7.81 mg/kg) and 17.0–48.5% (7.14–9.06 mg/kg), respectively. In untreated soil, an increment of 3.6–10.8% (6.32–6.76 mg/kg) was observed. The order of S enhancement was CPP + SP/CPP > CM + SP > CM/NPK + SP > NPK > NFT.In soils of Ogbomoso, CM application increased the available S from pre-incubation value of 5.2 mg/kg to 6.05 mg/kg at 21 DOI by 8.0% and continued till 105 DOI when the value reached 9.02 mg/kg, signifying 61.1 % when compared with the pre-incubation value of 5.7 mg/kg. Soil treated with CM + SP enriched S by 16.4–78.4% (6.52-9.99 mg/kg) when matched with initial value prior to incubation. Incubation of the soil with CPP increased S from 6.04 mg/kg at 21 DOI to 9.84 mg/kg at 105 DOI, signifying 14.3–75.3% increment in comparison with value before incubation. The fertilizer CPP + SP improved S with range of 12.9–78.9% (7.50–10.88 mg/kg whereas soil incubated with NPK and NPK + SP resulted in an increase of available S by 6.1.0–26.6% (5.84–7.09 mg/kg) and 6.3 – 35.7% (6.25–7.6 mg/kg) respectively. Untreated soil had an increment of 3.6–10.8% (6.32–6.76 mg/kg). The order in which S enhancement occurred was CPP + SP/CPP/CM + SP > CM > NPK + SP > NPK > NFT.

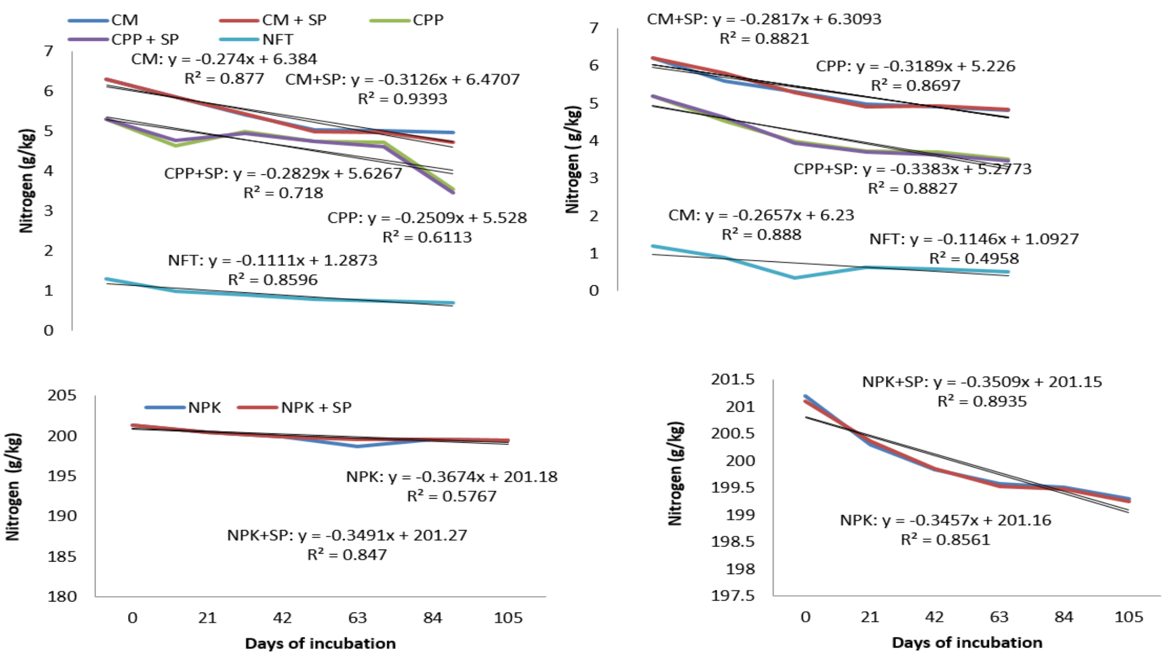
Table 4. Effects of fertilizers on available Sulphur (mg/kg) at successive incubation periods in soils of Ibadan and Ogbomoso locations

