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Research Article

Comparison of two kinetics models for estimating N mineralization affected by different quality of organic matter in Typic Hapludults

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Abstract: N availability in the soil is determined by the rate of mineralization. N mineralization can be estimated using several models. Aim of research is to compare of two kinetics models for estimating N mineralization affected by different inputs of organic matter and soil fertility in Typic Hapludults. Research used completely randomized design with two factors. The first factor was land use: (1). Soil from land cultivated by cassava crops for less than 10 years, and (2). Soil from land cultivated by cassava crops for more than 30 years. The second factor was type of organic matter: (1). Groundnut biomass, (2). Maize biomass, (3). Groundnut-maize biomass, with ratio of 1:1, (4). Groundnut – maize biomass, with ratio of 2:1, (5). Groundnut – maize biomass, with ratio of 1:2, and (6). Without organic matter. The result shows that based on the value of R², first-order kinetics equation is more suitable to decribe N mineralization than double-pool kinetics equation because R-square value higher than double-pool kinetics and is positively correlated with N mineralization parameters (N0, k and N0.k).

Keywords: kinetic equations, nitrogen mineralization, organic matter quality

Introduction

Ultisol has low fertility due to intensive leaching (Van Noordwijk et al., 1996). Ultisol has acid soil reaction, low of cation exchange capacity (CEC) and organic matter (Shaw et al, 2010). The addition of organic matter into soil through harvest remaining, compost, and cover crops prunings can improve total reserve of soil organic matter and soil fertility.

Agricultural practices will reduce total N in soil. Crops need N in large amount compared to other nutrients. However, N availability is low due to its mobility in soil is very high. N availability in soil is determined by the rate of mineralization where it is affected by various factors such as soil pH, moisture, temperature and quality of organic matter (Handayanto et al., 1997; Griffin and Honeycutt, 2000; Samuel et al., 2002; Cookson et al., 2002; Kyveryga et al., 2004; Fritschi et al. 2005; Agehara and Warncke, 2005).

There are several approaches to evaluate the kinetic of N mineralization as an indicator of N availability in soil. Two models widely known for

estimating N mineralization are first-order kinetics equation and double exponential model involving two parts describing fast and slow organic pools (Heumann and Bottcher, 2004; Cartes et al., 2009).

Recently. logarithmic, parabolic and hyperbolic models are also developed. However, the exponential model is more often used. Mineralization of organic matter process involves microorganism. Microorganism activity is determined by the dynamic of enzyme which is often described as exponential. Thus the mineralization process then described using exponential model (Li et al., 2003).

Several kinetic models are often used to estimate the kinetic of N mineralization, then a model is selected based on the highest correlation coefficient and the lowest standard error (Shariatmadari et al., 2006). Aim of research was to compare of two kinetics models for estimating N mineralization affected by different inputs of organic matter and soil fertility in Typic Hapludults.

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Materials and Methods

Soil preparation and experimental treatment

Sample of soil was taken from a depth of 0-20 cm (topsoil), belong to Typic Hapludults order (ICALRD, 2008). The result of soil analysis is presented in Table 1. Research used completely randomized design with two factors. The first factor was land use: (1). Soil from land cultivated

by cassava crops for less than 10 years, and (2). Soil from land cultivated by cassava crops for more than 30 years. The second factor was type of organic matter: (1). Groundnut biomass, (2). Maize biomass, (3). Groundnut-maize biomass, with a ratio of 1:1, (4). Groundnut -maize biomass, with a ratio of 2:1, (5). Groundnut -maize biomass, with a ratio of 1:2, and (6). Without organic matter.

