

**AN EVALUATION OF ALKALINE HYDROLYZABLE ORGANIC NITROGEN
AS AN INDEX OF NITROGEN MINERALIZATION AND AVAILABILITY IN
BIOCHAR-MANURE COMPOST AMENDED SOILS**

BY

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DECLARATION

I hereby declare that this thesis, “An evaluation of alkaline hydrolyzable organic nitrogen as an index of nitrogen mineralization and availability in biochar-manure compost amended soils” herein presented for a degree of Master of Philosophy in Soil Science is the result of my own investigation and that it has neither in whole nor in part been presented for another degree elsewhere. References to other authors have been duly acknowledged.

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DEDICATION

To my mother, thank you for giving me an opportunity to be there for you.



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ABSTRACT

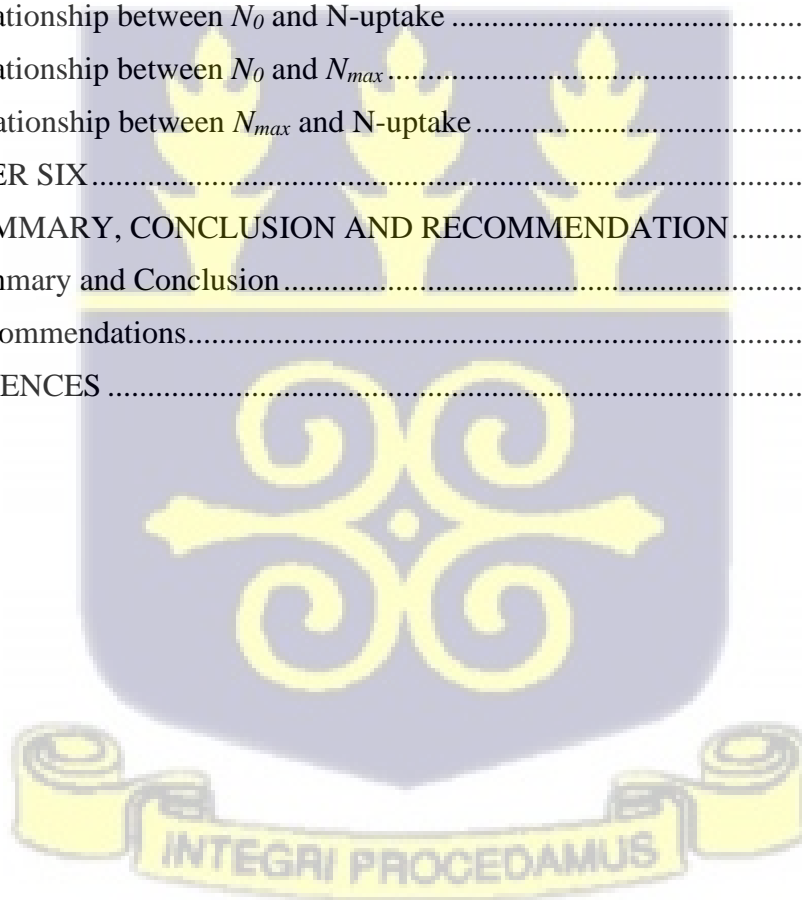
The ability to predict the amount of plant-available nitrogen (N) organic amendments can supply through mineralization are required to improve their efficient use as sources of N fertilizers. This study compared a rapid alkaline hydrolysis of organic nitrogen (ON) method for evaluating the chemical index of N mineralization in soils to the standard long-term biologically based aerobic incubation method in three contrasting soils amended with 12 different biochar-manure composts (BMCs) of varied C/N ratios. The cumulative N mineralized/hydrolyzed from the biological and chemical hydrolysis methods were fitted to the first-order exponential equation to determine the potentially mineralizable N (N_o) and an analogous “potentially hydrolyzable N (N_{max})” for the BMCs. Furthermore, the study also assessed the suitability of the alkaline hydrolysis method as a soil fertility index by comparing the results with actual N uptake by maize in a pot experiment. The results showed that the biological and chemical estimated N_o and N_{max} values differed significantly among the BMCs, suggesting that the chemical composition of the BMCs affected their reactivity and decomposability. It was also observed that the N_o and N_{max} values were positively and significantly correlated ($p \leq 0.01$). The correlation between N_{max} and actual N uptake by maize was also significant ($p \leq 0.05$). These results indicated that the rapid chemical hydrolysis method can be interpreted broadly for both mineralization process and soil fertility assessment. It was concluded that the rapid chemical hydrolysis method offers a time-effective surrogate approach for N mineralization and N supplying capacity of soil organic amendments.

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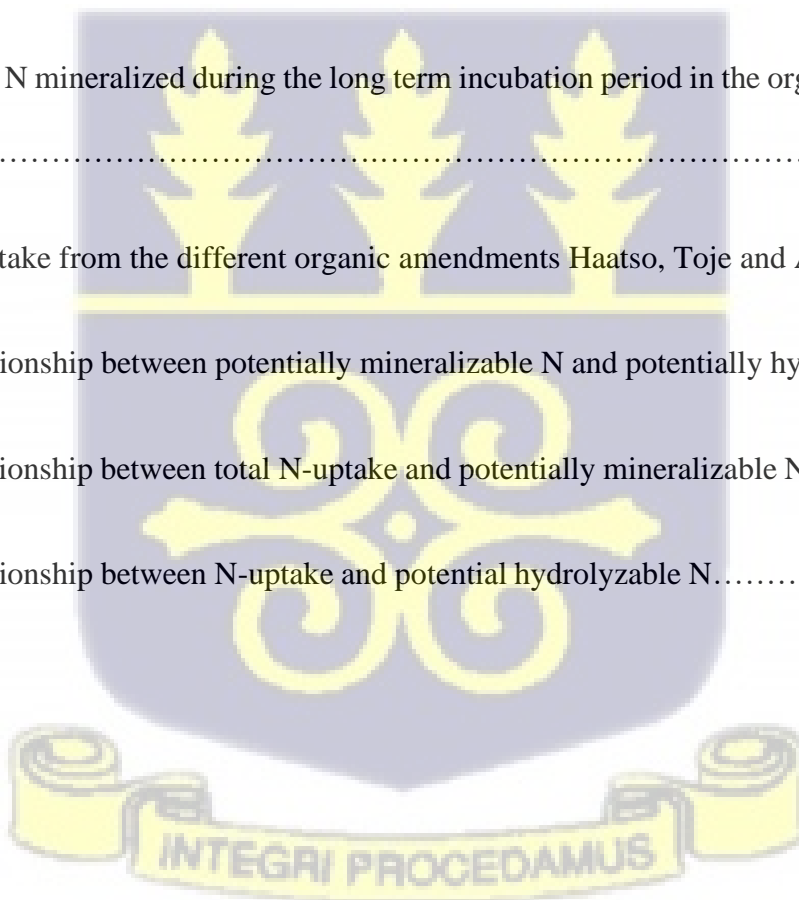
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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Among the various nutrients that are particularly required for good crop performance, nitrogen (N) remains one of the macronutrients that is often deficient in soils. Nitrogen plays major roles in plant nutrition, being a component of the chlorophyll that drives photosynthesis and plant growth (Fageria and Baligar, 2005). Except for leguminous plant that can convert atmospheric N to forms usable by the plants (Sylvia et al., 2005; Chesworth et al., 2008), N must be supplied externally to sustain plant growth. In intensive agricultural systems, large quantities of N fertilizer application remove the deficiency, though this approach is also associated with environmental consequences. Average quantities of N applied to cereal crops in the USA is about 480 kg N/ha, even more may be applied in other situations. With good soil water management, N use efficiencies (NUE) of up to 41% have been achieved in advanced counties (Omara et al., 2019). In developing countries, however, fertilizer N application continues to remain low, averaging 30 kg N/ha, and the NUE is often less than 50% (Baligar and Bennett, 1986).

For the majority of the low-input tropical agricultural systems, N is derived largely from the decomposition of organic materials (e.g., residue, soil organic matter). The dependence on N from organic resources has both advantages and disadvantages. On the one hand, the overall productivity of the soil in terms of physical (e.g., aggregation), fertility and microbial activity is enhanced by organic material application. On the contrary large quantities of organic resources must be applied at relatively short periods to sustain soil

productivity due to the high decomposition rates under high temperatures. In effect, the benefits derived from the applied organic materials is often short-lived. Another major handicap of the use of organic amendments for N supply relates to the slow release of the N via mineralization, with release patterns not synchronizing with plant uptake. Furthermore, the quantities of N that will actually mineralize from an added organic amendment is often unknown at the onset of the season, though this is required for management decision making. Thus, how much N can be mineralized from the organic sources is an issue of much scientific interest.

Several methods have been proposed over the years for assessing N mineralization potential of soils (Bundy and Meisinger, 1994), however, none of these have been widely adopted in general soil fertility testing. A biological method proposed by Stanford and Smith (1972) has become the accepted standard for assessing N mineralization and availability in soils. The method is based on long-term (>26 weeks) aerobic incubation of soils (and plus amendments), with the mineralized N determined intermittently and cumulated over the entire incubation period. By fitting the cumulative N mineralization data to the first order equation, kinetic parameters of the process, namely the potentially mineralizable N pool (N_o) and the mineralization rate constant k_m , which depends on the biochemical composition of the organic resource, can be determined.

The length of the incubation period, however, makes the Stanford and Smith (1972) procedure unrealistic and impractical for routine use in soil testing laboratories. Alternative methods have been developed to address this challenge. Among others, are chemical methods which have often proven to be fast and precise. Indeed, significant correlation between the amount of N extracted and/or hydrolyzed by chemical methods and the N_o

determined through the long-term biological incubation procedures have been reported (Gianello and Bremner, 1986, Smith and Li, 1993; Jalil et al., 1996).

Recently, a simple and precise alkaline hydrolysis method for evaluating the chemical index of N_o of soils has been proposed (Dodor and Tabatabai, 2019). The procedure involves direct steam distillation of 1 g field-moist soil treated with 1 M KOH or 1 M NaOH and the distillate collected in boric acid and analyzed for mineralized N at 5 min intervals for a total of 40 min. The NH_4^+ -N in the distillate is determined by titration with 0.005 M H_2SO_4 . The cumulative N hydrolysis data are fitted to a first-order equation akin to the Stanford and Smith (1972) procedure. This enables the determination of an alkaline hydrolyzable N pool, N_{max} as well as the hydrolysis rate constants k_h for the organic amendment. Kamara (2019) investigated the N mineralization of soils using both the Stanford and Smith (1972) procedure and the rapid chemical hydrolysis method of Dodor and Tabatabai (2019) and concluded that N_{max} and N_o are significantly correlated, and that the alkaline hydrolysis method offers a quick and reliable method for estimating N mineralization potential of soils and recommended that the technique can be used for assessing N-supplying potential of soils. The question of interest is whether the N_o and N_{max} derived for BMC amended soils would be significantly correlated to enable the N_{max} to be used as a surrogate index for N_o .

It is known that the transformation of organic N (ON) in soils are mediated by microorganisms through the action of extra-cellular enzymes. Therefore, the activities of specific enzymes that catalyze the hydrolysis of C-N bonds in linear and aryl-amides can be evaluated as indices of N mineralization in soils. Dodor and Tabatabai (2020) evaluated the relationship between the kinetically derived parameters of the alkaline hydrolysis

method for estimating the chemical index of N_o of soils and the activities of arylamidase and four amidohydrolases involved in hydrolysis of ON in soils. Their result indicated that the activities of arylamidase and amidohydrolases were coupled in mineralization of ON in soils. Based on the specificity of enzyme reactions and the strong relationship between estimated N_{max} values and the activities of arylamidase and amidohydrolases, Dodor and Tabatabai (2020) concluded that similar amide-N bonds were susceptible to enzymatic and alkaline hydrolysis, and that alkaline hydrolyzable ON can be used as an index of N mineralization in soils.

1.2 Problem statement and hypothesis

The use of organic sources for soil fertility maintenance is increasingly attaining research attention worldwide, given the renewed concerns of environmental challenges. Historically, composting has been recognized as a method of concentrating the nutrients, enabling a much more effective nutrient application than by direct application of fresh material. Composted materials are often very high in easily degradable N (Yee et al., 2018), yet the fast depletion of composts due to the high quantities of easily decomposable C remains a challenge, as compost materials must be constantly re-applied. In recent times, much more attention has focused on the use of biochar to stabilize soil C and enhance soil productivity. Biochar is a C-rich material pyrolyzed under limited oxygen condition (Lehmann et al., 2011) and has a high surface area. Chemically, biochar has high pH, high P content but low N, which apparently becomes volatilized during the pyrolysis process. Biochar carbon is stable and can remain in the soil for long periods of time (Dodor et al., 2019).

It is therefore conceivable that the combination of biochar and compost (composting) would produce a nutrient enriched material that is also carbon stable. Such a material, referred to as Biochar-Manure Compost (BMC) would be superior to its constituents in terms of soil fertility enhancement. Yet, when a mixture of organic materials of different N pools are mixed and composted, a complex set of interactions may occur, which can result in a final product with different organic N pools with varying degrees of susceptibility to mineralization or hydrolysis. In effect, the N_0 determined by the Stanford and Smith (1972) procedure for such a mixed material would be the sum of the contributions from the pool of the BMC constituents. Similarly, the N_{max} derived from the chemical hydrolysis procedure will also be the contributions from the different BMC constituents. It remains unclear if the hydrolysis method would preferentially hydrolyze the more easily decomposable constituents of the mixed BMC and not the more recalcitrant biochar components.

Given that the magnitude and rate of N mineralization depends on composition and amendment combinations, it is of research interest to assess the efficacy of the hydrolysis method in predicting N mineralization potential of soils amended with BMCs. To date, the applicability of the alkaline hydrolysis method to soils amended with compost and/or BMC have not been evaluated. This is needed to provide information on the management practices that optimize N mineralization in soils, while reducing environmental impact associated with excessive leaching of inorganic N, particularly NO_3^- -N, into aquatic environments. Furthermore, the practicality of any chemical index of N mineralization and accessibility depends on the degree to which it correlates with N uptake by plants. To date, no study has evaluated the relationship between the kinetic parameters derived from the

chemical hydrolysis method with plant N uptake. This constitutes another gap in research that requires attention, especially with regard to the application of organic materials of highly carriable composition, such as BMCs.

The hypothesis of this study is that though BMCs may be a composite of different types of constituents, the chemical hydrolysis method would still be applicable because the N_{max} is a discrete and definable portion of the labile and active N pool in organic amendments. In other words, a good correlation between the N_{max} and N_o is still expected. It is further postulated that alkaline hydrolyzable ON would be significantly correlated with actual plant N uptake under greenhouse condition.