Treatment	Ibadan					Ogbomoso				
	Days of incubation									
	21	42	63	84	105	21	42	63	84	105
CM	6.89de	7.59c	9.10b	9.76b	9.66e	6.05bc	6.35bc	8.66ab	9.02b	9.02b
CM + SP	7.53a	7.89ab	9.45a	10.15b	10.14b	6.52a	6.82b	8.98a	9.85a	9.99a
CPP	7.25bc	7.76bc	9.28ab	10.88a	10.88a	6.04bc	6.30c	8.42bc	9.42ab	9.84a
CPP + SP	7.50ab	8.03a	9.54a	10.95a	10.88a	6.32ab	7.55a	8.70ab	9.62a	10.02a
NPK	6.83e	7.03d	7.57d	7.79d	7.81d	5.64d	5.98e	6.96de	7.01d	7.09d
NPK + SP	7.14cd	7.62c	8.81c	8.81c	9.06d	5.95c	6.13de	7.24cd	7.46c	7.60c
NFT	6.32f	6.29e	6.54e	6.75e	6.76e	6.05bc	6.35bc	8.66ab	9.02b	9.02b

Note: CM- cattle manure at 90 kg N/ha, CPP- cattle manure at 90 kg N/ha, NPK20-10-10 – nitrogen phosphorus potassium fertilizer grade 20-10-10 at 90 kg N/ha, SP- Sulphur powder at 30 kg S/ha.
Means with similar letter along a column are not significantly different according to Tukey pairwise comparison at 5% level of significance.

3.5. Kinetics of Nitrogen (N) Release from Fertilizers across Incubation Periods

Figures 1, 2, and 3 present zero, first- and second-order kinetics evaluations of N, respectively, throughout the incubation periods in soils of Ibadan and Ogbomoso locations. In soil of Ibadan location, the data fitted into regression curves indicated that N release from all fertilizers complied with zero, first, and second order kinetics considering the values of their respective significant coefficients of determination (R^2) within the ranges of 0.58 – 0.94, 0.58 – 0.91, and 0.57 – 0.96, while their release kinetics constants (k_0, k_1, k_2) ranged from 0.0053 to 0.0175, 0.0008 to 0.0056, and 2.9 x 10^{-10} to 0.0007 g/kg/day, respectively for zero, first, and second order kinetics along with their estimated releasable quantity-q_0 of 1.17 – 200.92, 1.18 – 200.92, and 1.19 – 200.0 g/kg (Table 5). In soils of Ogbomoso location, N release from incubated soils was suitably described by zero, first, and second-order kinetics models with R^2 values ranging from 0.50–0.89. As regards first and second order kinetics, all treatments conformed to respective R^2 values of 0.86–0.92 and 0.86–0.95, respectively. Kinetics constants ranged from 0.0054 to 0.0165, 0.0009 to 0.0038, and 2.85 x 10^{-10} to 0.0085 g/kg/day, respectively, for zero, first- and second-order kinetics (Table 6). The estimated releasable quantities (q_0) were of the ranges 0.98–200.81, 0.90–200.82 and 0.79–200.0 g/kg for zero, first- and second-order kinetics, respectively (Table 6).



Ibadan Ogbomoso

Figure 1. Zero order kinetics of nitrogen in soils of Ibadan and Ogbomoso locations.

Note: CM- Cattle manure, CPP- Cocoa pod powder, NPK- Nitrogen phosphorus potassium fertilizer 20-10-10, SP- Sulphur powder.