Table 1. Chemical properties of soil samples

Soil analysis	Soil from land cultivated by cassava crops for less than 10	Soil from land cultivated by cassava crops for more than 30		
	years	years		
pH (H ₂ O)	5.1	4.6		
N-total (%)	0.073	0.037		
C –organic (%)	2.06	0.70		
P-Bray 1 (ppm P_2O_5)	15.9	6.8		
CEC (cmol (+)/kg)	6.54	4.12		
K (cmol (+)/kg)	0.14	0.05		
Ca (cmol (+)/kg)	1.68	0.50		
Mg (cmol (+)/kg)	0.33	0.15		
Al exchange (cmol (+)/kg)	1.40	2.50		
Al saturation (%)	33	54		

Dosage of all selected biomasses applied were equivalent to 5 t/ha. Samples of soil sieved through a 2 mm sieve. 10 g of soil was weighed and kept into a plastic bottle then each treatment of organic matter was given. The moisture content of soil samples were maintained same as in field capacity.

These bottles were stored in incubators with various temperatures of 20°C, 25°C and 30°C. After 0, 2, 4, 8, 6, 10 and 12 weeks, content of N (NH₄⁺ and NO₃⁻) was observed using 1 M KCl extract with Kjeldahl method . The relationship between kinetics parameters of N mineralization and nutrient uptake were obtained by treated cassava in greenhouse same as incubators. Crops were cultivated in pots contained 15 kg of soil in field capacity. Crops were harvested at the age of four months and analyzed for the N uptake and soil analysis involving microbial biomass C and N, water-soluble C and N, Particulate Organic Carbon (POC) and Particulate Organic Nitrogen (PON) (Soon et al., 2007; Okore et al., 2007).

Observation of N mineralization kinetic

Kinetics was observed by two models, i.e. irstorder kinetics equation and double-pool kinetics equation. First-order kinetics equation was estimated by determining N mineralization potential (N0. in mg/kg), mineralization rate constant (k in day⁻¹), the apparent energy activation (Ea in J mol⁻¹), using a simple reaction-type model developed by Sugihara et al. (1987):

$$N = N0 [1 - \exp(-kt)]$$
 (1)

N is the amount of inorganic N (mg N kg-1) on day t, N0 is the N mineralization potential (mg/kg), k is mineralization rate constant (day⁻¹).

Double-pool kinetics equation was estimated by Ando et al. (1992) and Heumann and Bottcher (2004):

$$N = Na(1 - Exp - kat) + Nr(1 - Exp - krt)$$
 (2)

N is the amount of inorganic N (mg N/kg) on day t, Na is fast pool mineralization (mg/kg), ka is fast pool mineralization rate constant (day⁻¹), Nr is slow pool mineralization (mg/kg), kr is slow pool mineralization rate constant (day⁻¹).

Statistical analysis

First-order kinetics and double-pool kinetics equations were fitted with the curve fit procedure using SigmaPlot 12 program (SYSTAT software inc, 2011).

Results and Discussion

First-order and double-pool kinetics equations to estimate N mineralization

N mineralization estimation using first-order kinetics equation shows that organic matter from groundnut and maize biomasses affected mineralization rate constant (k). The k value of soil from land cultivated by cassava crops for less than 10 years has same pattern as soil from land cultivated by cassava crops for more than 30 years. Organic matter from mix of groundnut: maize (2: 1) has the highest k value. It is followed by groundnut biomass, groundnut: maize (1: 1), groundnut: maize (1: 2), maize and without organic matter (Table 2).

These results indicates that the mix of organic matter from groundnut biomass with low C:N ratio and maize biomass with high C:N ratio can increase mineralization rate compared to only maize biomass. It is due to C:N ratio decrease. Sholihah et al. (2012) reported that mineralization rate has correlation to C:N ratio (0.582*). Organic matter with low C:N ratio has higher mineralization rate compared to organic matter with high C:N ratio (Abera et al., 2012). A similar pattern is found for N potential observation.