1.3 Objectives

The general objective of this study is to evaluate the rapid alkaline hydrolysis method as an index of N mineralization in soils amended with different BMC materials. The study was designed to:

- i. derive the potentially mineralizable N, N_o for soils amended with different BMCs, following the Stanford and Smith (1972) procedure,
- ii. derive the potentially hydrolyzable N, N_{max} using the rapid chemical hydrolysis procedure proposed by Dodor and Tabatabai (2019), and
- iii. validate the use of the alkaline hydrolyzable ON as an index of N availability to plant using maize as the indicator crop.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Nitrogen in nature

Nitrogen in nature occurs largely as a gas, constituting about 78% of the atmospheric gas. In this natural state, nitrogen occurs in an unreactive form N_2 , which must be reduced or involved in some chemical transformation to become useful for plant use. One way of this transformation is by biological nitrogen transformation, whereby soil bacteria (*Rhizobia spp*) living in symbiosis with leguminous plants reduce N_2 in the soil air to other forms that can be utilized by the plants. The legume plant materials become enriched in nitrogen and when they die, the decomposed material contributes to the soil N economy (Cooperband, 2002). Another way of transforming the N_2 is by the industrial chemical reduction process (Haber Bosch) resulting in the manufacture of nitrogen fertilizers. The dramatic increase of cereal yields observed worldwide over time can be partly attributed to N fertilizer application. The various oxidative state of N is summarized in Table 2.1

Table 2. 1: Main forms of N in soil and their oxidation states

Name	Chemical Formula	Oxidation State
Nitrate	NO_3^-	+5
Nitrogen dioxide (g)	NO_2	+4
Nitrite	NO_2^-	+3
Nitric oxide (g)	NO	+2
Nitrous oxide (g)	N_2O	+1
Dinitrogen (g)	N_2	0
Ammonia (g)	NH_3	-3
Ammonium	NH_4^+	-3
Organic N	R_{NH_3}	-3

Gases (g) occur both free in the soil atmosphere as well as dissolved in soil water

Adopted from (Crohn, 2004)

2.1.1 *Forms of N in soil*

Though more than 90% of the N in surface soils occurs in organic forms and plays an important role in plant nutrition and soil fertility through its effects on microbial activity and nutrient availability (Kelley & Stevenson, 1995), much of the organic N is relatively not available to plants. The forms of organic N present in the soil can be grouped into two wide types: organic residues, comprising of undecayed plant and animal deposits and fractional decomposition products, and soil organic matter or humus (Kelley and Stevenson, 1995). Identifiable organic N compounds are the amino acids and amino sugars (Stevenson, 1996). Acid-insoluble N is the N remaining in the soil residue. The N not accounted for in the above forms is referred to as the HUN fraction (hydrolyzable unknown N). In addition to amino acids and amino sugars, soils contain trace quantities of nucleic acids and other known nitrogenous biochemicals. However, specialized techniques are needed for their separation and identification (Kelley & Stevenson, 1995).

Organic N must be transformed or broken down and converted to inorganic forms before taken up by plants. The N transformation process is microbial-mediated and is described in detail below. It is worth noting also that due to microbial growth requirements, portions of nitrogen applied as inorganic fertilizers can become immobilized by microorganisms and hence become organic N, while some percentage of the fertilizer N applied to soil becomes stabilized by integration into humic substances (Kelley and Stevenson, 1995).

2.1.2 *Inorganic forms of N in Soil*

Inorganic N in most soils occur as nitrate (NO_3^- -N) and ammonium (NH_4^+ -N). Although nitrite (NO_2^- -N) may also be present, the amount is usually negligible except in cases

where $\text{NH}_4^+\text{-N}$ or $\text{NH}_4^+\text{-N}$ forming fertilizers are applied to neutral or alkaline soils (Mulvaney, 1996). Other forms of inorganic N in soils have been proposed as intermediates during microbial transformations. These forms include hydroxylamine (NH_2OH), hyponitrous acid ($\text{H}_2\text{N}_2\text{O}_2$), and nitramide (NH_2NO_2), but these compounds have not been detected in soils as they are thermodynamically unstable (Mulvaney, 1996). The dynamics of inorganic N ($\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$) and research on the changing aspects of organic N in cultivated soils has been studied (Mulvaney, 1996; Karuku and Mochoge, 2018). Inorganic N is frequently less than 2% of the entire N in surface soils and experiences speedy fluctuations in structure and quantity (Mulvaney, 1996). Regardless of its minimum size, the inorganic portion is the source of N nutrition for plants (Mulvaney, 1996; Chung and King, 2004).

2.1.3 Nitrogen mineralization and immobilization

An understanding of N transformation in soils is important for managing ecosystem productivity and health. Research has shown that the transformation of organic to inorganic N in soils involves both mineralization and immobilization. Nitrogen mineralization is a biological process that involves conversion of organic N to inorganic N by soil microbial biomass (M. M. Bregliani et al., 2010). Microbes “consume” dead biomass (detritus) that is primarily carbon to sustain their growth and as a source of energy. Microbial needs are effortlessly met, and N is released if plant detritus is rich in N. If plant detritus is low in N, microbes must scavenge inorganic N from their surroundings leading to immobilization of N into their biomass. This latter process is referred to as immobilization. Mineralization and immobilization occur at the same time within comparatively small volumes of soil.

The quality of organic matter (the availability of C in the material relative to its available N) controls the balance between N mineralization and immobilization. Immobilization occurs concurrently in most ecosystems (e.g., soil) where organic material is undergoing microbial decomposition (Karuku and Mochoge, 2018).

The overall mineralization process occurs in two steps: ammonification and nitrification (Canali et al., 2011). Hence the overall process can be represented by the equation:



Ammonification is the intermediate step between the depolymerization of large organic molecules and the nitrification step. Mineralization is often referred to as ammonification in older literatures and traditionally ammonium has been viewed as the immediate product of mineralization (Crohn, 2004). It is the conversion of organic N into $\text{NH}_4^+\text{-N}$ and is solely achieved by heterotrophic microorganisms able to function both in aerophilic and anaerobic conditions (Canali et al., 2011). It is commonly considered that the majority of, if not all, microorganisms (bacteria and fungi) are capable of ammonification (Romillac, 2018).

Nitrification is the microbial oxidation of ammonia to less reduced forms principally NO_3^- -N and NO_2^- -N (Crohn, 2004). It occurs through the action of autotrophic aerobic bacteria: Nitrosomonas (from $\text{NH}_4^+\text{-N}$ into NO_2^- -N) and Nitrobacter (from NO_2^- -N into NO_3^- -N) (Canali et al., 2011). According to Bregliani et al. (2006), at low soil pH the degree of nitrification is lesser and higher amounts of $\text{NH}_4^+\text{-N}$ are possible. It is worth highlighting that nitrification is central to the flows, losses or utilization of N through the conversion of

NH_4^+ -N into labile NO_3^- -N. Understanding nitrification is an important further step in maximizing N efficiency and losses reduction particularly in grassland, but also as a main interactive process linked by flows of substrates and spatial distributions in all ecosystems (Jarvis et al., 1996).

2.2 Importance of N mineralization

Nitrogen mineralization is a significant process and a vibrant part of soil fertility. It is the process by which organic N is transformed to plant available inorganic forms. It is regarded as a potential indicator to comprehend the soil's response to biological change. Mineralization permits the release of nutrients contained in dead organic matter into inorganic forms and is significant in their uptake by growing organisms, particularly plants. Soils often amended with organic wastes will accumulate organic N until they reach a steady-state condition, a concept useful for planning N management approaches. An understanding of these patterns is necessary to match crop N demands by improving manure management while lessening the potential for regulatory concerns regarding groundwater pollution (Crohn, 2004). There is current attention in soil N mineralization since it has influence on soil N supply, potential for NO_3^- -N leaching and as a characteristic of soil quality (Soon et al., 2007).

2.3 Factors controlling N mineralization

Numerous factors affect N mineralization in the soil. Predominant environmental factors include temperature and soil moisture (Charoulis et al., 2005). Temperature influences the rate of reactions, whereas soil moisture will control soil aeration. Given that the

mineralization is an aerobic process, then high moisture will be detrimental as aeration will be impaired. The end product of N mineralization under anaerobic conditions are nitrous oxides, which are underside Greenhouse Gases. Research has also shown that salt content (electrical conductivity/EC) can also influence mineralization rate, denitrification or leaching.

The quality of the soil organic resource (e.g., C/N ratio) also significantly affects mineralization. The quality of the organic material can affect the N mineralization rate and would affect N availability (Franklin et al., 2015). The degree and rate of mineralization of N from organic sources is mutable because a variety of materials compose the organic resources (Gale et al., 2006; Helgason et al., 2007). For most organic resources, the C/N ratio is greater than unity (1.0), implying that there is more carbon than nitrogen. The C/N ratio of the material has a direct impact on residue decomposition and also N cycling in soils. The effect of C/N ratio on mineralization of organic N has been studied by many scientists. Review by Bartholomew (1965) concluded that a high C/N ratio material causes net N immobilization and a low C/N ratio causes net N mineralization of organic N in soils. In the early 1990s, it was accepted that the critical value below which mineralization of organic N takes place ranges from 20 to 25 (Jensen, 1929). If the ratio exceeds 25, mineralization is delayed until decomposition brings the ratio closer to 25 (Kelley and Stevenson, 1995). As important as the C/N ratio is, it cannot describe all transformations in N mineralization since organic materials with comparable C/N ratios may mineralize different amounts of N (Diacono and Montemurro, 2010).

2.4 Effects of organic amendment on N mineralization

It is important to apply appropriate rates of organic amendments to avoid contaminating the environment. The application of organic amendments is common in organic farming systems. These amendments when added to the soil enhance plant growth and may lessen the need for mineral fertilizers, which reduces costs for farmers. Organic amendments slowly release nutrients, restore, and reclaim degraded soils by maintaining organic matter and sustaining soil fertility for agricultural production, particularly in the long-term. The two main reasons for exploring N mineralization dynamics of amendments are to avoid excess fertilizer application and reduce N losses to the environment; and second, to optimize residue management to maximize crop production, especially in low-input agriculture based on nutrient recycling (Bruun et al., 2006). The amount of N mineralized and available to crops depends on the chemical composition of organic matter such as N content, C:N ratio, contents of cellulose and hemicelluloses, lignin, and polyphenols (Calderón et al., 2005; Mohanty et al., 2011) and on the physical, chemical, and biological properties of soil microbes (Manojlović et al., 2010).

2.5 Nitrogen mineralization indices

A number of indices have been proposed as measures of N mineralization. These indices depend on the methods used to assess the mineralization process (Jarvis et al., 1996). Methods for determining N mineralization in soils have not always been decisive, although a lot of research has been carried out to develop standardized approaches to facilitate comparison and interpretation of results. Method that could estimate the N that mineralizes in the soil at a time. Reviews of some indices of N mineralization can be found in (Bremner

& Keeney, (1965), Cornfield, (1960). These indices for determining N have been grouped into two, the biological indices and the chemical indices.

2.5.1 *Biological indices of N-mineralization*

The most precise method of estimating N availability under laboratory conditions is to incubate soil-amendment mixtures and determine the quantity of inorganic N produced (Magdoff and Amadon, 1980; Castellanos and Pratt 1981a). One of the most extensively used approaches is the biological method and the protocols for doing this are many and varied. It is assumed that there is an organic N pool which can be mineralized by micro-organisms in a finite time under optimal conditions. Many methods rely on aerobic conditions and several incubation methods for determination of N mineralization have been proposed. However, the method developed by Stanford and Smith (1972), which involves the incubation of soils for 26-weeks has remained the most widely method used. This method involves incubation of sieved soil sample to determine the soil's N mineralization potential, (N_o) and its first-order rate constant of mineralization, (k). The method assumes that the soil organic N comprise of a single homogenous pool mineralizing according to first order kinetics (Kelley and Stevenson, 1995).

Another biological method is to crop N uptake as a sink for any N released by mineralization. Uptake and removal into the crop are then assumed to equate with mineralized N. Plant N uptake can be derived from data on fertilizer response trials that have been extensively published in the literature.; A number of researchers have recorded good correlations between N released during incubation and uptake in pot studies (Douglas and Magdoff, 1991; Jarvis et al., 1996; Cordovil et al., 2007).

Using data from laboratory incubations to predict field mineralization rates has had unpredictable success. However, incubation procedures are quite laborious and time-consuming, and therefore, rapid and convenient chemical extraction procedures are proposed as suitable indices of N availability (Magdoff and Amadon, 1980; Castellanos and Pratt 1981b; Dodor 2002). The usefulness of any chemical index of this type depends on the degree to which it can be correlated with reliable biological measurements (Keeney, 1982).

2.5.2 *Chemical indices of N mineralization*

There has been a long need for satisfactory laboratory methods to obtain reliable estimates of potentially available N resulting from mineralization of soil organic matter (Chae and Tabatabai, 1986; Dodor, 2002). Some chemical methods have been proposed (Douglas and Magdoff, 1991; Gianello & Bremner, 1986; Dodor & Tabatabai, 2019). It is commonly acknowledged that the most consistent methods currently available are those involving the determination of the mineral N produced during the aerobic or anaerobic incubation of soil over various times, but these biological methods are not rapid and simple enough for use in routine testing. Thus, there is an imperative need for a rapid chemical method of assessing potentially available soil organic N that is suitable for commercial laboratories. These chemical methods equally define the totality of soil N availability indices that have been proposed for defining the N-supplying abilities of soils.

The alkaline hydrolysis method for evaluating the chemical index of N of soils has been proposed (Dodor and Tabatabai, 2019). The technique includes direct steam distillation of 1 g field-moist soil treated with 1 M KOH or 1 M NaOH. The distillate was collected in

boric acids, which was changed every 5 min for an overall of 40 min. The $\text{NH}_4^+\text{-N}$ present in the distillate was determined by titrating with 0.005 M H_2SO_4 . When the data is cumulated and fitted to a first-order kinetic, two parameters of importance can be derived. The first is the potential hydrolysable N (designated as N_{max}), which is akin but not equal to the 26-week Stanford and Smith (1972) potential mineralizable N (N_o). The second parameter is the rate constant k_h , akin to the 26-week derived km . Kamara (2019) validated this chemical index by evaluating the relationship between the amounts of N hydrolyzed by the alkaline hydrolysis method and that mineralized under the Stanford and Smith, (1972) biologically based method for 12 soils under different land use systems from the Coastal Savannah zone of Ghana. Based on the strong association between estimated N_{max} and N_o , coupled with the significant reduction in the incubation time, Kamara (2019) concluded that the alkaline hydrolysis method offers a quick and reliable method for estimating N mineralization potential of soils, and recommended that the technique should be considered for routine use in soil testing laboratories for estimating N-supplying potential of soils.

However, where the organic resource is very heterogenous, as in the case of composts involving high resistant carbon (e.g., biochar), the applicability of the procedure remains in doubt. Whether the chemical method would preferentially hydrolyze only some constituents of the compost mixture is unknown. In general, whether the chemical method would serve as good index of mineralization for all types of organic residue is a challenge that this study seeks to address. To this extend, there is a need to evaluate the applicability of the chemical method proposed by Dodor and Tabatabai (2019) in soils amended with biochar-manure compost.

