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Nutrients mineralization from sludge amended acid soil in Thailand

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ABSTRACT An appropriate sludge application depends on the rate of the mineralization process which will release nutrients to the cropland. This study was aimed at investigating the nitrogen and phosphorus mineralization from two sludges, septage and sewage mixed into an agricultural acid soil. The research design was multiple independent variables with two types of sludge, three sludge application rates, two levels of lime addition, and four incubation times under aerobic condition. A non-linear least square regression was used for prediction of mineralization parameters. Within six weeks, only 26% and 17% of nitrogen were mineralized in the soil applied with septage sludge and sewage sludge, respectively. The application of septage sludge gave higher potentially mineralizable nitrogen (N_0) 247 mg N/kg with mineralization rate constant (*k*) 0.046 week^{-1} but slightly lower phosphorus mineralization rate (48%) than that of the sewage sludge (51%). Nutrients mineralization increased with an increasing sludge application rate and incubation time. Other factor influencing nitrogen mineralization was lime addition, while phosphorus mineralization depended on sludge type. After six weeks of incubation, the soil had reached neutral pH and added 3-4% organic matter. It contained higher total heavy metals but still under the allowable metals concentrations, and phytotoxic threshold for plant growth.

(Nitrogen, phosphorus, mineralization, sludge, acid soil)

INTRODUCTION

Land spreading of organic waste such as sludge on agricultural lands is now receiving the extensively interest. This was due to the high cost of sludge disposal and lack of area for landfill. Moreover, the sludge contain a substantial amount of nutrients such as N, P, trace elements and organic matter, which are essential major and minor nutrients for plant growth. The large amounts of organic matter in sludge can act as a soil conditioner to improve the soil physical properties that essential for agricultural soils in Thailand, which has organic materials content normally very low. However, one of the most important determinants of application rate is the nutrient supplying capacity of the materials applied. The information about rate of nutrients especially nitrogen mineralization is necessary to predict nitrogen ability during a cropping season.

Previous investigators have reported the mineralization of nitrogen in sludge. Application of sewage sludge to a sandy soil would have beneficial effects on the microbial activity and nutrient mineralization. Inorganic nitrogen and phosphorus contents in the soil increased with the addition of sewage sludge [1]. Laboratory incubation experiments designed to estimate nutrient mineralization rate in the field have been partially successful in predicting nitrogen availability to crops from sludge amended soil. Stanford and Smith [2] incubated soil under optimal conditions to determine the nitrogen mineralization potential *(N_0)* and rate constant *(k)* of soils. The first-order rate constant *(k)* and potentially mineralizable nitrogen *(N_0)* was estimated by an iterative statistical method from a first order rate equation. Others have used this technique and found similar results [3, 4]. Smith et al [5] improved this method and found that a nonlinear least square equation provided more accurate estimation of *k* and N_0. This is proved by a study of Magdoff and Amadon [6] who found that there was 54% of organic nitrogen loss in 17 weeks from aerobically digested sludge under laboratory conditions and 55% loss under field conditions.

The objectives of this study were to investigate mineralization of nitrogen and phosphorus from an application of sludge to agricultural soil and also determine factors influencing nutrients mineralization.

MATERIALS AND METHOD

Sample Collection and Characterization

The plough layer (0-20 cm depth) of Rangsit soil and dewatered septage and sewage sludge from Nong Khame septage treatment plants and Yannawa municipal wastewater treatment plants, respectively were sampled and studied. They were air-dried at ambient temperature 25-30°C, crushed by hand and sieved through a 2 mm. stainless steel screen. The chemical properties of sample were determined using the following technique;

Soil pH values were measured by electrometric method in a 1:2 soil: $CaCl_2$ mixture. Organic matter was analyzed by the Walkley-Black method. Total organic nitrogen was determined by semi-micro Kjeldahl method. Inorganic nitrogen was extracted by KCl and measured by colorimetric method. Total and available forms of phosphorus were analyzed by digestion with conc. H_2SO_4 and extraction with Bray II solution, respectively. P was then measured colorimetrically. Total and available heavy metals were digested with 7 M nitric acid and extracted with DTPA pH 7.3 respectively, then measured by atomic absorption spectrophotometer (AAs).

Incubation Study

The soil was thoroughly applied with sludge at a rate of 10, 20 and 30 ton/ha, respectively. The mixture was divided to two groups: treated with lime at rate of 3.12 g /400 g soil and without lime addition. They were incubated in the experimental containers for 6 weeks in aerobic condition at 30°C temperature, maintained 60% field moisture capacity and provided 24 hrs. artificial light sources. During 0, 2, 4 and 6 week of incubation times, the samples of mixture had been analyzed for pH, total nitrogen, ammonium nitrogen, nitrate nitrogen, total phosphorus, available phosphorus and available heavy metals.

Statistical Analysis

A descriptive statistic, mean and percentage, were used for explanation of soil and sludge characteristics. The inorganic N data measured at each of six incubation periods were statistically analyzed by using a nonlinear regression approach which described by Smith et al [5]. A computer program was used to solve the following equation. Stepwise multiple regressions was also used for find out the factors influencing sludge mineralization process.

$$N_m = N_o(1-e^{(-kt)})$$

Where;

N_m is amount of nitrogen mineralized at a specific time
N_o is the potentially mineralizable nitrogen
k is the rate of mineralization (first-order rate constant)
t is time of incubation

RESULTS AND DISCUSSIONS

The general characteristics and metals content of sludges and soil are listed in Table 1. The studied sludges had suitable pH range and enriched with organic matter and plant nutrients. The soil, on the other hand, had poor characteristics for planting. However, these sludges contained higher amount of heavy metals than the soil but there were not exceeded the allowable ranges for applying on agricultural land [7].