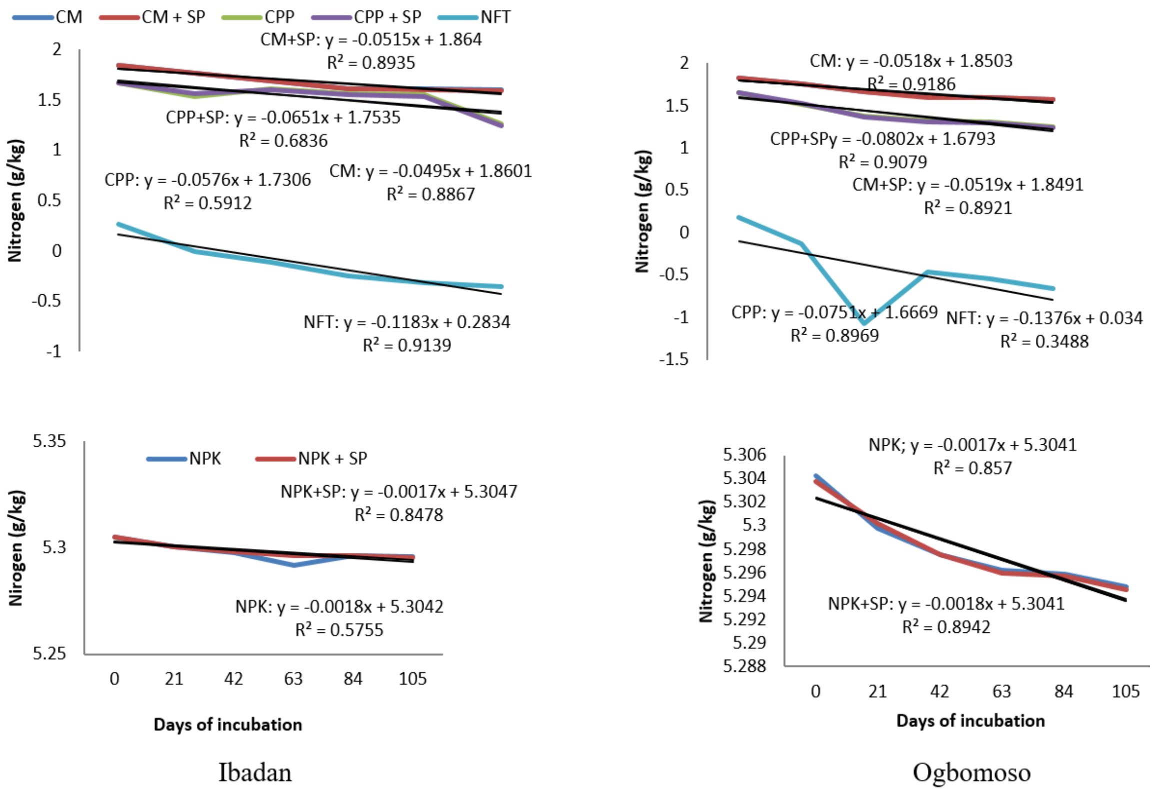


Figure 2. First order kinetics of nitrogen in soils of Ibadan and Ogbomoso locations.

Note: CM- Cattle manure, CPP- Cocoa pod powder, NPK- Nitrogen phosphorus potassium fertilizer 20-10-10, SP- Sulphur powder.