2.6 Kinetic parameters of N mineralization

2.6.1 Potentially mineralizable N

The potentially mineralizable N (N_o) is interpreted as an approximation of the amount of N that will mineralize in infinite time under optimal temperature and moisture (Stanford et al., 1977). Mineralizable N is composed of a varied array of organic substrates including humus, residues of recent crops and microbial biomass (Campbell and Curtin, 2008). Several studies have been conducted to relate N_o to soil properties (Curtin and Wen, 1999), environmental conditions (El Gharous et al., 1990) and agricultural practices such as tillage, fertilization, organic waste application and cropping (Bonde and Rosswall, 1987). Though the value of the first-order model in describing N production kinetics is generally accredited for soils free from recently added high C/N ratio organic materials, the usefulness of N_o in rating N mineralization capacity of different soils has been questioned by many researchers (Wang et al., 2003). According to Bregliani et al. (2006) soils vary extensively with regard to the potential N supply since mineralization is a microbial process while N supply of a specific soil hinges on factors such as temperature and moisture content of the soils. Also, the N_o represents not only the measure, but also the superiority of substrates and their interaction with the soil matrix (Wang et al., 2003).

Irrespective of the advantages or otherwise, Canali et al. (2004) concluded that the potentially mineralizable N showed significant differences between the slowly fertilized soil and not slowly fertilized soils when they assessed the consequence of compost and organic fertilizer utilization on soil quality. The potentially mineralizable N is calculated using a first-order kinetic model (Stanford and Smith, 1972):

$$N_{min} = N_o[1 - \exp(-kt)] \quad 2.3$$

where N_{min} is cumulative N mineralized in time t , N_o is potentially mineralizable N, and k is the mineralization rate constant. This equation has two unknowns (N_o and k), which are usually estimated by least-squares iteration using appropriate statistics software.

2.6.2 Mineralization rate constant

The mineralization rate constant km , reflects the general progress of the mineralization process (Manojlović et al., 2010). Though the km is related to the residue quality (C/N), some researchers observed that k is more related to the N content of the organic resource. A critical level of 1.7% N has been suggested for net mineralization (Frankenberger and Abdelmagid, 1985b). Subsequent studies (Griffin and Laine, 1983; Smith et al., 1977) showed that k is also influenced by soil temperature and moisture. However, km values are not universal but differ significantly among different soils (Juma et al., 1984).

2.7 Nitrogen availability indices and plant N-uptake

Pot experiments give straight evidence about the amount of plant-available N in organic products. A better information about the plant-availability of N in organic products might help to increase the resourceful use of these products as fertilizers (Plant et al., 2021). According to Sharifi et al. (2011) soil receiving repeated manure applications normally have high fertility. However, repetitive application of excess manure in the long-term can build up the soil N supply in excess of crop N requirements and may surpass the capacity of soil to retain manure N. However, Bregliani et al. (2006) established that the uptake of N by maize plants (roots and shoots) measured in a short-term pot experiment was poorly correlated with the N mineral fraction in soil. Also, a research by Sharifi et al., (2011) did

not find significant relationship between the tested measures of N availability in the laboratory and the field-based indices of N supply. Moreover, the use of chemical indices of N availability has been limited because of the poor correlation with crop N uptake, probably due to the inability to selectively release the fraction of soil organic N that is made available for plant growth by soil microorganisms (Dodor and Tabatabai, 2019). Nitrogen fertilizer recommendations are estimated from the relationship between inorganic N fertilizer inputs and crop yield response (Whalen et al., 2019). This information is required to develop crop-specific N fertilizer recommendations that consider the N use efficiency of inorganic N fertilizers based on the proportion of additional N that was recovered in the crop (Whalen et al., 2019)

2.8 Composting of organic materials

Composting process is a very effective way to help make good use of organic waste. Two different amendments that can be able to supplement each other are used for composting. Compost properties differ depending on the composting process, feedstock quality and pile age (Lazicki et al., 2020), controls plant diseases and improves nutrients in the soil (Seyedbagheri, 2010). The increasing cost of inorganic fertilizers coupled with their inability to condition the soil has directed attention to organic manures in recent times (Boateng et al., 2009). Application of organic amendments in cultivated soils can modify greenhouse gas emissions (GHG) whereas improving soil physical, chemical, and biological properties (Thangarajan et al., 2015).

Organic material application to cropland could affect soil properties, but the effects generally may not be apparent over a short time period (Miller et al., 2000). The release of

these nutrients are slow and they are responsible for the increase in crop yields in the subsequent years, thus determining the difficulty of quickly evaluating the true agronomic value of these organic materials as amendments (Diacono & Montemurro, 2010). In order to swiftly supply a crop with the required nutrients, a chemical fertilizer may be needed. Organic manures first have to be broken down into nutrients (by soil-organisms) before they can be utilized by the plants (Ameloot et al., 2013). Research by Bregliani et al. (2006) concluded that just after manure or fertilizer application, higher amounts of $\text{NH}_4^+\text{-N}$ can be initiated. According to Chadwick et al. (2000), the total N content and forms of N in manures are likely to differ in relation to animal type, age, diet and manure management system.

2.8.1 Benefits of composting with animal manures

Animal composts vary in their total N contents and N forms because of differences in animal age, feed conversion by different animal species, bedding material, feed and water intake (MAFF, 1994). Although typical values of total N and plant available N in manures are provided by MAFF (1994) to farmers, published values are subject to large uncertainty due to variabilities between manures even from the same animal species (Chadwick et al., 2000). Organic fertilizers such as farmyard manure, sheep manure and poultry manure may be used for crop production as a substitute of the chemical fertilizers because the reputation of the organic manures cannot be disregarded (Farhad et al., 2009). Crop residues, cattle manures, and compost are all organic sources of N and when applied to soil, they play crucial roles in supporting soil fertility and crop productivity (Soumaré et al., 2003). Also, manure contains $\text{NH}_4^+\text{-N}$ which enters the plant-available N pool in manure-amended soil and organic N compounds that mineralizes to release plant-available N for crops (Whalen

et al., 2019). Kang et al. (2005) noticed an increase in wheat-based cropping system and concluded that mineralization of organic manures may be responsible for such increases in crop yields.

Compost make available an added N source that compliments fertilizer N to provide a more sustainable farming system (Seyedbagheri, 2010). Some studies specify that the usage of compost on soil may recover several plant and soil parameters, which would make compost an exciting choice for soil restoration purposes, as well as take advantage of its fertilizer properties (Martínez-Blanco et al., 2013). For increase crop yield, Kang et al. (2005) noticed that the application of inorganic and organic fertilizers improved soil health and improved the yield and nutrient uptake by corn in the pot experiment. He also highlighted that the upsurge in dry matter yield and nutrient uptake was noteworthy with organic fertilization.

2.8.2 *Biochar*

Biochar is pyrolyzed organic resource (Lehmann et al., 2011). Biochar is increasingly researched as a soil amendment because it has a more stable carbon, which unlike compost, decomposes slowly and has a longer impact on the soil. Studies on biochar application in Ghana showed that maize yield increased by 51% (Yeboah et al., 2016; Cooperband, 2002). It is known that when biochar is added to compost, it adds micronutrients to the soil and slows mineralization rate. Largely, the C/N ratios of biochar vary between 7 to 400, with a mean of 61 Johannes Lehmann (2009). The C/N ratio of biochar is frequently used as an indicator of its ability to mineralize and release inorganic N when applied to soils.

Recently, researchers have studied composting with biochar and its benefits to the soil. The use of biochar co-applied with compost to the soil is being promoted due to its ability for long term improvement in soil physical and chemical properties. Review by Steiner et al. (2011) revealed that biochar could act as a bulking agent which enables oxygen availability and aid as a suitable habitat for active microbial activity, growth and respiration.

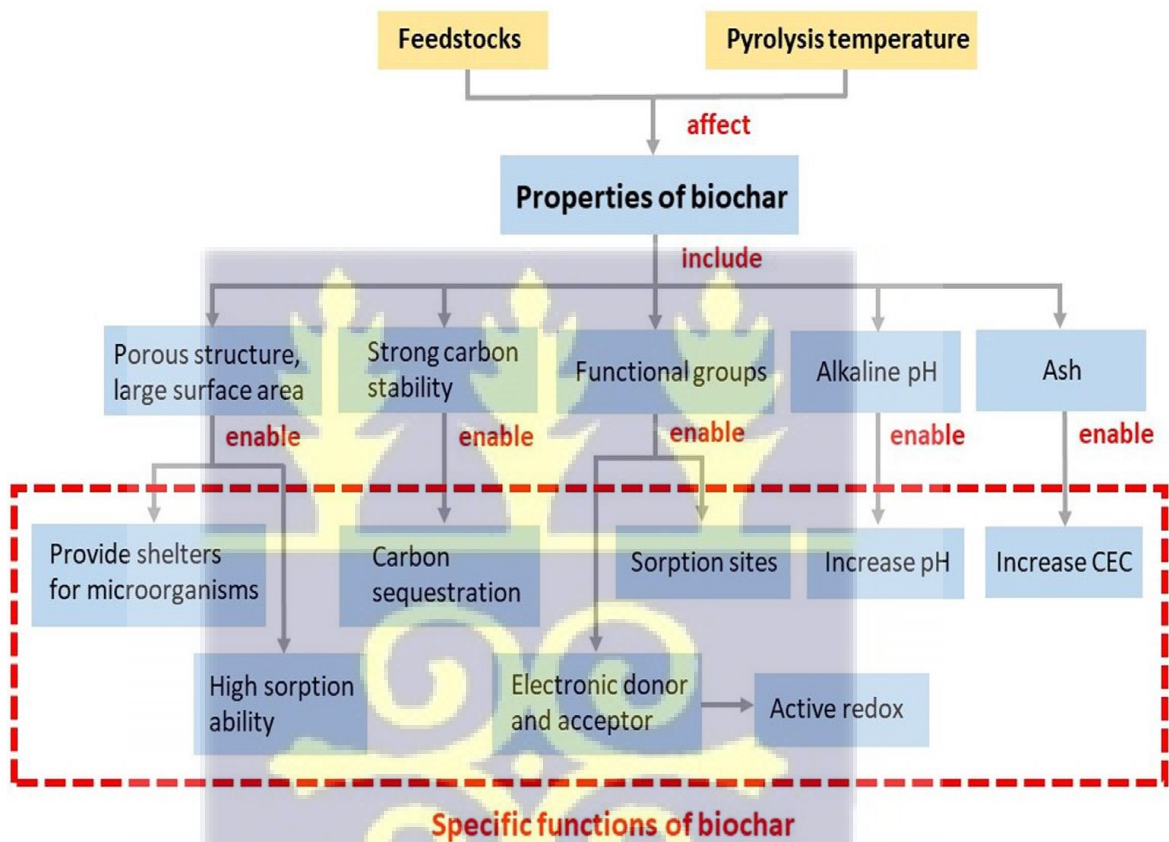


Figure 2. 1: Diagram showing biochar properties and their relevant functions.

Adopted from (Guo et al., 2020)

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Soils and sampling

The soils used in the study were sampled from different locations at the University of Ghana Farms, Legon, located within the Accra Plains of Coastal Savannah zone of Ghana with Latitude $05^{\circ} 39' 31.7''$ N and $05^{\circ} 39' 36.4''$ N and within Longitude $05^{\circ} 38' W$ and $05^{\circ} 41' W$ (Eze, 2015). The area experiences a bi-modal rainfall pattern with an annual mean rainfall of about 800 mm and mean annual temperature of $27^{\circ} C$ (Eze, 2015). The rainfall regime comprises of two rainy seasons: a main wet season which falls between March to June/July, and a minor season around September to October.

A total of three soils were used in the study. The first soil, Toje series (Rhodic Kandistalf) is located at the mid-lower to upper slope positions along the Legon catena and has quartzite schist as its underlying parent material. The second soil, Adenta series (Typic Kandistalf) is located at the middle slope of the Legon catena. It is formed from sedimentary differentiation of colluvial deposits of tertiary age superimposed on Togo quartzite schist (Eze, 2015). Haatso series (Kandic Paleustalf), located at the foot of the Legon catena was used as the third soil. It is formed from deposits of alluvial and colluvial materials underlain by sandstone and iron-stained quartzite schist.

3.1.1 Soil sampling

Soil samples (0 – 20 cm) of each soil type were collected randomly from 3 – 5 locations using an auger and a spade, and composited. Undecomposed plant materials such as roots, leaves, sticks, and other debris were removed, and the remaining soil gently ground and passed through a 2 mm sieve to obtain the fine earth fraction. The sieved soils were placed in polythene bags and transported to the Department of Soil Science Laboratory, University of Ghana. The soils were divided into two portions, with the first portion which was used in the N mineralization and hydrolysis studies stored under field-moist condition at 5°C in the refrigerator; the second portion was air dried at room temperature and used for the determination of physical and chemical properties.

3.2 Determination of soil physical properties

3.2.1 Particle size analysis

The particle size distributions of the soils were determined by the Bouyoucos hydrometer method as modified by Day (1965). Forty grams (40 g) of air-dried soil was weighed into dispersing bottles and 100 mL of 5% sodium hexametaphosphate solution was added. The suspensions were shaken on a mechanical shaker for 2 hours, then transferred into sedimentation cylinders and distilled water was added to the 1 L mark. The suspension was mixed thoroughly using a plunger, left to stand on the bench for 5 minutes, then a hydrometer reading for clay and silt was taken. The suspension was left on the bench uninterrupted for 5 hours after which the hydrometer reading for only clay was taken. After the second reading had been taken, the suspensions were poured into a sieve and the

effluent collected in a container. The residue was washed thoroughly with tap water to get rid of any remaining silt or clay particle and then poured into a moisture can with known weight and oven dried at 105 °C for 24 hrs. The dried sand was placed in desiccators to cool down and then weighed. All the experiments were done in triplicates. The percent sand, silt and clay fractions of the soils were calculated as follows:

$$\% \text{ clay} = \frac{\text{hydrometer reading at 5 hrs}}{\text{soil weight}} \times 100 \quad 3.1$$

$$\% \text{ silt} = \frac{\text{hydrometer reading at 5 min} - \text{hydrometer reading at 5hrs}}{\text{soil weight}} \times 100 \quad 3.2$$

$$\% \text{ sand} = \frac{\text{weight of oven dried sample}}{\text{soil weight}} \times 100 \quad 3.3$$

3.2.2 Field capacity

A 500 g of the soil was weighed into triplicates of perforated plastic pots of 20 cm height and 15 cm diameter lined with filter paper and saturated with water. The top of the pot was covered with a plastic to prevent evaporation and allowed to drain for 3 days. On the third day, subsamples were taken, weighed and oven dried at 105 °C for 24 hr. After 24 hr, the oven-dried soil samples were placed in a desiccator to cool down and the dry weights measured. The gravimetric water content was determined as the difference in mass between the moist soil and oven-dried soil. The percentage water content at field capacity was computed as follows:

$$\% \text{ water content} = \frac{\text{weight of wet soil} - \text{weight of oven dried soil}}{\text{Weight of the wet soil}} \times 100 \quad 3.4$$

3.2.3 Bulk density (ρ_b)

The bulk density of the soils used was determined using the core method following Blake and Hartge (1986). The surface of the soil in the field was cleared, and a core sampler was gently driven into the soil using a mallet. The surrounding of the core sampler was gently dug and removed carefully to avoid any disturbance. The sampler was capped and levelled at both ends with a knife, labelled, placed in polybags, and transported to the laboratory. The soil samples were emptied into moisture cans with known weight (W1), oven dried at 105 °C for 72 hrs (3 days) and the weight taken after cooling in a desiccator (W2). Bulk density was calculated as:

$$\rho_b(\text{kg/m}^3) = \frac{M}{(\pi d^2/4)h} \quad 3.5$$

where:

ρ_b = bulk density of soil (g/cm^3)

M = mass of soil = W2-W1

W2 = weight of oven dried soil and moisture can.