Mineralization rate constant (k) has positive correlation with temperature. The k value increases around 32% by temperature rise from 20°C to 30°C for the less than 10 years cassava crops cultivation and about 27% for the more than 30 years cassava crops cultivation. Guntinas et al. (2012) reported that k value is strongly influenced by temperature and sharply increase for temperature between 25°C and 35°C. It is due to the increase of organic matter decomposition rate (Nordmeyer and Richter, 1985) resulted by changes in biochemical composition of organic matter and transport processes e.g. diffusion process as well as increasing the number of microorganisms (MacDonald et al., 1995). The highest k value for the mix organic matter of groundnut: maize (2:1) from the less than 10 years cassava crops cultivation is 0.098 and from the more than 30 years cassava crops cultivation is 0.0083. The low k value can be assumed come from the low activity of soil microorganisms (Nira and Nishimune, 1993) and it shows poor N mineralization (Nishio et al., 1994).

N mineralization measured by double-pool kinetics equation estimates mineralization rate of fast and slow pools. This study indicates that mineralization rate constant (ka and kr) and N mineralization (Na and Nr) are affected by temperature and organic matter. Increasing of temperature will be followed by the increase of k

and N value. The ka value of the less than 10 years cassava crops cultivation is 0.028 per day at temperature of 20°C and 0.031 per day at temperature of 30°C, while kr value respectively are 0.026 and 0.029 per day. The ka value of the more than 30 years cassava crops cultivation is 0.023 per day at temperature of 20°C, 0.025 and 0.029 per day at temperature of 25°C and 30°C. while kr value respectively are 0.021, 0.023 and 0.026 per day at temperature of 20°C, 25°C and 30°C (Table 2). Temperature is one of factors affecting N mineralization rate (Sierra, 2002). Study of Stanford and Smith (1972) showed that range of k values is 0.035 up to 0.095 per week, with the average of 0.054 per week. In addition, Sierra (2002) finds that the range of k value in tropical soil is 0.007 up to 0.014 per day.

In this study, N mineralization is also determined by type of organic matter. N mineralization of groundnut biomass is greater than maize biomass. The mix of organic matter from groundnut and maize biomass increase N mineralization compared to only maize biomass. Mineralization of the fast pool (Na) was higher than slow pool (Nr). The range of Na value of the less than 10 years cassava crops cultivation is 943 - 1253 mg/kg, while the range of Nr value is 560 -1016 mg/k. At temperature of 30°C, application of groundnut: maize biomass (1:1) has the highest N mineralization (3.570 mg/kg), 284% higher than no biomass application. The range of Na value of the more than g 30 years cassava crops cultivation-soil sample is 579-1011 mg/kg, while the range of Nr value is 549-792 mg/kg. Application of groundnut biomass has the highest N mineralization (2318 mg.kg⁻¹), 147% higher than no biomass application. Plant biomass affects N mineralization. Groundnut biomass or the mix of groundnut and maize biomasses increase N mineralization. Groundnut is a legume crop having a low ratio of C: N that is easy to be mineralized.

Based on double-pool kinetics equation, N mineralization of fast pool is higher than the slow pool, same as mineralization rate constant (k) of fast pool that was greater than slow pool. This indicates that mineralization of decomposted-organic matter can happen quickly compared to some resistant organic which can be mineralized linearly with time. The results are consistent with study of Li et al. (2003) which the value of Na and ka is greater than the value of Nr and kr. Result of this study shows that the average of R-square value in first-order kinetics equation is higher than double-pool kinetics equation. It implies N mineralization estimation using firstorder kinetics equation is better than double-pool kinetics equation (Table 2).