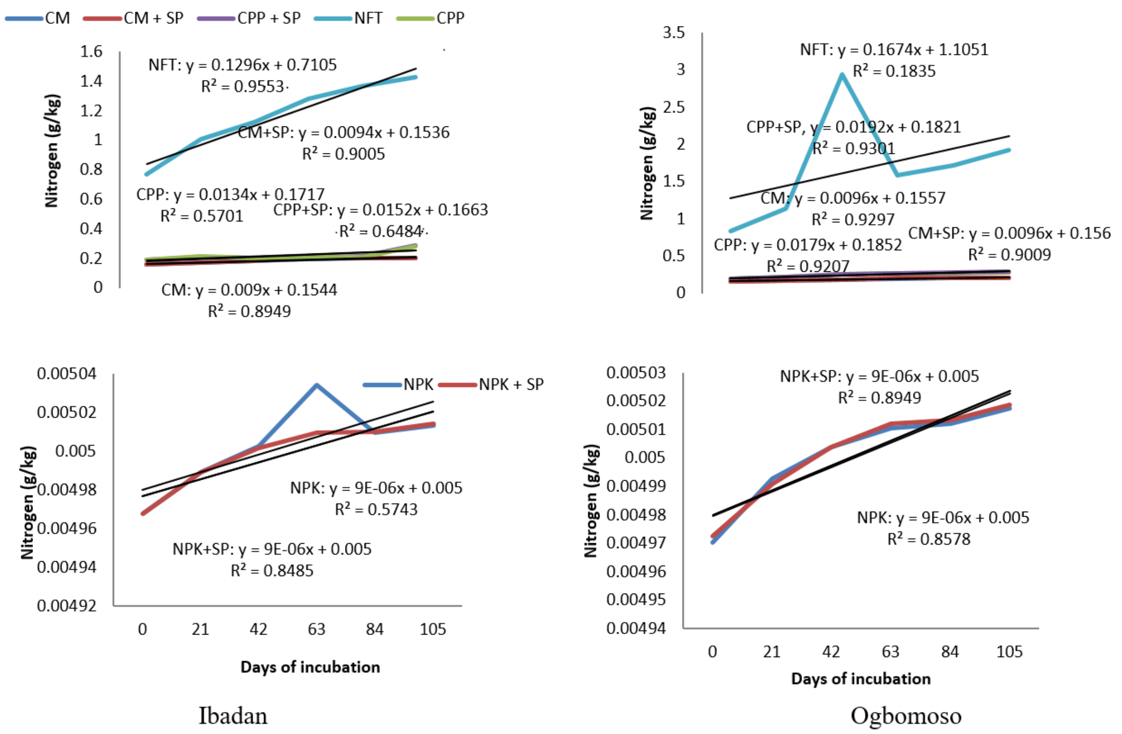


Figure 3. Second order kinetics of nitrogen in soils of Ibadan and Ogbomoso locations.

Note: CM- Cattle manure, CPP- Cocoa pod powder, NPK- Nitrogen phosphorus potassium fertilizer 20-10-10, SP- Sulphur powder.

Table 5. Releasable potential of nitrogen (q0), kinetics constants (k0 k1 & k2) and R2 for zero, first and second order kinetics in soil of Ibadan location.

Fertilizer	Zero order			First order			Second order		
	q_0 g/kg	k_0 g/kg/Day	R^2	q_0 g/kg	k_1 g/kg/Day	R^2	q_0 g/kg	k_2 g/kg/Day	R^2
CM	6.11	0.013	0.877	6.11	0.0024	0.887	6.12	0.0054	0.631
CM+SP	6.12	0.0135	0.939	6.13	0.0025	0.893	6.13	0.0004	0.901
CPP	5.27	0.0119	0.611	5.33	0.0027	0.591	5.40	0.0006	0.570
CPP+SP	5.34	0.0135	0.718	5.41	0.0031	0.684	5.51	0.0007	0.648
NPK	200.81	0.0175	0.577	200.80	0.0009	0.576	200.0	2.9×10^{-10}	0.574
NPK+SP	200.92	0.0166	0.847	200.92	0.0008	0.848	200.0	2.9×10^{-10}	0.849
NFT	1.17	0.0053	0.859	1.18	0.0056	0.914	1.19	0.0062	0.955
SE ±	36.2	0.002	0.053	36.2	0.0007	0.056	40.9	0.001	0.061

Table 6. Releasable potential of nitrogen (q0), kinetics constants (k0 k1 & k2) and R2 for zero, first and second order kinetics in soil of Ogbomoso location.

Fertilizer	Zero order			First order			Second order		
	q_0 g/kg	k_0 g/kg/Day	R^2	q_0 g/kg	k_1 g/kg/Day	R^2	q_0 g/kg	k_2 g/kg/Day	R^2
CM	5.96	0.0127	0.888	5.98	0.0025	0.919	6.05	0.0055	0.950
CM+SP	6.03	0.0134	0.882	6.03	0.0025	0.892	6.04	0.0046	0.901
CPP	4.91	0.0152	0.870	4.91	0.0036	0.897	4.92	0.0085	0.921
CPP+SP	4.94	0.0160	0.883	4.95	0.0038	0.908	4.97	0.0230	0.930
NPK	200.81	0.0165	0.856	200.82	0.0009	0.857	200.0	2.86×10^{-10}	0.858
NPK+SP	200.80	0.0167	0.894	200.80	0.0009	0.894	200.0	2.85×10^{-10}	0.894
NFT	0.98	0.0054	0.496	0.90	0.0006	0.349	0.79	0.0080	0.184
SE ±	36.2	0.0020	0.055	36.2	6×0^{-4}	0.078	36.1	0.002	0.104

Note: CM- Cattle manure, CPP- Cocoa pod powder, NPK- Nitrogen phosphorus potassium fertilizer 20-10-10, SP- Sulphur powder, NFT- No fertilizer treatment.