W1 = weight of empty moisture can.

$\pi d^2/4$ = area of core base

d = diameter of core

h = height of core

$\pi = 3.142$

3.3 Determination of soil chemical properties

3.3.1 Soil pH

Twenty grams (20 g) of 2 mm sieved soil was weighed into a 50 mL beaker and 20 mL of distilled water was added to give a soil: water suspension ratio of 1: 1. The soil-water suspension was stirred continuously for about 30 min and then left to stand for about one hour. The glass electrode pH meter (pH-mV-Temp PL-700 PV) was calibrated using two aqueous solutions of pH 4 and 7 before use to measure the pH of the soils.

3.3.2 Available N

Ten grams (10 g) of the 2 mm-sieved soil sample was weighed into a 100 ml extraction bottle and 50 ml of 2 M KCl was added. The soil suspension was shaken for 60 min at 180 strokes per min on a reciprocating shaker. The supernatant was filtered using a No 42 Whatman filter paper. Ten milliliters (10 mL) aliquot of the filtrate was then taken into a 250 mL Kjeldahl distillation flask and 0.2 g of MgO powder was added, swirled, and distilled for ammonia (NH₃)-N. The NH₃-N liberated was collected in 5 mL of 2% boric acid containing a mixture of methylene blue and methyl red indicators.

After about 30 mL of the distillate was collected, 0.2 g of Devarda's alloy (to reduce the NO₃⁻-N to NH₄⁺-N) and 1 mL of 0.2 M sulphuric acid (H₂SO₄) (to destroy nitrite) were added. The distillation was continued until additional 30 mL of the distillate was collected into a second beaker containing 5 mL of 2 % boric acid indicator mixture. The two (2) distillates were titrated with 0.01M HCl and the concentration of NO₃⁻ / NH₄⁺ (mg L⁻¹) in the soil was calculated as follows:

$$\text{NO}_3^-/\text{NH}_4^+ - \text{N (mg/kg soil)} = \frac{M_{\text{HCl}} \times V_{\text{HCl}} \times 10^{-3} \times 14 \times V_{\text{KCl}} \times 1000 \text{ mg}}{\text{Volume of Aliquot} \times \text{Weight of soil (g)}} \quad 3.6$$

where:

M HCl = Molarity of the HCl

V HCl = Titre value of the HCl

V KCl = Volume of KCl extractant

14 = Molecular weight of N

3.3.3 Cation exchange capacity

Ten grams (10 g) of the soil samples (2 mm-sieved) were weighed into 200 mL extraction bottles and 100 mL of ammonium acetate (NH₄OAc) solution buffered at pH 7.0 was added. The bottles were capped and then shaken on a reciprocating shaker at 180 strokes per min for 1 hr. The soil suspension was then filtered through a No. 42 Whatman filter paper. The soil residues remaining on the filter paper were leached immediately with 50 mL portions of methanol into empty plastic bottles. The soils were then leached with 50 mL of acidified 1 M KCl into different plastic bottles. Each portion of the acidified KCl was added at a time and allowed to pass through before adding the next. Ten milliliters (10 mL) of the leachate were then transferred into a Kjeldahl flask and 5 mL of 40 % NaOH was added and distilled. The distillate was collected in 5 mL of 2 % boric acid-indicator mixture in a conical flask to about 30 mL. The distillates were back titrated with 0.01 M HCl and the ammonium ion concentration in the filtrate was determined as described in section 3.3.2. The CEC of the soil in cmol kg⁻¹ soil was calculated as follows:

$$\text{CEC}_{(\text{cmolc kg}^{-1} \text{ soil})} = \frac{V_{\text{HCl}} \times V_{\text{HCl}} \times 10^{-3} \times \text{Volume of extrate} \times 10^3 \times 10^2 \text{ cmol}}{\text{Volume of Aliquot} \times \text{Weight of soil (g)}} \quad 3.7$$

3.3.4 Initial $\text{NH}_4^+\text{-N}$

The initial $\text{NH}_4^+\text{-N}$ present in the soils were determined by the addition of 20 mL of 2 M KCl and 0.2 g of MgO to 5 g of field moist soil and direct steam distilled for 4 minutes (Dodor, 2002). The ammonium in the distillate was determined as described in section 3.3.2.

3.3.5 Total carbon and nitrogen

The total C and N contents of the samples were determined on <180 μm air-dried samples by dry combustion using LECO CNS Analyzer (LECO Corp, St Joseph, MI, USA).

3.4. Compost materials

Rice husk was collected from the Soil and Irrigation Research Centre (SIREC) Kpong, University of Ghana. Market wastes was collected from Madina market which lies within 5.67° N, 0.17° W. Cowdung and poultry manures were collected from the Livestock and Poultry Research Centre (LIPREC) Nungua, University of Ghana. Biochar was prepared from the charring of rice husks using a locally made *Kon tiki* biochar kiln at a temperature of 400 °C at Kpong. Biochar was allowed to cool after pyrolysis, sieved and packaged for subsequent use. All materials were air-dried before composting. Descriptions of the materials used in the preparation of the MBCs are summarized in Table 3.1.

Table 3. 1: Description of composting materials

NAME	CODE	DESCRIPTION
Rice husk	RH	Organic fraction of rice husk separated at the source and used for composting.
Market waste	MW	Mixture of watermelon, pear, mangoes, oranges, onions, tomatoes, green vegetables mixed and air-dried for 21 days.
Cowdung	CD	Dry cow dung manure
Poultry manure	PM	Chicken droppings without litter
Rice-husk biochar	RHB	Rice husk pyrolyzed at 400 °C

3.5 Composting

The biochar used for composting was produced from rice husk. After drying, the feedstock was cut into small pieces and pyrolyzed at a temperature of 400 °C using a kiln. The resulting biochar was allowed to cool to room temperature, crushed and passed through 2 mm sieve to give a uniform size fraction. Cattle and poultry manures were air-dried and crushed to pass through 2 mm sieve. Market wastes consisting of fruits and vegetables were cut into small sizes, and air-dried. The composts were prepared based on market waste or rice husk as the main materials (>50%). The dried market waste and rice-husk were mixed with either cattle or poultry manure in different ratios (Table 3.2) and composted for three months to maturity.

3.5.1 Compost characterization

Chemical characterizations of the matured compost materials for pH (water), available N, TC and TN were done as described in section 3.3.1, 3.3.2 and 3.3.5, respectively.

3.6 Indices of N mineralization

3.6.1 Long-term aerobic incubation

The procedure described by Stanford and Smith (1972) was adopted for the long-term aerobic incubation study. Duplicate mixtures of 75 g field moist soil and 75 g acid washed sand amended with appropriate amount of the BMC material to provide 200 mg N kg⁻¹ soil were placed in a leaching column lined with non-absorbent wool at the bottom to avoid soil loss. The soil-BMC mixtures were incubated at 25 °C in the dark for a total of 26 weeks. At every 2 weeks interval, the soil-amendment mixtures were leached with 75 ml 0.05 M CaCl₂ and 25 ml of N-free nutrient solution. After leaching, 10 mL aliquot of the leachate was taken and distilled as described in section 3.3.2.

3.6.2 Alkaline hydrolysis of organic N

The procedure described by Dodor and Tabatabai (2019) was used for the alkaline hydrolysis ON. Briefly, 1 g of field-moist soil (on oven-dried basis) containing 200 mg N kg⁻¹ BMC was placed in a distillation flask and 20 ml of 10 M NaOH or KOH was added. The soil-amendment mixture was direct steam distilled and the NH₃-N liberated was collected in 5 mL of 5% boric acid containing a mixture of methylene blue and methyl red indicators. The boric acid was changed successively every 5 min for a total of 40 minutes.

Ammonium in the distillate was titrated with 0.001 M HCl and its concentration determined as described in section 3.32.

3.6.3 Screenhouse pot experiment

3.6.3.1 Soils used for planting

The three soils; namely Toje, Adenta and Haatso series used in the laboratory incubation and hydrolysis studies were used in conducting the pot-experiment in the screenhouse at the University of Ghana, Legon campus. Buckets of 20 cm inner top diameter, 18 cm height and 16.5 cm bottom diameter were filled with 5 kg air-dried soils. The soils were repacked to their field bulk densities of 1.31 Mg/m³, 1.38 Mg/m³, and 1.37 Mg/m³ for Toje, Adenta and Haatso series, respectively. Holes were drilled at the bottom of the pots and non-absorbent cotton inserted in them to allow free water drainage but prevent soil loss. The upper 2-cm layer of the soil was mixed with 120 kg N /ha equivalent of the different amendments. The pots were watered daily and left to stand for 10 days to stabilize before planting.

3.7 Design of the study

The experimental design used was a completely randomized with three replications, giving a total 117 experimental units: (12 amendments × 3 soils × 3 reps) + 3 controls per soil. The twelve organic amendments were assessed alongside a control that received no amendment. The treatment layout used for both the biological and chemical method are shown in Table 3.2. The numbers denote organic amendments applied to the soil.

Table 3. 2: Description and abbreviations of the different organic amendments

Treatment	Abbreviation	Code
Rice husk + cow dung	RH + CD 10: 0	1
50% (Rice husk + cow dung) + 50% rice husk biochar	RH + CD 5:5	2
70% (Rice husk + cow dung) + 30% rice husk biochar	RH + CD 7:3	3
Rice husk + poultry manure	RH + PM 10:0	4
50% (Rice husk + poultry manure) + 50% rice husk biochar	RH + PM 5:5	5
70% (Rice husk + poultry manure) + 30% rice husk biochar	RH + PM 7:3	6
Market waste + cow dung	MW + CD 10:0	7
50% (Market waste + cow dung) + 50% rice husk biochar	MW + CD 5:5	8
70% (Market waste + cow dung) + 30% rice husk biochar	MW + CD 7:3	9
Market waste + poultry manure	MW+ PM 10:0	10
50% (Market waste + poultry manure) + 50% rice husk biochar	MW + PM 5:5	11
70% (Market waste + poultry manure) + 30% rice husk biochar	MW + PM 7:3	12



3.7.1 *Planting and agronomic practices*

Maize (*Zea mays* L.) seed variety *Obatanpa* was used as the test crop. Germination test was conducted to prevent poor stand. Seeds were poured into a 500 mL beaker, 70% alcohol was added, stirred for a few minutes, and washed thoroughly with distilled water to get rid of any alcohol left on the seed. A few drops of 1% acidified HgCl₂ was added to the seeds and diluted with distilled water, stirred and decanted. The seeds were washed thoroughly with a lot of distilled water to remove any excess 1% acidified HgCl₂ left on them. The seeds were transferred onto clean petri dishes lined with sterile moist filter paper using sterile forceps at twenty seeds per petri dish. The petri dishes were kept in a dark room at 25 °C for 3 days to germinate.

Three maize seeds were planted per pot (4 cm depth) and after complete germination (14 days), the two most vigorous seedlings were retained. A basal P and K fertilizers were applied at 60 kg P₂O₅ and 60 kg K₂O, respectively at two weeks after planting. Weeds on the soil surfaces were uprooted by hand. Soil moisture was maintained at 85% water holding capacity (WHC) throughout the experiment.

3.7.2 *Dry matter yield determination*

Maize biomass was harvested after 6 weeks of planting by cutting the above ground stalk at 3 cm above the surface of the soil. The root was removed from the soil by wetting the contents of the pot and washing the roots under running water to remove soil particles attached to it. The fresh green weight of the shoots and roots packed into quarto-sized envelopes and dried in an oven at 65 °C for 72 hours, weighed to determine the above ground biomass and root dry matter yields. The harvested shoots and roots

were ground in a stainless-steel mill and sieved through 0.1 mm mesh and stored for determination of total N.

3.7.3 Total N determination

Total N content of the shoot and root biomass were determined using Kjeldahl digestion. One gram (1 g) of the milled dry mass of either the shoots or roots were weighed into a digestion tube, followed by addition of 5 mL concentrated H₂SO₄. The mixture was heated at low heat on a digestion block, and 2 mL of hydrogen peroxide was added. The heating temperature was then increased to 360 °C and maintained till the mixture changed to a colorless solution. The digest was allowed to cool and transferred into a 100 mL volumetric flask and made up to mark with distilled water. A 20 mL aliquot of the digest was transferred into a distillation flask, 10 mL of 40% NaOH was added and distilled. The ammonia liberated was collected in a 5 mL boric acid its concentration determined as described in section 3.3.2.

3.8 Modelling of N mineralization and hydrolysis

The cumulative N mineralized in the long-term aerobic incubation was fitted to the first order kinetics equation describe by Stanford and Smith (1972) :

$$N_{min} = N_o[1 - \exp(-k_m t)] \quad 3.8$$

where, N_{min} (mg N/kg) is the cumulative amount of N mineralized at time, t (week) and N_o (mg N/kg) is the potentially mineralizable N and k_m is the mineralization rate constant (k).

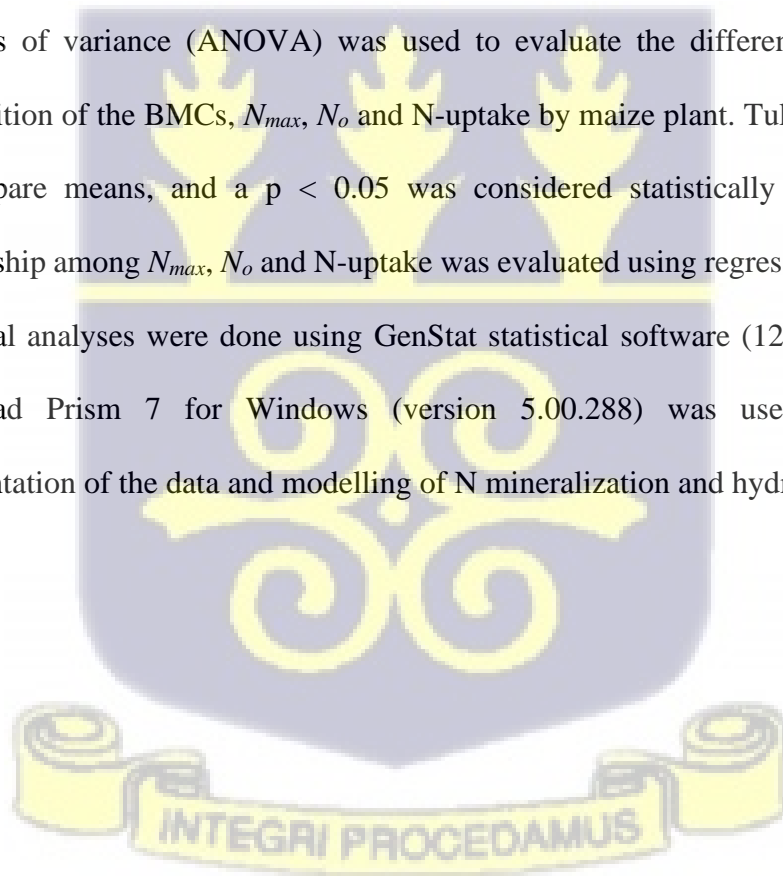
Likewise, the cumulative N hydrolyzed by the alkaline reagents with time of distillation was fitted to the non-linear first order equation proposed by Dodor and Tabatabai (2019):

$$N_{hyd} = N_{max}[1 - \exp(-k_h t)] \quad 3.9$$

where, N_{hyd} (mg N/kg) is the cumulative amounts of N hydrolyzed in time, t (min), N_{max} (mg N/kg) is the potentially hydrolyzable N, and k_h is the first-order alkaline hydrolysis rate constant.