Table 2. Value of k and potential N mineralization on first-order kinetics equation and double pool kinetics equation in Typic Hapludult, Lampung

Treatments	First-order kinetics			Double-pool kinetics equation					
	equation								
	k	N0	\mathbb{R}^2	Na	ka	Nr	kr	\mathbb{R}^2	
The less than 10 year	ars cassava c	rops cultiva	tion-soil sar	mple					
Groundnut (G)	0.0090	743.0	0.996	1719	0.027	1078	0.023	0.980	
Maize (M)	0.0074	989.8	0.989	1222	0.030	959	0.028	0.955	
G: M(1:1)	0.0090	1000.9	0.995	1969	0.027	1601	0.025	0.982	
G: M(2:1)	0.0098	1150.5	0.994	1569	0.034	1301	0.032	0.956	
G: M(1:2)	0.0078	1056.2	0.989	519	0.026	737	0.025	0.897	
Without OM	0.0063	641.1	0.966	519	0.027	417	0.025	0.964	
Means	0.0082	930.3	0.988	1253	0.029	1016	0.026	0.957	
The more than 30 y	The more than 30 years cassava crops cultivation-soil sample								
Groundnut (G)	0.0080	587.5	0.996	1374	0.030	944	0.027	0.980	
Maize (M)	0.0067	825.9	0.990	766	0.029	625	0.027	0.977	
G: M(1:1)	0.0076	650.7	0.997	1192	0.031	796	0.027	0.982	
G: M(2:1)	0.0083	1057.8	0.998	1251	0.033	1037	0.031	0.987	
G: M(1:2)	0.0072	994.1	0.982	996	0.035	898	0.033	0.939	
Without OM	0.0058	544.7	0.981	485	0.027	451	0.027	0.925	
Means	0.0073	776.8	0.991	1011	0.031	792	0.029	0.965	

Relationship between kinetics parameters of N mineralization with N uptake

The parameters of N mineralization kinetics are positively correlated with plant dry weight and N uptake (Table 3). It implies that N mineralization kinetics can be used to estimate N uptake by plants. Organic matter addition into soil will increase microorganisms activity in N and C mineralization processes. The increase of N0, k and N0.k will increase N mineralization kinetics. Moreover, it can increase the availability of N in the soil resulting N uptake by plants increase

(Geisseler et al., 2009). De-Zhi et al. (2006) reported that N mineralization has positive correlation with N uptake in paddy in which without N source-fertilizer, approximately 98% of N absorbed by paddy is taken from N mineralization. In double-pool kinetics equation, N mineralization kinetics parameter.e.g, fast (Na) and slow (Nr) pools mineralization has positive correlation with plant dry weight and N uptake (Table 3). In this study, fast and slow pools N mineralization is contributed to cassava plant growth.

Table 3. Correlation between N kinetics parameters in firstorder and double-pool kinetics equations with plant dry weight and N uptake

Observations	Fir	First-order kinetics equation			Double-pool kinetics equation			
	N0	k	N0.k	Na	ka	Nr	kr	
The less than 10 year	rs cassava cr	ops cultivation	on-soil samp	le				
Plant dry weight	0,510*	0,534*	0,521*	0,785**	0,579*	0,756**	0,501	
N uptake	0,549*	0,516*	0,516*	0,693**	0,454	0,656**	0,537*	
The more than 30 ye	ars cassava c	rops cultivat	tion-soil sam	ple				
Plant dry weight	0,560*	0,674**	0,543*	0,648**	0,171	0,564*	0,675**	
N uptake	0,552*	0,832**	0,616**	0,646**	0,205	0,457	0,796**	

Based on the result of correlation between kinetics parameters of N mineralization with plant dry weight and N uptake, first-order kinetics equation has better correlation than double-pool kinetics equation. The first –order kinetics equation has

the value of N0, k and N0.k which is positively correlated with plant dry weight and N uptake, while the double pool kinetics equation has the value of Na, Nr and Kr which is correlated with plant dry weight and N uptake (Table 3).

Comparison between first order and double-pool kinetics equations

R-square value is generally used for estimating equation. R-square value closer to 1.00 indicates good equation. Table 2 shows that the average value of R square at various temperatures in the first-order kinetics equation is higher than the double-pool kinetics equation.