3.6. Kinetics of Sulphur (S) Release from Fertilizers across Incubation Periods

The zero and first and second order kinetics analysis of S across the incubation periods in soil of Ibadan and Ogbomoso locations are shown in Figures 4 and 5, respectively. In soils of Ibadan location, S release in soils incubated with various fertilizers was in conformity with zero, first- and second-order kinetics when put into consideration the values of their corresponding coefficients of determination (R^2) which fell within the ranges of 0.78–0.95, 0.31–0.96 and 0.77–0.95.

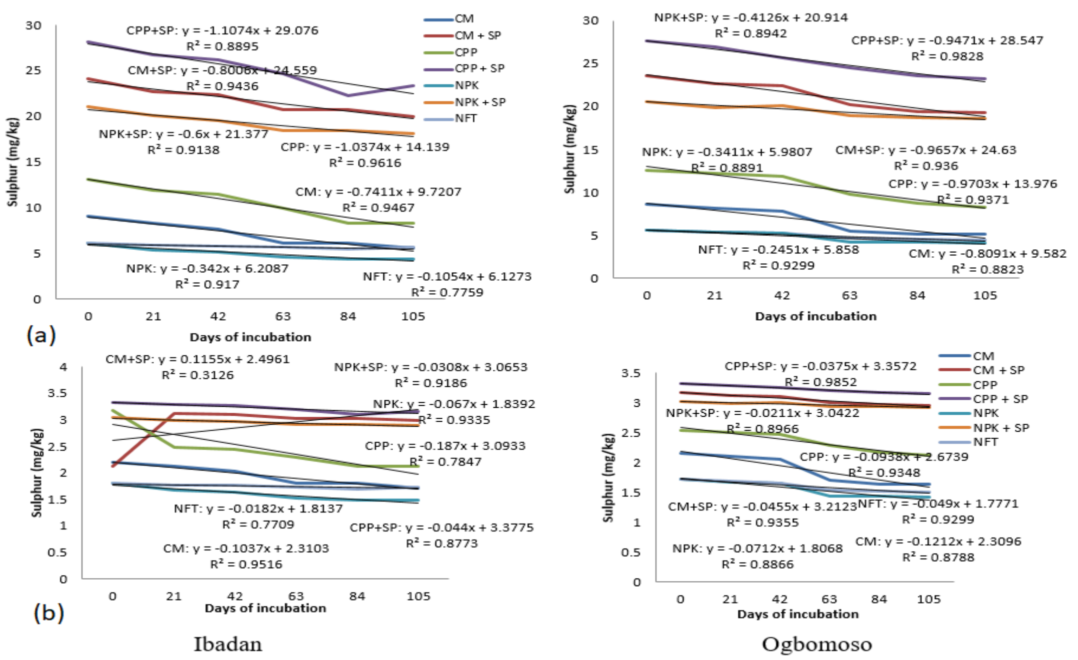


Figure 4. (a) Zero order and (b) first order; kinetics of sulphur in soils of Ibadan and Ogbomoso locations.

Kinetics constants (k_0, k_1, k_2) ranged from 0.005 to 0.038, 0.0015 to 0.0089 and 0.00009 to 0.0007 mg/kg/day, respectively for zero, first- and second-order kinetics, while their estimated initial (releasable) quantity (q_0) had the range of 8.9 – 27.97, 5.88–28.02 and 5.91–28.09 g/kg in soil of Ibadan location (Table 7).