3.9 Statistical analysis

Analysis of variance (ANOVA) was used to evaluate the differences in chemical composition of the BMCs, N_{max} , N_o and N-uptake by maize plant. Tukey test was used to compare means, and a $p < 0.05$ was considered statistically significant. The relationship among N_{max} , N_o and N-uptake was evaluated using regression analysis. All statistical analyses were done using GenStat statistical software (12th edition, 2009). GraphPad Prism 7 for Windows (version 5.00.288) was used for graphical representation of the data and modelling of N mineralization and hydrolysis.



CHAPTER FOUR

4.0 RESULTS

4.1 Chemical and physical characteristics of the soils

Some chemical and physical characteristics of the soils are presented in Table 4.1. The three soils are moderately acidic with pH values of 5.7, 6.1 and 6.3 for Adenta, Haatso and Toje, respectively. The particle size distribution of the soils showed that Haatso and Adenta series are sandy clay loam, while Toje series is sandy loam. The bulk densities of the three soils are 1.25, 1.26 and 1.33 Mg/m³ for Haatso, Toje and Adenta series, respectively. Organic carbon contents are 1.07 g/kg, 1.03 g/kg, and 0.86 g/kg for Haatso, Toje and Adenta series, respectively. Haatso series recorded the highest total carbon and N. The NH₄⁺-N and NO₃⁻-N contents were high in Toje series.

Table 4. 1: *Selected chemical and physical properties of the soils*

Parameters	Soils		
	Haatso	Toje	Adenta
pH	6.1	6.3	5.7
Total C (g/kg)	8.9	4.5	4.8
Total N (g/kg)	1.1	1.1	0.9
NH ₄ ⁺ -N (mg/kg)	15.6	34.5	20.8
NO ₃ ⁻ -N (mg/kg)	16.7	35.8	20.2
Organic N (g/kg)	1.07	1.03	0.86
Bulk density (Mg/m ³)	1.25	1.26	1.33
Sand (%)	70	60	70
Clay (%)	22.5	35	22.5
Silt (%)	7.5	5	7.5
Textural class	Sandy clay loam	Sandy clay	Sandy clay loam

4.2 Characteristics of the organic amendments

Some chemical properties of the organic amendments are shown in Table 4.2. The organic amendments are alkaline with pH values ranging from 8.1 in amendments 5 and 6 to 9.5 in amendments 7, 10 and 11. Amendment 2 had the highest TC content of 276.7 g/kg and the minimum TC was recorded by amendment 1 with a value of 120.2 g/kg. Total N varied among the amendments, with the maximum and minimum values of 17.5 g/kg and 6.8 g/kg in amendments 10 and 1, respectively. The $\text{NH}_4^+\text{-N}$ content did not vary among the organic amendments, with values ranging from 110.1 to 118.5 mg/kg. The $\text{NO}_3^-\text{-N}$ content of the amendments varied, however, with values ranging from 73.7 to 224.0 mg/kg in amendments 2 and 12, respectively. The C: N ratio of the amendments varied significantly, with values ranging from 30.9 to 12.1 in amendments 1 and 10, respectively.

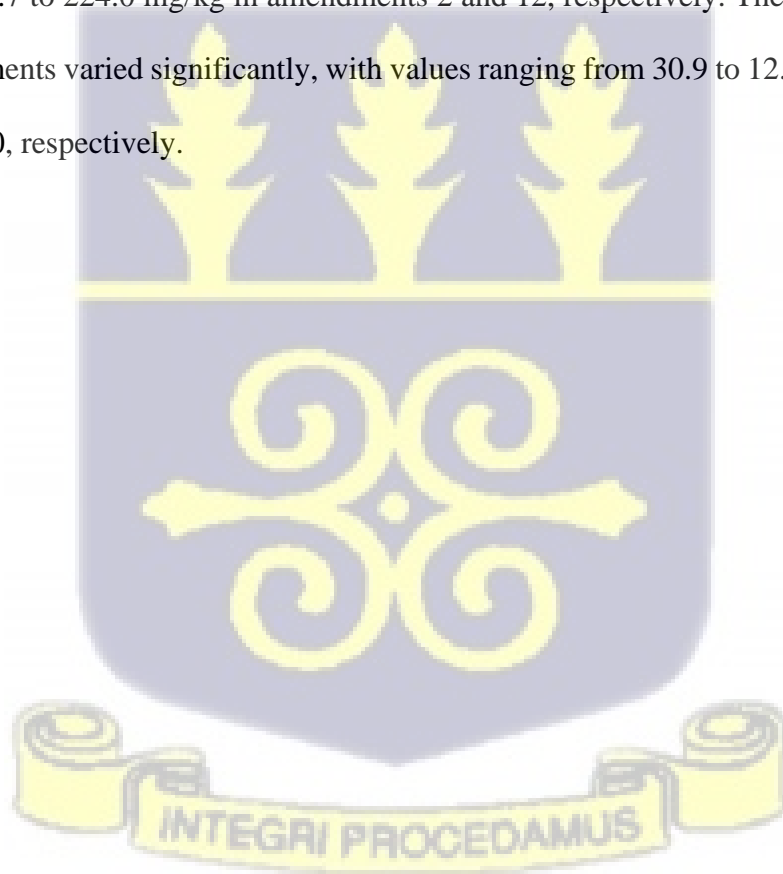
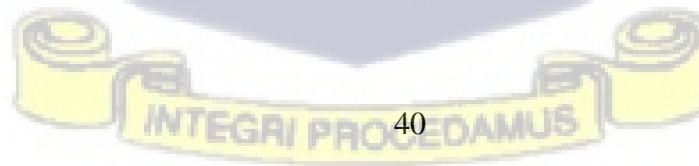


Table 4. 2: Selected chemical properties of the organic amendments

Organic amendment	Code	pH	Total C (g/kg)	Total N (g/kg)	NH ₄ ⁺ -N (mg/kg)	NO ₃ ⁻ -N (mg/kg)	C: N
RH + CD 10: 0	1	8.6 abc	120.6 a	6.8 a	110.1 a	80.3 a	17.7 abc
RH + CD 5:5	2	8.4 ab	276.7 k	8.9 bc	111.1 a	73.7 a	30.9 g
RH + CD 7:3	3	8.4 ab	159.6 b	6.9 ab	108.3 a	73.7 a	22.8 fg
RH + PM 10:0	4	8.6 abc	262.0 i	9.5 cd	109.2 a	86.8 a	27.1 efg
RH + PM 5:5	5	8.1 a	261.0 i	9.5 cd	110.1 a	82.1 a	25.6 fg
RH + PM 7:3	6	8.1 a	254.0 h	9.5 cd	109.2 a	82.1 a	27.1 efg
MW + CD 10:0	7	9.5 e	177.3 c	13.7 f	114.8 a	179.2 bcd	13.0 a
MW + CD 5:5	8	9.1 cde	237.7 g	11.0 de	112.0 a	175.5 bc	21.7 ef
MW + CD 7:3	9	8.7 bcd	198.6 d	12.9 ef	112.9 a	170.8 b	15.3 ab
MW+ PM 10:0	10	9.3 de	212.9 e	17.5 g	116.7 a	220.3 cd	12.1 a
MW + PM 5:5	11	9.5 e	267.0 j	13.7 f	114.8 a	220.3 cd	19.4 bcd
MW + PM 7:3	12	9.5 e	227.3 f	13.7 f	118.5 a	224.0 d	16.5 abc
LSD (0.05)		0.33	1.53	1.14	10.40	25.72	3.64

RH = Rice husk, CD = cow dung, PM = poultry manure, MW = Market waste, 7:3 = 70% compost + 30% rice husk biochar, 5:5 = 50% compost + 50% rice husk biochar, 10:0 = compost + no rice husk biochar. Means with same alphabets within a column are not significantly different at 0.5%.



4.3 Organic N hydrolysis

The patterns of organic N (ON) hydrolysis by the two alkaline reagents with time of distillation in five of the organic amendments in the three soils used are shown in Figure 4.1. The shapes, trends and patterns for the other organic amendments are similar and fall between those shown. The graphs show that there was an initial high rate of organic N hydrolysis by the two alkaline reagents during the first 20 minutes of steam distillation, and then declined to a low constant rate thereafter.

4.3.1 Total organic N hydrolyzed by the alkaline reagents

The total amount of N hydrolyzed by the two alkaline reagents in the organic amendments in the three soils used are shown in Figure 4.2. Within each soil and reagent, statistical analysis indicated that there were significant differences ($p < 0.05$) among the total amounts of organic N hydrolyzed from the amendments, with NaOH generally hydrolyzing more N compared to KOH. The amount of ON hydrolyzed ranged from 255.36 to 272.91 mg/kg in amendments 4 and 7 to 276.87 and 255.73 mg/kg in amendments 3 and 5 for NaOH and KOH, respectively. Generally, the total amount of N hydrolyzed from the organic amendments using KOH slightly exceeded those obtained with NaOH and the order of magnitude of the amounts of N released followed the same trend in all the organic amendments.



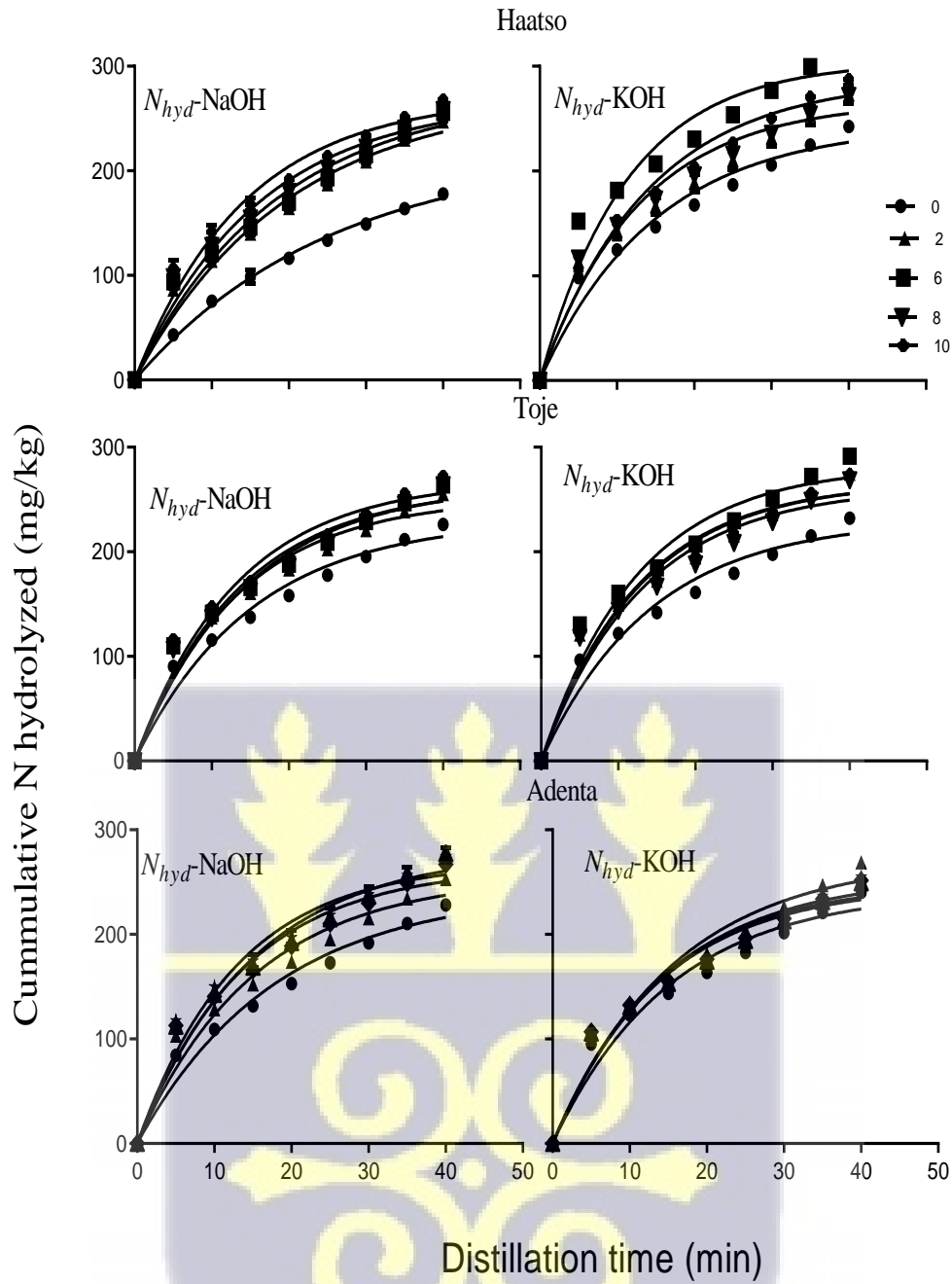


Figure 4.1: Cumulative N hydrolyzed with time of distillation using NaOH and KOH in five of the organic amendments.