First order kinetics equation for explaining the dynamics of soil N mineralization was first introduced by Stanford and Smith (1972), which was developed through laboratory procedures with experimental incubation for 30 weeks under aerobic condition with controlled humidity and temperature. In first-order kinetics equation, N mineralization potential is defined as an easily-mineralized pool N in soil (Gill et al., 2011). In recent years, incubation procedure to estimate N mineralization in a controlled laboratory developed by Stanford and Smith (1972) has been followed by many researchers (Li et al., 2003; Cordovil et al., 2007; Dessureault-Rompre et al., 2010; Guntinas et al., 2012).

In 1980, another equation introduced by Molina et al. (1980) and Richter et al. (1980) is a model with two components or double exponential equation. This equation is developed based on two components of organic N fraction, namely active and resistant fractions. Active fraction is rapidly undergoing a process of mineralization (fast pool), while the resistant fraction is relatively difficult in mineralization (slow pool). This equation assumes that N mineralization process always involves microbial and enzyme activities which is growing exponentially so that the estimation of N mineralization should be based on the exponential equation (Li et al., 2003).

Research of Ando et al. (1992) suggested that first order equation can be used to estimate N mineralization in soil with anaerobic (wet condition), otherwise in aerobic condition, double exponential equation is more suitable to estimate N mineralization. Dou et al. (1996) suggested that N mineralization depends on incubation time. For 30 weeks-incubation, double exponential equation is a good model to explain N mineralization, while for 15 weeks-incubation either first-order kinetics or double exponential equation can be used to estimate N mineralization.

Benbi and Richter (2002) reported that for incubation during 82 days, double exponential equation could not be used to estimate N mineralization, because organic N pool consists of various components which can be characterized by its half-life. If the incubation time is too short compared to the half-life of organic N fraction, N

mineralization may look as linear. Related to incubation time, Gill et al. (2011) suggested that double-pool kinetics equation is better to estimate N mineralization if the incubation period is between one to two years, and even for long-term experiment which need more than two years-incubation time. Benbi and Richter (2002) suggested that for much longer incubation time until mineralization rate is approaching a constant value.

Quality of organic matter also affects equation model. Organic matter with wide C:N ratio is more suitable using double-pool kinetics equation for describing N mineralization. In organic matter with wide C:N there are two organic N pools, i.e. fast pool consisting organic matter with low C: N ratio and slow pool consisting high C: N ratio (Benbi and Richter, 2002). Azeez and Van Averbeke (2010) found that N release rapidly on days 0-30, constant on days 45-55 then decrease on days 70-90 when analyzing N mineralization from three manures respectively chicken (C:N ratio = 9.6), cow (C:N ratio = 10.3) and goat (C:N ratio = 11.3).

Some researchers have suggested that soil samples preparation also affects N mineralization. In undisturbed soil, first-order kinetics equation is suitable to describe N mineralization, while double pool kinetics equation is suitable to describe disturbed soil. The high release of N in disturbed soil due to micro aggregate destruction during soil samples handling (Benbi and Richter, 2002).

Based on explanation above, there are several factors that cause N mineralization can be estimated with an equation, namely: (1) incubation time, (2) type of organic matter or organic matter quality, (3) soil condition (dry, wet, disturbed and not disturbed). In this study, the incubation time was only 12 weeks and categorized as short-term. This caused the first-order kinetics equation to have R square value higher than double-pool kinetics equation.

Conclusion

In this study, N mineralization is depend on soil fertility, temperature and organic matter quality. N mineralization is higher at fertile soil, high temperature (30°C) and low of C:N ratio. First-order kinetics equation is more suitable to describe N mineralization than double-pool kinetics equation. The first-order kinetics equation has higher R-square value (correlation coefficient) than double-pool kinetics equation and positively correlated with N mineralization parameters (N0, k and N0.k). Several factors that

cause N mineralization can be estimated with an equation, namely: (1) incubation time, (2) type of organic matter or organic matter quality, and (3) soil condition (dry, wet, disturbed and not disturbed).

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