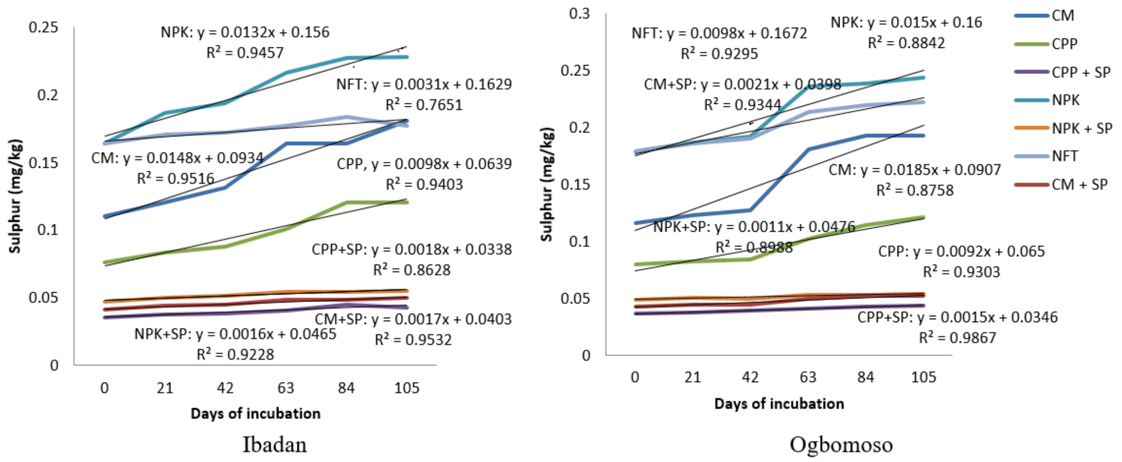


Figure 5. Second order kinetics of sulphur in soils of Ibadan and Ogbomoso locations.

Note: CM- Cattle manure, CPP- Cocoa pod powder, NPK- Nitrogen phosphorus potassium fertilizer 20-10-10, SP- Sulphur powder.

Table 7. Releasable potential of sulphur (q0), kinetics constants (k0 k1 & k2) and R2 for zero, first and second order kinetics in soil of Ibadan location.

Fertilizer	Zero order			First order			Second order		
	q_0 mg/kg	k_0 mg/kg/Day	R^2	q_0 mg/kg	k_1 mg/kg/Day	R^2	q_0 mg/kg	k_2 mg/kg/Day	R^2
CM	8.98	0.035	0.947	9.08	0.0049	0.952	9.24	0.00070	0.952
CM+SP	23.75	0.038	0.943	13.62	0.0055	0.313	23.81	0.00008	0.953
CPP	13.10	0.049	0.962	18.28	0.0089	0.785	13.57	0.00009	0.940
CPP+SP	27.97	0.052	0.890	28.02	0.0029	0.877	28.09	0.00047	0.863
NPK	15.87	0.016	0.917	5.88	0.0032	0.940	5.91	0.00063	0.916
NPK+SP	20.78	0.029	0.913	20.05	0.0015	0.919	20.79	0.00008	0.923
NFT	6.02	0.005	0.775	6.02	0.0009	0.771	6.02	0.00014	0.765
SE ±	3.01	0.006	0.020	3.10	0.0009	0.090	3.38	0.00001	0.026

Note: CM- Cattle manure, CPP- Cocoa pod powder, NPK- Nitrogen phosphorus potassium fertilizer 20-10-10, SP- Sulphur powder, NFT- No fertilizer treatment.

In soil of Ogbomoso location, S release from fertilizers complied with the various kinetics orders, with R^2 values ranging from 0.88–0.98, 0.87–0.99 and 0.88-0.99 for zero, first and second order kinetics models. Kinetics constants ranged from 0.012 to 0.046, 0.001 to 0.0058 and 0.00007 to 0.0009 mg/kg/day, respectively for zero, first- and second-order kinetics, respectively (Table 8).

Table 8. Releasable potential of sulphur (q0), kinetics constants (k0 k1 & k2) and R2 for zero, first and second order kinetics in soil of Ogbomoso location.