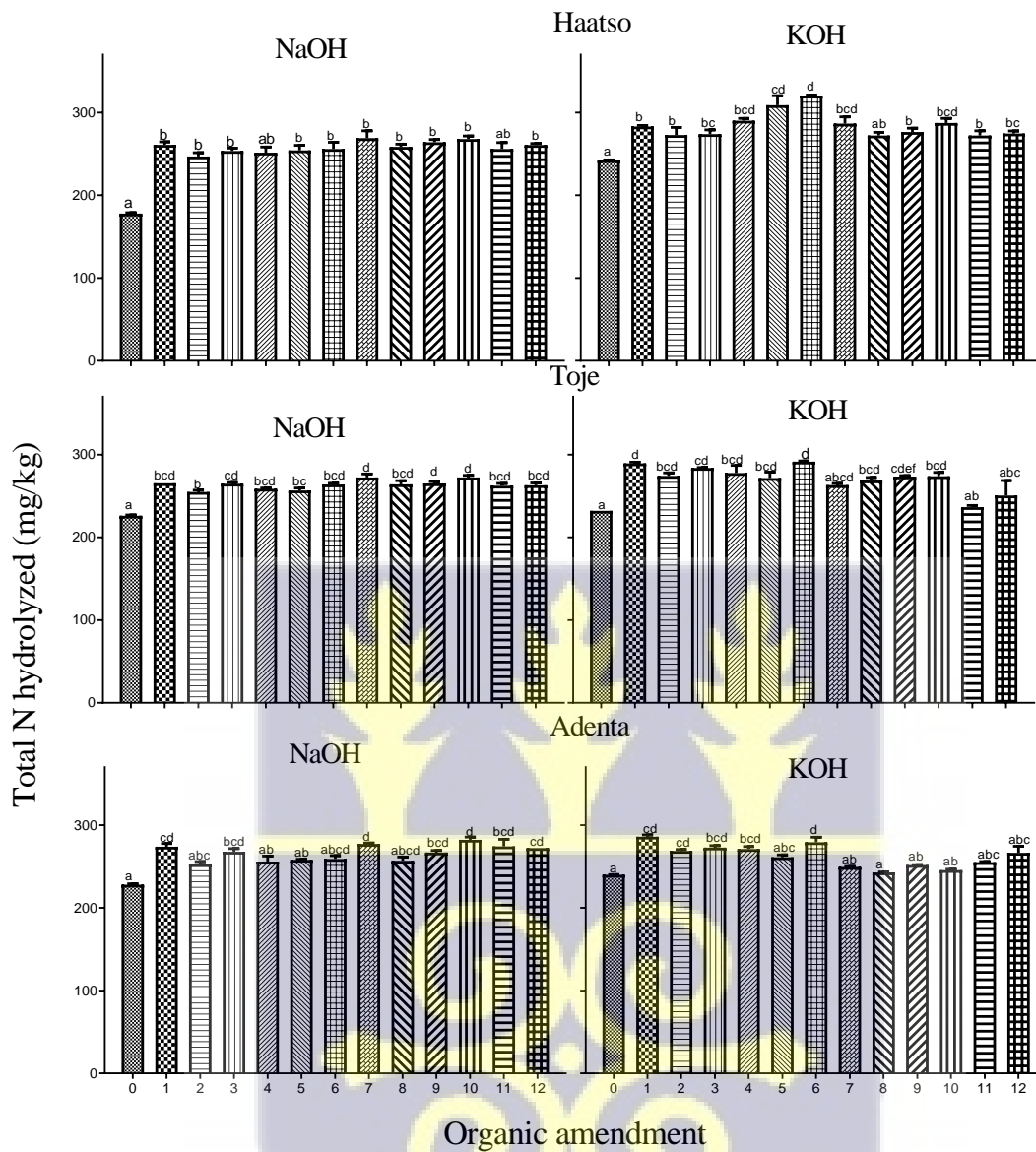


Figure 4.2: Total N hydrolyzed from the organic amendments. Within each reagent, same letter (s) above bars indicate no significant difference at $p = 0.05$. Vertical bars represent standard error of the means ($n = 2$). Numbers denote organic amendments applied to the soil, respectively.

4.4 Nitrogen mineralization under long-term incubation

The patterns of N mineralization from five of the organic amendments under the long-term aerobic incubation condition in the soils are shown in Figure 4.3. Generally, N mineralization increased sharply during the first 10 weeks followed by a steady decrease thereafter till the end of the 26 weeks incubation period. The shapes, trends, and patterns of N mineralization from the other organic amendments are similar and fall between those shown.



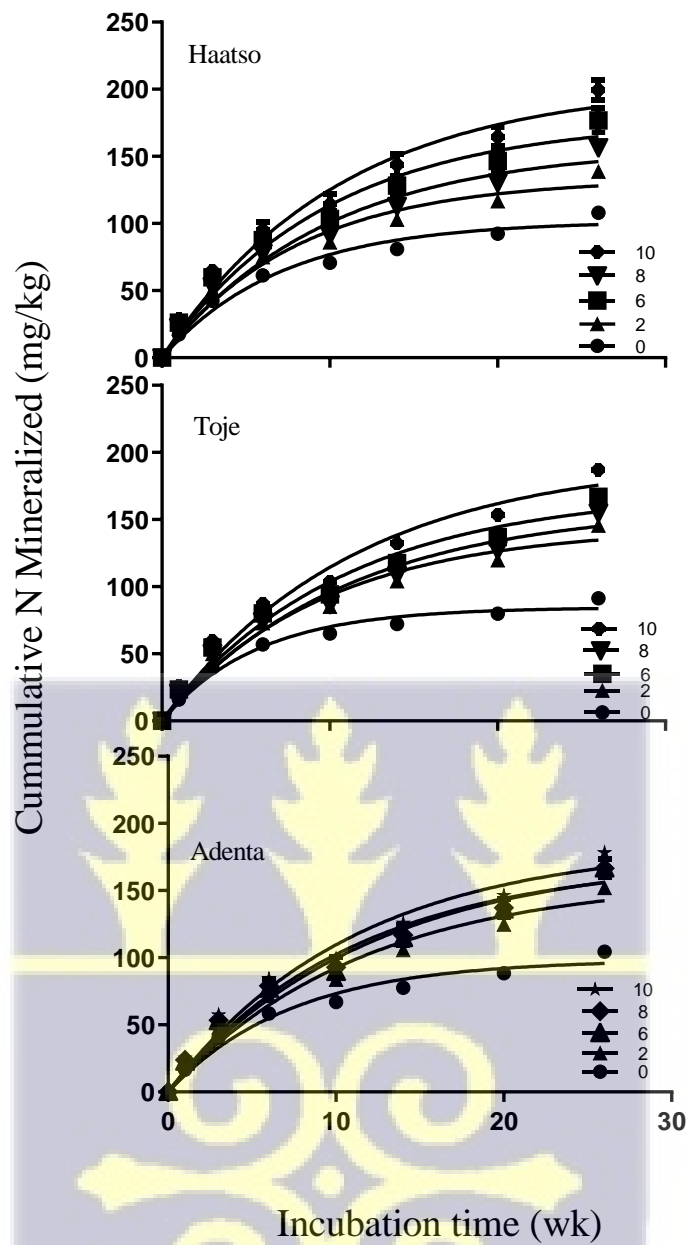


Figure 4.3: Patterns of N mineralization during the long term incubation period in five of the soil-compost mixtures in Haatso, Toje and Adenta series.



4.4.1 Total N mineralized under long-term incubation

The total N mineralized from the organic amendments in the long-term aerobic incubation condition in the soils are shown in Figure 4.4. Regardless of the type of organic amendments, the amount of N mineralized from the non-amended control soils were significant ($p < 0.05$) lower than those from the amended soils. Statistical analysis indicated that the amount of N mineralized from the amendments are significantly ($p < 0.05$) different within each reagent and soils. The order of magnitude of the amounts of N released followed the same trend in all the organic amendments, with slightly greater amounts of N mineralized from amendment 10 compared to the others in the three soils used.



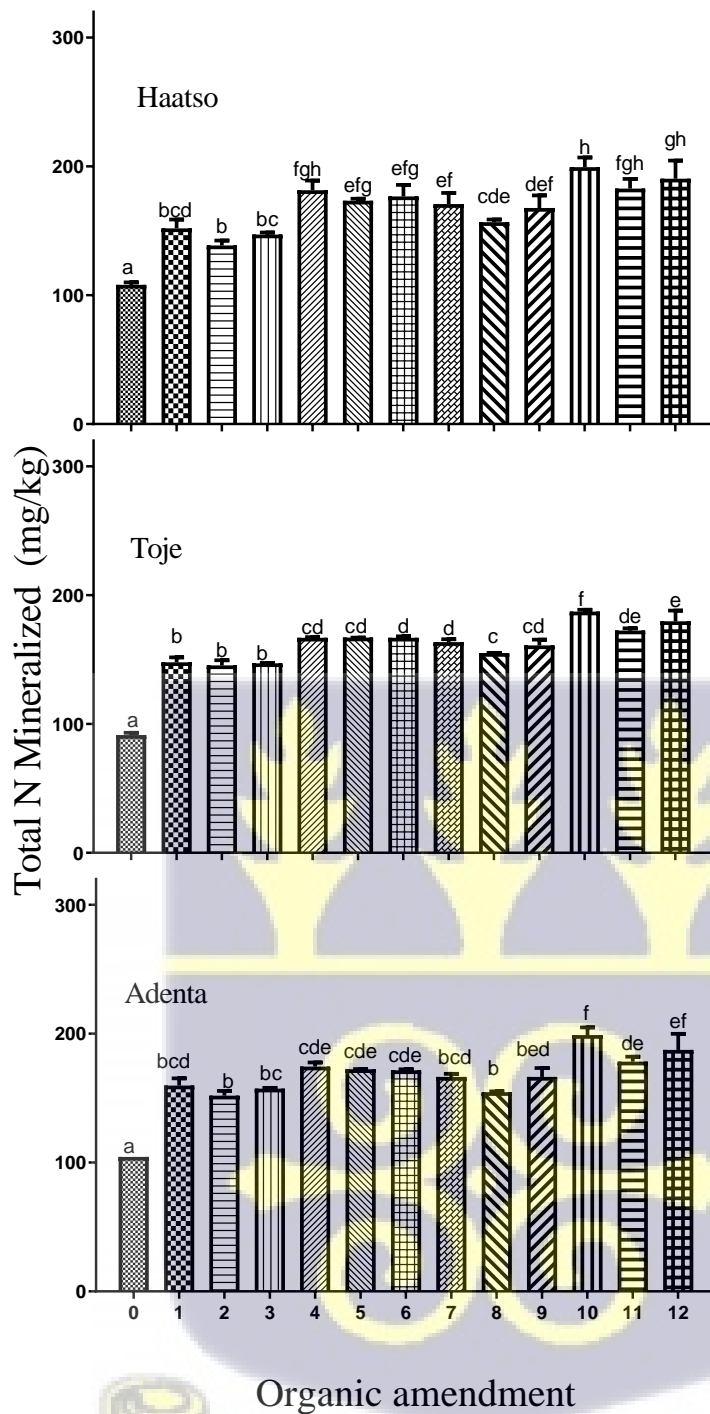


Figure 4.4: Total N mineralized during the long term incubation period in the organic amendment in Haatso, Toje and Adenta series. Within each amendment, same letter (s) above the bars indicate no significant difference at $p = 0.05$.

4.5 Kinetics parameters of N mineralization/ hydrolysis

The calculated kinetic parameters of N mineralization and hydrolysis from the amendments by the two reagents are presented in Tables 4.3 – 4.5 for Haatso, Toje and Adenta, respectively. Data from N mineralization in the long-term incubation study fitted the nonlinear regression model very well, with convergence of the model occurring with 20 iterations or less and R^2 values ranging between 0.970 – 0.987 across the three soils used. Within each soil, estimated N_0 values differed significantly among the amendments, and were significantly different from those of the control soils without amendment. Generally, and across all soils and amendments, estimated N_0 values were significantly higher for Haatso compared to Toje and Adenta series. Estimated N_0 values range from 133.0 – 205.0 mg/kg in amendments 2 and 10, respectively in Haatso series. The corresponding values for Toje and Adenta series ranged between 144.5 (amendment 2) and 196.0 mg/kg (amendment 10), and between 106.3 and 140.0 mg/kg for amendments 2 and 10, respectively. Analysis of variance indicated that k_m values differed significantly among the amendments, with values ranging from 0.095 – 0.141, 0.088 – 0.177, and 0.058 – 0.091 week⁻¹ for Haatso, Toje and Adenta series, respectively.

Application of the nonlinear exponential regression equation to estimate the kinetic parameter of ON hydrolysis by NaOH and KOH from the organic amendments also conformed very to the model, with all R^2 values > 0.98 across all soils. Estimated N_{max} values for NaOH (N_{max} -NaOH) and KOH (N_{max} -KOH) were significantly correlated with each other ($p < 0.001$) across the three soils and differed significantly among the amendments. The estimated N_{max} values using NaOH (N_{max} -NaOH) ranged from 262.3 – 271.9 mg/kg in amendments 1 and 9, respectively in Haatso series, from 251.8 – 270.1

mg/kg for amendments 2 and 9, respectively for Toje, and from 256.2 – 279.9 mg/kg for amendments 2 and 7, respectively for Adenta series. The corresponding N_{max} -KOH values varied between 267.0 – 304.7 mg/kg in amendments 8 and 6, respectively in Haatso series, between 240.0 – 282.8 mg/kg for amendments 11 and 6, respectively for Toje series, and between 247.5 – 286.9 mg/kg for amendments 7 and 6, respectively for Adenta series. The calculated k_h values varied among the amendments across the three soils, with values ranging from 0.059 to 0.075 min^{-1} for NaOH, and from 0.066 to 0.082 for KOH hydrolysis.



Table 4. 3: First-order kinetic parameters of N mineralization/alkaline hydrolysis from the amendments in Haatso series

Organic amendment	N_0				$N_{hyd-NaOH}$				$N_{hyd-KOH}$			
	N_0	k_m	$t_{1/2}$	R^2	N_{max}	k_h	$t_{1/2}$	R^2	N_{max}	k_h	$t_{1/2}$	R^2
0	102.1	0.141	5.0	0.974	222.2	0.039	18.1	0.997	244.4	0.067	10.4	0.915
1	147.0	0.121	5.8	0.974	262.3	0.069	10.0	0.971	274.5	0.080	8.6	0.901
2	133.0	0.123	5.6	0.973	273.6	0.050	13.8	0.979	272.1	0.069	10.0	0.901
3	141.5	0.122	5.7	0.972	285.1	0.047	14.7	0.977	276.3	0.067	10.3	0.922
4	183.0	0.101	6.9	0.987	254.7	0.068	10.3	0.976	286.4	0.072	9.6	0.884
5	173.0	0.106	6.6	0.986	267.7	0.058	12.0	0.973	300.5	0.079	8.9	0.868
6	177.0	0.103	6.8	0.975	275.2	0.054	12.9	0.974	304.7	0.088	7.9	0.846
7	172.0	0.102	6.8	0.977	273.5	0.067	10.3	0.977	285.9	0.071	9.7	0.908
8	157.5	0.102	6.8	0.975	268.8	0.062	11.2	0.977	267.0	0.078	8.9	0.910
9	168.5	0.103	6.8	0.976	271.9	0.064	10.9	0.975	274.9	0.073	9.6	0.916
10	205.0	0.095	7.4	0.977	271.3	0.070	10.0	0.977	288.2	0.072	9.7	0.923
11	184.0	0.101	6.9	0.977	256.7	0.069	10.0	0.969	274.3	0.069	10.1	0.916
12	195.0	0.095	7.3	0.977	265.4	0.069	10.2	0.975	278.6	0.068	10.3	0.920
LSD	22.1	0.013	0.75	0.010	20.5	0.010	3.0	0.010	13.6	0.010	1.27	0.010

0 = no amendment, 1 = RH + CD 10:0, 2 = RH + CD 5:5, 3 = RH + CD 7:3, 4 = RH + PM 10:0, 5 = RH + PM 5:5, 6 = RH + PM 7:3, 7 = MW + CD 10:0, 8 = MW + CD 5:5, 9 = MW + CD 7:3, 10 = MW + PM 10:0, 11 = MW + PM 5:5, 12 = MW + PM 7:3

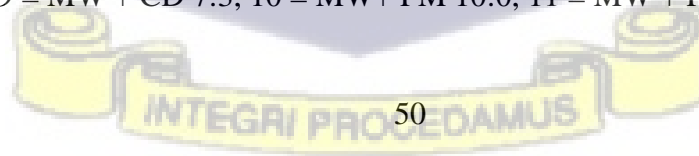


Table 4. 4: First-order kinetic parameters of N mineralization/alkaline hydrolysis from the amendments in Toje series

Organic amendment	N_0				$N_{hyd-NaOH}$				$N_{hyd-KOH}$			
	N_0	k_m	$t_{1/2}$	R^2	N_{max}	k_h	$t_{1/2}$	R^2	N_{max}	k_h	$t_{1/2}$	R^2
0	84.6	0.177	3.9	0.979	231.2	0.066	10.5	0.972	231.0	0.070	9.9	0.964
1	147.5	0.103	6.8	0.973	262.7	0.075	9.2	0.971	280.1	0.082	8.5	0.959
2	144.5	0.104	6.7	0.972	251.8	0.075	9.2	0.968	267.6	0.077	9.0	0.960
3	147.0	0.101	6.9	0.970	267.6	0.071	9.8	0.972	276.4	0.078	8.9	0.959
4	170.0	0.096	7.2	0.975	257.6	0.073	9.6	0.967	267.9	0.082	8.5	0.961
5	169.0	0.098	7.1	0.976	253.2	0.076	9.1	0.969	260.5	0.087	8.0	0.962
6	171.0	0.093	7.4	0.974	262.5	0.073	9.5	0.970	282.8	0.080	8.7	0.959
7	172.5	0.084	8.2	0.973	269.8	0.074	9.4	0.971	256.4	0.077	9.0	0.957
8	160.0	0.091	7.6	0.974	265.3	0.069	10.0	0.971	262.0	0.076	9.1	0.957
9	168.0	0.088	7.9	0.974	270.1	0.066	10.5	0.975	267.4	0.078	8.9	0.966
10	196.0	0.088	7.9	0.976	269.1	0.076	9.2	0.967	266.9	0.079	8.8	0.959
11	176.0	0.095	7.3	0.975	263.5	0.071	9.8	0.972	240.0	0.067	10.4	0.972
12	185.0	0.093	7.5	0.977	261.5	0.074	9.4	0.971	249.3	0.071	9.9	0.964
LSD	10.6	0.006	0.4	0.00	13.6	0.010	1.27	0.010	15.8	0.010	1.4	0.010

0 = no amendment, 1 = RH + CD 10:0, 2 = RH + CD 5:5, 3 = RH + CD 7:3, 4 = RH + PM 10:0, 5 = RH + PM 5:5, 6 = RH + PM 7:3, 7 = MW + CD 10:0, 8 = MW + CD 5:5, 9 = MW + CD 7:3, 10 = MW + PM 10:0, 11 = MW + PM 5:5, 12 = MW + PM 7:3

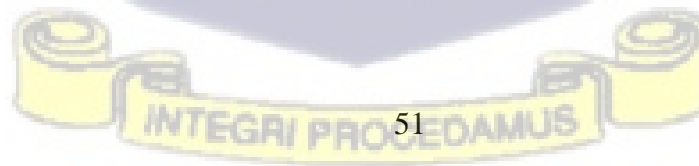
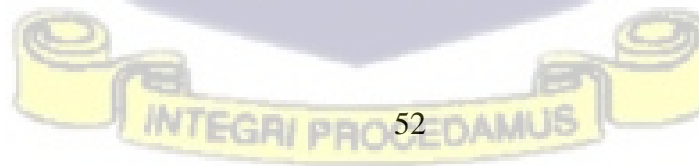


Table 4. 5: First-order kinetic parameters of N mineralization/alkaline hydrolysis from the amendments in Adenta series

Organic amendment	N_0				$N_{hyd-NaOH}$				$N_{hyd-KOH}$			
	N_0	k_m	$t_{1/2}$	R^2	N_{max}	k_h	$t_{1/2}$	R^2	N_{max}	k_h	$t_{1/2}$	R^2
0	65.7	0.091	3.4	0.972	242.1	0.056	12.4	0.974	242.3	0.065	10.7	0.966
1	111.3	0.058	5.3	0.972	276.4	0.065	10.6	0.964	276.3	0.078	8.9	0.954
2	106.3	0.058	5.3	0.973	256.2	0.065	10.6	0.966	273.1	0.063	11.0	0.962
3	109.7	0.058	5.3	0.971	269.9	0.066	10.5	0.964	267.5	0.075	9.3	0.959
4	120.7	0.060	5.1	0.974	253.4	0.071	9.7	0.962	267.7	0.074	9.4	0.967
5	119.3	0.060	5.1	0.983	254.0	0.074	9.3	0.961	259.6	0.069	10.0	0.960
6	119.3	0.058	5.3	0.974	263.1	0.067	10.4	0.968	286.9	0.063	11.0	0.960
7	117.7	0.055	5.6	0.972	279.9	0.067	10.4	0.968	247.5	0.071	9.7	0.970
8	106.3	0.060	5.1	0.971	258.9	0.067	10.3	0.966	242.9	0.069	10.1	0.963
9	115.3	0.060	5.2	0.976	265.3	0.072	9.6	0.967	249.5	0.072	9.6	0.964
10	140.0	0.056	5.5	0.975	278.5	0.076	9.1	0.970	246.5	0.068	10.2	0.963
11	123.3	0.060	5.1	0.974	269.2	0.078	8.9	0.968	256.1	0.068	10.2	0.964
12	130.3	0.060	5.2	0.974	276.7	0.067	10.4	0.974	262.9	0.073	9.5	0.960
LSD	18.1	0.009	0.84	0.010	12.1	0.003	0.57	0.010	12.3	0.004	0.57	0.010

0 = no amendment, 1 = RH + CD 10:0, 2 = RH + CD 5:5, 3 = RH + CD 7:3, 4 = RH + PM 10:0, 5 = RH + PM 5:5, 6 = RH + PM 7:3, 7 = MW + CD 10:0, 8 = MW + CD 5:5, 9 = MW + CD 7:3, 10 = MW + PM 10:0, 11 = MW + PM 5:5, 12 = MW + PM 7:3



4.6 Maize N-uptake

4.6.1 N-uptake by maize

The N-uptake by maize during a cultivation period of 6 weeks is shown in Fig.4.5. In general, N-uptake followed the order Haatso>Toje>Adenta series, with values ranging from 2 to 11.52 mg/pot across the three soils. Maize N-uptake varied sufficiently among the amendments, with uptake values in BMC amended soils being significantly higher than those of the control across all soils.

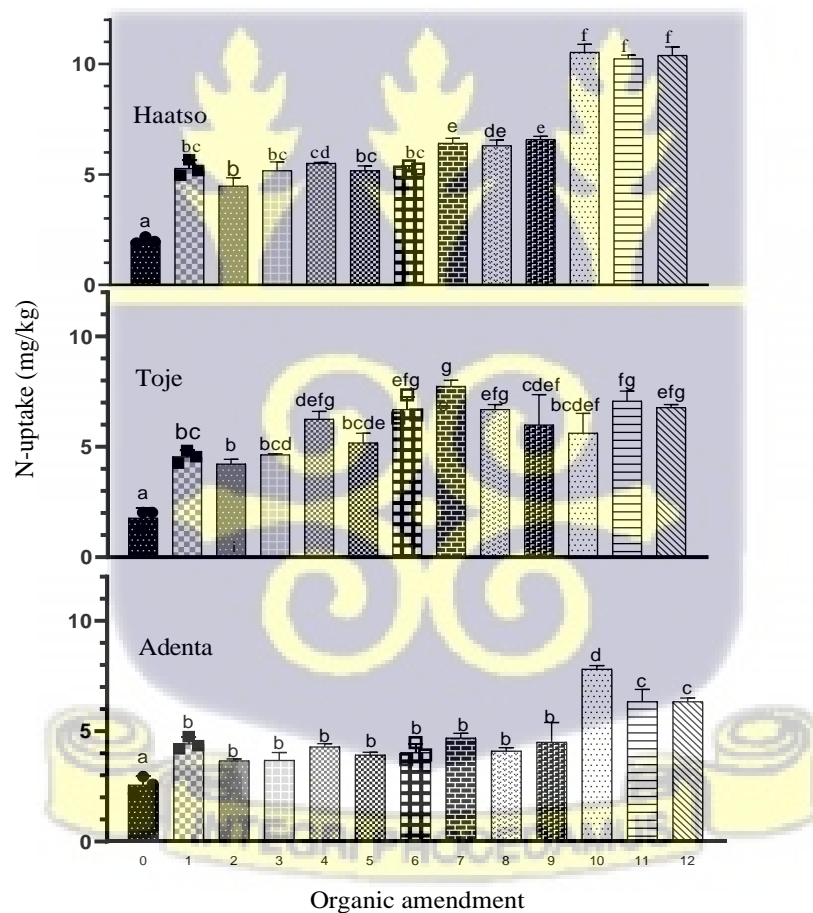


Figure 4.5: N-uptake from the different organic amendments in the soils. Vertical bar represent standard error of three replicates. Within each soil, bars followed by the same letter are not significantly different at $p = 0.05$.

4.7 Relationship among N_o , N_{max} , and N-Uptake

When data across the three soils were pooled together, the results indicated that relationship between N uptake by the maize was positively and significantly ($p < 0.0001$) correlated with the N_o (Fig 4.7).

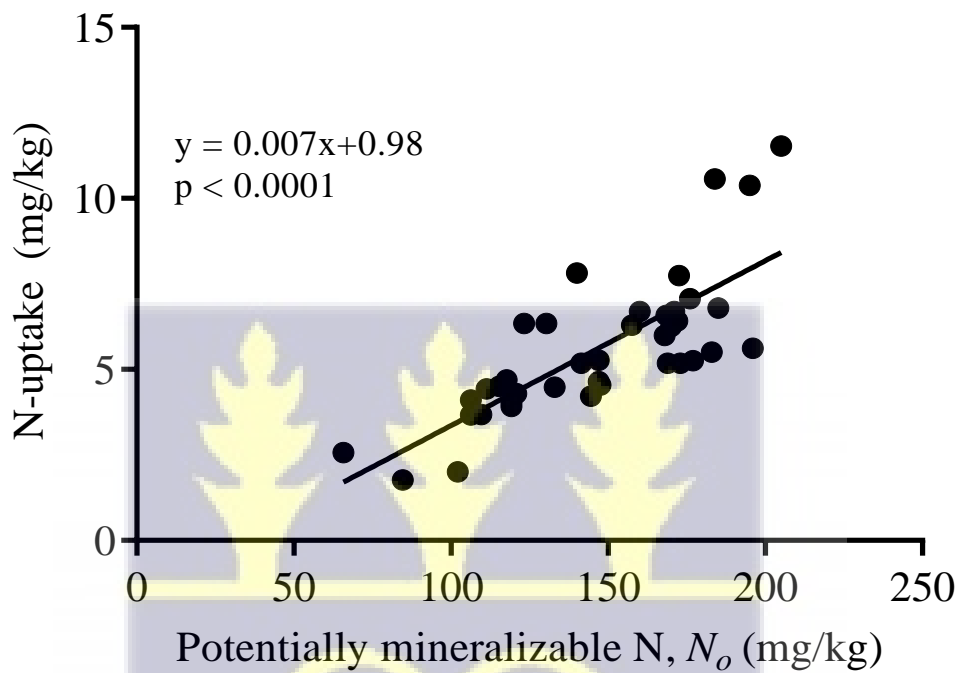


Figure 4.6: Relationship between total N-uptake and potentially mineralizable N, N_o

The relationship between N_0 and N_{max} in the three soils are shown in Fig 4.6. The results indicated that N_0 was positively and significantly ($p < 0.001$) correlated with N_{max} -NaOH and N_{max} -KOH; however, the correlation with N_{max} -NaOH showed a closer association.

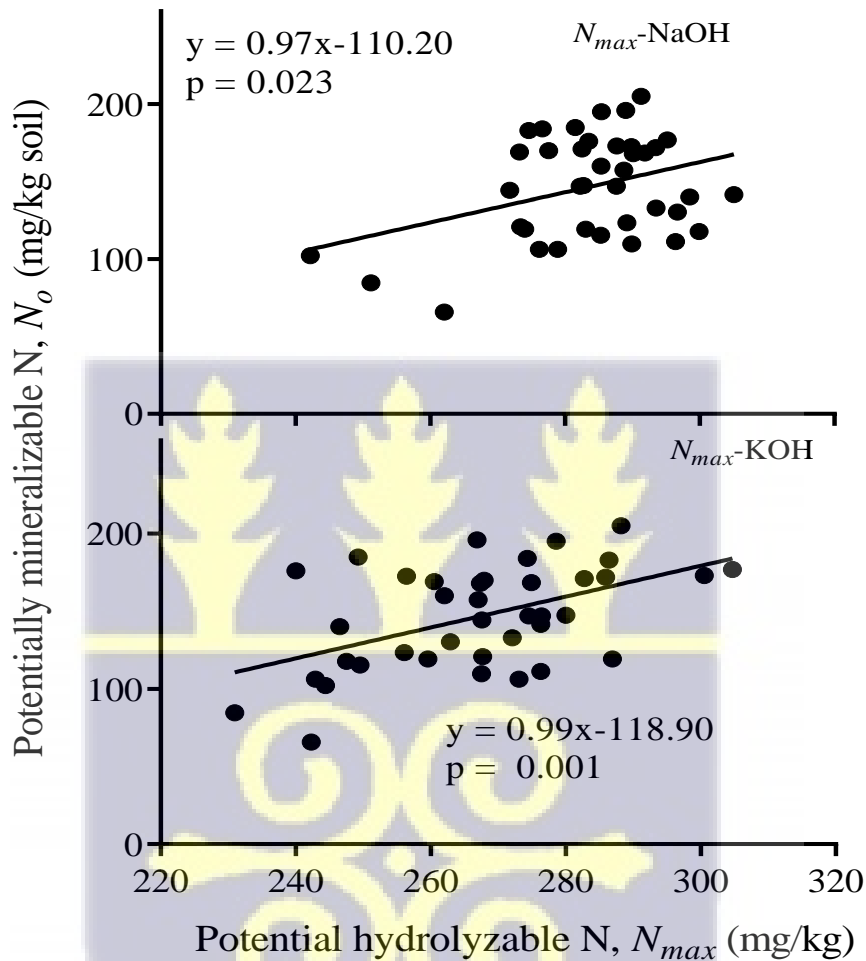
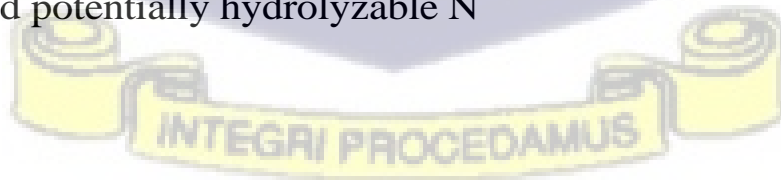


Figure 4.7: Relationship between potentially mineralizable N and potentially hydrolyzable N



The relationship between N_{max} and N uptake in the three soils are shown in Fig 4.8. Results indicated that N_{max} -NaOH was positively and significantly correlated with the N-uptake. Although the relationship between N-uptake and N_{max} -KOH was also positive, the association was not significant.