Fertilizer	Zero order			First order			Second order		
	q_0 mg/kg	k_0 mg/kg/ Day	R^2	q_0 mg/kg	k_1 mg/kg/ day	R^2	q_0 mg/kg	k_2 mg/kg/ Day	R^2
CM	8.77	0.038	0.882	8.92	0.0058	0.877	9.15	0.00090	0.876
CM+SP	23.66	0.046	0.936	23.73	0.0022	0.936	23.87	0.00010	0.934
CPP	13.00	0.046	0.937	13.20	0.0045	0.935	13.48	0.00040	0.930
CPP+SP	27.60	0.045	0.983	27.65	0.0018	0.985	28.78	0.00007	0.987
NPK	5.64	0.016	0.889	5.67	0.0034	0.887	5.71	0.00070	0.884
NPK+SP	20.50	0.020	0.894	20.51	0.0010	0.897	20.53	0.00005	0.899
NFT	5.61	0.012	0.930	5.80	0.0023	0.930	5.65	0.00047	0.930
SE ±	3.39	0.006	0.014	3.38	0.0006	0.014	3.48	0.00001	0.017

Note: CM- Cattle manure, CPP- Cocoa pod powder, NPK- Nitrogen phosphorus potassium fertilizer 20-10-10, SP- Sulphur powder, NFT- No fertilizer treatment.

The estimated releasable potentials (q_0) were of the ranges 5.61 – 27.6, 5.67 – 27.65 and 5.65 – 28.78 g/kg for zero, first- and second-order kinetics, respectively. The release dynamics and kinetics analysis provided basis of estimation for release pattern prior to field evaluation in that the releasable rate constant could be used to estimate the potentiality of soil N and S status of the field at a particular day even besides specified days of incubation. The kinetics evaluation indicated that pre-incorporation of sole and S-augmented CM and CPP could be done 21 days prior to field trials.

In the incubation study, all fertilizers (sole and sulphur-augmented cattle manure-CM, cocoa pod powder-CPP and NPK) enhanced total N and available S of the soil across successive incubation periods in soils of Ibadan and Ogbomoso locations. This can be ascribed to periodic release of the elements in the fertilizer over time. The release dynamics revealed that N enhancement followed the order: NPK + SP/NPK/CPP + SP/CPP > CM + SP/CM > NFT in soils of the two locations, implying that NPK and NPK + SP treatments were comparable to those of CPP + SP and CPP even though they had higher values of N contents at the end of the incubation period. The orders of S enhancement were CPP+SP/CPP > CM+SP > CM/NPK+SP > NPK> NFT and CPP+SP/CPP/CM+SP > CM > NPK+SP > NPK > NFT in soils of Ibadan and Ogbomoso, respectively. Among fertilizer treatments, it was evident that NPK was least in terms of S enhancement. This can be ascribed to the fact that NPK did not contain sulphur, unlike other fertilizer sources, even though it is not unexpected that N constituent of NPK would interact with the inherent soil S to an extent. In soil of Ibadan and Ogbomoso locations, kinetics of N and S release of all fertilizers conformed with zero, first, and second order kinetics considering the values of their respective significant coefficients of determination (R^2) within the range of 0.20–0.99 across location soils. The implication is that releasable potentials of N and S did not depend on initial contents of the elements in incubated soils, and their release rates differed from one another with occurrence of interaction between N and S. Ghafoor, et al. [23] had earlier reported that zero and first-order kinetics equations suitably described K release from various organic manures. According to Dey, et al. [19] zinc release from vermicompost and biochar was in conformitywith first-order release kinetics like that of magnesium from farmyard manure, whereas S release from vermicompost, farmyard manure, mushroom compost, poultry manure, biogas slurry, biochar, and *Lantana spp* suitably fitted well into second-order kinetics in addition to zero and first-orders.

4. CONCLUSION

This study established that N and S release from sole and sulphur-augmented cattle manure, cocoa pod powder, and NPK 20-10-10 suitably fitted well into zero, first- and second-order kinetics, thus determining periodic release level, initial releasable potential, as well as kinetic rate constant, all of which could serve as bases for timing of pre-planting soil incorporation of the fertilizer materials for crop growth, which require N and S for optimal performance. Sulphur-augmented cattle manure and cocoa pod powder are substitutes of sulphur-augmented NPK for production of crops with high N and S demand and could be applied at least 21 days before planting.

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