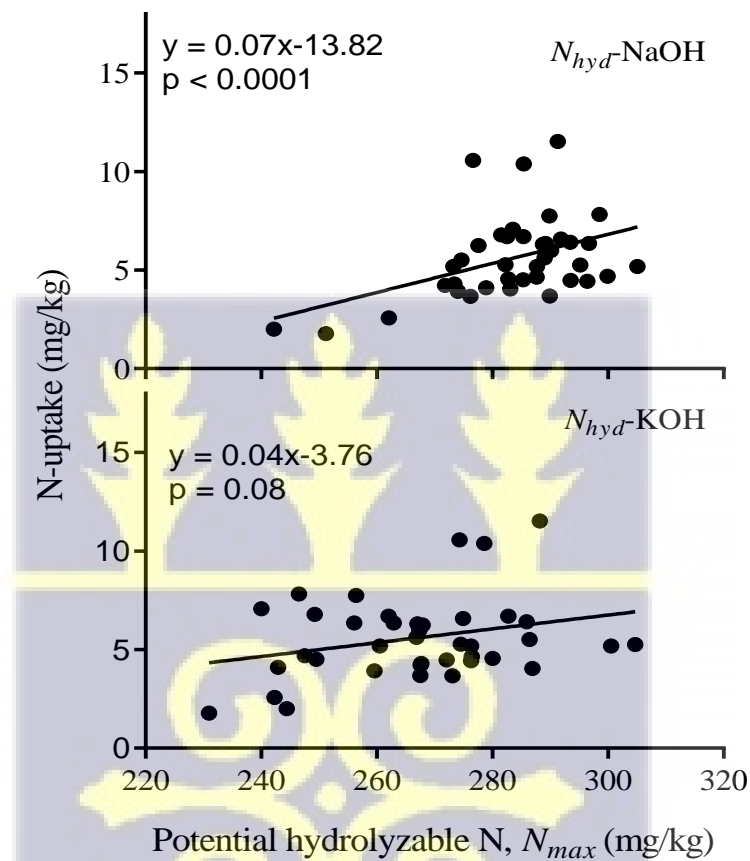
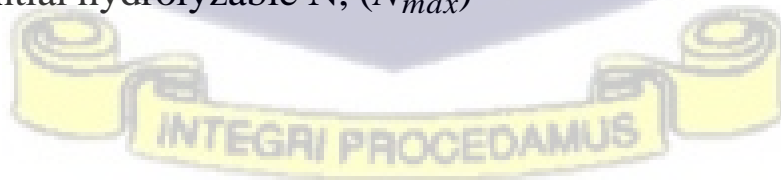


Figure 4.8: Relationship between N-uptake and potential hydrolyzable N, (N_{max})



CHAPTER FIVE

5.0 DISCUSSION

5.1 Soil properties

The medium bulk densities of the soils, ranging between 1.25 and 1.33 Mg m⁻³ reflects the sandy clay loam characteristic of soils in the coastal savanna agro-ecological zone of Ghana. The pH values of the soils are similar to those reported by Eze (2008) and Kamara (2019) who worked on soils from this agroecological zone. The moderate acidic to near neutral pH of the soils are within the pH \geq 5.5 required for optimum N mineralization in soils (Weil and Rady, 2017), suggesting that mineralization of ON in the BMCs will not be constrained by soil reaction.

The organic carbon (OC) content of the soils are within the range reported by other researchers for soils from the same area (Eze, 2015; Kamara, 2019), and can be considered very low based on the classification criteria proposed by Jones et al. (2004). The low OC content of the soils are characteristic of soils in the coastal savanna agro-ecological zones where the rates of mineralization are high due to the high temperatures and moisture which reduces the accumulation of organic carbon (Dowuona et al., 2012).

The rating of N levels in soils based on the classification scheme defined by Landon (2014); >10 g/kg very high; 5 - 10 g/kg high; 2 - 5 g/kg medium; 1 - 2 g/kg low and <1 g/kg very low, were used to compare the N levels in the three soils. On the bases of this rating, it can be concluded that the N levels in the soils are generally low which is characteristic of soils in the sub-Saharan Africa.

5.2 Characteristics of the organic amendments

The alkaline pH of the organic amendments can be attributed to the presence of appreciable amounts of liming materials such as KHCO_3 , MgCO_3 and small quantities of MgO in the feedstock. These liming materials could help increase nutrient availability, improve soil structure (Diacono and Montemurro, 2010) and quality (Eusufzai and Fujii, 2012).

All amendments with a steep initial release suggest a relatively high proportion of initial mineralizable N, indicating that a good amount of N would be immediately available for plant uptake. The organic N in the different amendments differ nevertheless, the amount of added organic N mineralized shows consistency after incorporation into the soils. In general, the greater the total N content of the amendment, the greater the proportion of its organic N that was mineralized after incorporation (Hartz et al., 2000).

Decomposition of the organic amendments are known to be affected by their initial chemical composition and quality such as C/N ratio, lignin and soluble polyphenol concentrations (Kumar and Goh, 2003). The C/N ratio is one of the most commonly recommended properties in describing compost quality and has been found by numerous studies to be closely relate to N mineralization from a wide range of organic amendments (Gale et al., 2006; Delin et al., 2012; Lazicki et al., 2020). In general, the organic amendments had varying C/N ratios due to differences in their composition, consistent with the finding of other researchers (Yulipriyanto, 2011; Azim et al., 2017). Organic amendment with low N release could be as a result of high amount of lignin content present in the materials used, lignin being reported to be a more resistant and

less biodegradable compound which slow the rate of N mineralization (Tuomela et al., 2000).

5.3 Patterns of organic N mineralization/hydrolysis

The initial high rate of organic N mineralization, which declined to a slow constant rate after 10 weeks of incubation can be attributed to the rapid mineralization of the easily mineralizable N compounds present in the amendments. This findings is in agreement with Bartholomew (2015) who stated that in the early stages of decomposition of fresh plant residues, the more readily available organic N materials are rapidly attacked and the N mineralized are made available for use by the microflora. Furthermore, the more stable protein complexes typical of soil organic matter are assumed to be formed during the process of decomposition, largely from proteins produced by microorganisms. Significant evidence has accumulated to support this hypothesis although much of it is indirect. Also, the observed decline in the rate of mineralization with time suggest that the more recalcitrant N were being mineralized. In other words, following the exhaustion of the initially easily decomposable ON, there remained ON compounds with stronger biological stability, resulting very slow net mineralization (Bartholomew, 2015; Dodor and Tabatabai, 2019). The similar patterns of OH hydrolysis by the alkaline reagents suggest that they are selectively and sequentially hydrolyzing similar ON forms present in the amendments. The results of the present study agree with those of Kamara (2019) who reported similar trend and patterns in N mineralization and hydrolysis in soils from the same agroecological zone.

5.4 Kinetic parameters of N-mineralization/hydrolysis

The high R^2 values obtained in application of the non-linear regression equation to the N mineralization data indicate that the model is a useful approximation of N mineralization and hydrolysis in BMC amended soils. These results are similar to those reported by Serna and Pomares (1991). The N_o values reported in the present study are comparable to those of Schomberg et al. (2009) and N_{max} values are similar to those reported by Dodor and Tabatabai (2019). The observed significant differences in the N_o and N_{max} values among the organic amendments reflects the variation in the composition and the amount of mineralizable N. This finding is in agreement with research by Frankenberger and Abdelmagid (1985a) who reported significant differences among the kinetic parameters of N mineralization rates of leguminous crops incorporated into soil. Differences among the specific fractions of the organic amendments in releasing N may be attributed to several factors such as N content of the materials, lignoprotein complexes and their resistance to microbial decomposition, variation existing among organic materials with respect to their partitioning photosynthates (Frankenberger and Abdelmagid, 1985a).

The differences among the first order N mineralization rate constants, k_m indicates that the mineral N fractions of the organic amendments were released at different rates. The relatively high k_m values for the organic amendments in the present study as compared with those of Gale et al. (2006) can be explained by climatic conditions. This might have had an effect on microbiological activities causing more intensive mineralization. These values are similar in magnitude to the data obtained by Griffin & Laine (1983) when they worked on N mineralization in soils previously amended with organic wastes. The calculated $t_{1/2}$ values for N_o data are comparable to those reported by

Frankenberger and Abdelmagid (1985a) in their studies dealing with N mineralization of crop residues in soils.

5.5 Relationship between N_o and N-uptake

The strong positive and significant ($p < 0.001$) correlation between N_o and N-uptake by maize indicates that N_o could be a reliable estimator of N requirement by maize grown in soils amended with BMCs. The result is in agreement with Cordovil et al. (2007) who reported close agreement between N uptake in a pot experiment and the net N mineralization trend observed in aerobic incubations of organic wastes. However, the results disagree with the research by Bregliani et al. (2006) that uptake of N by maize plants (roots and shoots) measured in a short-term pot experiment was poorly correlated with the N mineral fraction in soils. Also, research by Sharifi et al. (2011) did not find significant relationship between the tested measures of N availability in the laboratory and the field-based indices of N supply.

5.6 Relationship between N_o and N_{max}

The positive relationship between N_o and N_{max} indicates that the alkaline hydrolysis method proposed by Dodor and Tabatabai (2019) can reliably be used as an index of organic N mineralization when soils are amended with BMCs. The relationship between N_o and N_{max} by the use of NaOH and KOH were significant, however, the closer relationship observed with KOH could be due to the fact that similar pools of N are being hydrolyzed in the amended soils as compared to those mineralized in the long-term incubation method. Furthermore, KOH could be hydrolyzing N pools that are more closely related to soluble N-fractions in the soils (Dodor and Tabatabai, 2019). Therefore, it can be concluded that this simple and precise method using NaOH and

KOH as chemical extractant could be suitable for use in routine laboratory conditions for the determination of hydrolyzable N in BMC.

5.7 Relationship between N_{max} and N-uptake

The positive relationship between N_{max} and N-uptake indicates that the alkaline hydrolysis method proposed by Dodor and Tabatabai (2002) can be used as an index of organic N mineralization and plant N-uptake when soils are amended with BMCs. Hydrolysis of N by NaOH was effective as compared to KOH in terms of N-uptake during the growing season. Also, highly significant correlation ($p < 0.0001$) was established by the use of NaOH, indicating that NaOH hydrolyzable ON is a better predictor of N-uptake. Similar results were reported by Magdoff and Amadon (1980) who found positive relationship between the amount of N mineralized in a pot experiment and that released by the use of autoclave as a chemical index of N availability. Also, the results are in consonance with those of other researchers who reported at various times high correlations between extracted organic N and liable N fractions (Castellanos and Pratt 1981a ; Antep, 1997; Martínez et al. 2018).

The insignificant relationship between N_{max} -KOH and N uptake in the pot experiment agrees with the results of Sharifi et al. (2011) who reported no significant relationship between the tested measures of N availability in the laboratory and the field-based indices of N supply to plant. This weak correlation between the two indices of N mineralization and availability can be attributed the chemical method hydrolyzing N pool that may not be mineralized by microbial action to release N for plant uptake.

In general, the use of chemical indices of N availability has been limited because of the poor correlation with crop N uptake, probably due to the inability to selectively release

the fraction of soil organic N that is made available for plant growth by soil microorganisms (Dodor and Tabatabai, 2019). This difficulty in relating chemical hydrolysis of N to plant N uptake and growth is probably due the differences in processes that control the rate of mineralization of N under field conditions compared to chemical hydrolysis. The process of N mineralization in the presence of plants growing in the soils could also be confounded by several unpredictable environmental factors (aeration, moisture, and temperature) that are not present in *in-vitro* chemical hydrolysis of N. In spite of this, there are many instances in which favorable results were obtained using N-availability tests (Robinson, 1968; Saito and Ishii, 1987).

The research question of this study was to investigate whether the rapid chemical hydrolysis method was applicable as N mineralization irrespective of the composition of the organic resource. The results of the study showed strong and significant correlation among the kinetic parameters N_{max} and N_o , irrespective of the composition of the organic amendment. It was also shown that though the correlation of N_{max} with the N uptake by maize was somewhat weak, the NaOH hydrolysis was significant. These findings support the notion that the rapid chemical hydrolysis method has wide validity and applicability. This has important management implication, in that even before crop cultivation, a reliable initial assessment of N supply capacity of the soil can be estimated, to guide other fertilizer application decisions. To date, no soil tests are conducted by farmers to determine fertilizer application. The farmers who do apply fertilizer simply follow blanket recommended rates (Aflakpul et al., 1997). In effect, fertilizer may be applied to soils which already have high ON that can mineralize to resource the plants.

A major issue which could not be determined within the scope of this study relates to the dynamics of the N released. As the times scales greatly differ between the standard biological (26 weeks) and chemical methods (40 minutes), it may not be possible to relate the k_m and k_h in any meaningful manner. Indeed, given that the k_h will depend on amendment composition, soil temperature, soil moisture, among others, no conclusions can be drawn at this stage of the research. However, it is essential to also estimate not only the N supply capacity but also the release pattern, given that synchrony of N release and uptake by the plant is necessary to ensure optimum nutrient use. The data obtained by the Stanford and Smith procedure (Table 4) gave half-lives of between 3 to 7 weeks. For cereals, such a slow N release rates may be problematic, as early growth stage N demands by cereals may be high. Further research effort is required in this regard.



CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

6.1 Summary and Conclusion

1. This study evaluated the alkaline hydrolyzable ON as an index of the potential mineralizable organic nitrogen pool size in soils amended with organic resources of varying chemical composition. Furthermore, the suitability of the chemical hydrolysis method as an index of N supplying capacity of such amended soils was also investigated. Three different soils with different previous management were used in the study. Also, a wide range of organic resources were used as soil amendments. In general, it could be concluded that the alkaline hydrolysis method provided a reliable and time-effective procedure for assessing the N_0 as well as N supplying capacity, irrespective of organic resource quality. The alkaline hydrolysis with 2 M NaOH could be used in routine laboratory analysis as a swift method for determining N mineralization when soils are amended with BMCs.
2. The chemical method has shown promise for management decision making with regard to fertilizer N application.

6.2 Recommendations

From the results obtained in this study, the following recommendations were made:

1. The effect of composted biochar on soils requires further study. In this study, compost was limited to only rice husk biochar. Therefore, additional studies that

would evaluate the influence of various biochar types on N mineralization would be highly recommended.

2. The results should be applicable to other regions; however, combinations of indices may be slightly dissimilar due to types of clays that may be present in the soil and organic matter present in soils from other regions. Therefore, it is recommended that N mineralization using the alkaline hydrolysis method should be studied in soils other than those located on the Legon catena.
3. Furthermore, not only the potential mineralizable N but also the N release dynamics and their sensitivity to temperature and soil moisture requires further research attention.
4. Field experiments should be conducted in the future to ascertain the applicability of the procedure under field conditions.



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