Sludge amendment could increase the NH_4^+-N content of soil, especially for those amended with higher sludge application rate. The NH_4^+-N concentration of all treatments increased along the incubation time from week 0 to week 4, after that they were decreased till the end of experiment. Regarding to the nitrate nitrogen (NO_3), they were slowly increasing from week 0 to week 4 of incubation time. Since then, they were rapidly increasing until the end of operation. The initial increase in NH_4^+-N content was due to the mineralization of organic nitrogen in the sludge and the soil that release NH_4^+-N as one of the degradation product [1]. The decline in NH_4^+-N content at the later period might be due to decreasing nitrogen mineralization rate as the amount of initial organic nitrogen decreased. In addition, this

Table 1. Characteristics of sludges and acid soil.

Parameters	Septage sludge	Sewage sludge	Acid soil
PH	6.37	6.69	4.42
OM (%)	33.91	13.52	2.86
C/N ratio	4.61	3.30	57.02
TKN (%)	7.35	4.10	0.05
NH_4 (mg/kg)	124	151	46
NO_3 (mg/kg)	1,544	1,408	0
Total P (mg/kg)	10,930	10,737	33
Available P (mg/kg)	3,412	1,034	7
Total heavy metals (mg/kg)			
- Cd	4.36	3.84	1.10
- Cu	477	768	34
- Fe	14,394	38,341	20,882
- Mn	376	2,286	79
- Pb	72.46	1,938.47	51.61
- Zn	2,167	2,317	24
Available heavy metals (mg/kg)			
- Cd	0.08	0.37	0
- Cu	0.63	14.97	2.38
- Fe	203.18	44.97	101.44
- Mn	17.14	91.09	16.99
- Pb	0.38	1.18	1.73
- Zn	159.81	233.36	3.16

sudden drop of ammonium nitrogen was caused from the process of nitrogen volatilization and immobilization rather than nitrification.

Most of nitrogen mineralization rates at the end of operation were increased with increasing of sludge application rate. Thus highest was found at sludge application rate 30 ton/ha. A previous study [1] also showed that the higher sludge application rate could release higher amount of nitrogen. However, in some case, the nitrogen mineralization rate decreased as the sludge amendment rate increased, it was due to the increase in organic nitrogen content was exceeded the microbial degradation capacity [1]. In addition, the poor receiving soil structure in a high sludge application rate might inhibit biodegradation [8, 9].

The nitrogen mineralization rates in the treatments applied with septage sludge were ranged from 21.46% to 31.33%, with a mean value of 26.21%. They were within the ranged of a study of Qafoku et al [9]. Concerning lime addition, the mean value of nitrogen mineralization rates in the treatments without lime addition was 29.87% while those of treatment with lime addition was 22.54%. When applied with sewage sludge, the nitrogen mineralization rates were ranged from 10.36% to 22.41%, with a mean value only 17.36%. It was agreed with a study of Garau et al [10]. Without addition of lime could also receiving higher nitrogen mineralization rate (21.05%) than those treatments with lime addition (13.88%). This might due to the acidity or alkalinity of the soil has a considerable influence on nutrient availability.

Kinetics of Nitrogen Mineralization

The curvilinear relationship between cumulative amount of nitrogen mineralization and incubation time indicated that this nitrogen mineralization can be approximately explained by the first-order kinetics. Estimation for the amount of potentially mineralizable nitrogen (N_0) and the first-order rate constant (k) for the 6-week incubation time using a nonlinear regression technique that described by Smith et al [5] are shown in Table 2. The potentially mineralizable nitrogen (N_o) obtained form the treatment applied with septage sludge and sewage sludge was ranged from 215 to 292 mg/kg soil and 132 to 310 mg/kg soil, respectively. The application of septage sludge could give higher amount of N_o than the sewage sludge since it contained higher amount of nitrogen. However, they were within the range

Table 2. Kinetics of nitrogen mineralization in the treatments applied with studied sludges by incubation time.

Types of Sludge	Lime Addition	Application Rates (ton/ha)	N_0	k	R^2
Septage sludge	0 g	10	264.50	0.037	0.28
		20	275.20	0.040	0.29
		30	292.07	0.055	0.39
	3.12 g	10	206.00	0.040	0.35
		20	214.99	0.050	0.42
		30	231.04	0.053	0.40
Sewage sludge	0 g	10	214.23	0.044	0.46
		20	206.06	0.046	0.47
		30	309.55	0.061	0.50
	3.12 g	10	184.03	0.046	0.57
		20	132.26	0.052	0.76
		30	233.87	0.061	0.69

Notes:
N_0 = Potentially mineralizable N obtained from nonlinear least square regression (mg/kg soil).
k = The first-order rate constant obtained from nonlinear least square regression (week^{-1}).
R^2 = Correlation coefficients as a result of nonlinear least square regression, significant at the 0.05 level of confidence.

(71-394 mg/kg soil) that reported by Serna et al [11]. According to a higher mineralization rate of treatments without lime addition, the N_o was also higher than those treatments with lime addition. It was increased with the increasing of sludge application rate. This result was similar to the study of Garau et al [10] and Parker et al [12].

Although the N_o values were varied among different types of sludge and soil, it has very closely relationship with the cumulative amounts of nitrogen mineralization [11]. The higher N_o value increases nitrogen mineralization. Such these results, the N_o value of sludge treated soil is assumed to be a definable quantity that can be useful for estimating the nitrogen supplying capacities of soils under specific environmental conditions [13].

The k values obtained from the treatment applied with septage and sewage sludge were ranged from 0.037 to 0.055 week^{-1} and 0.044 to 0.061 week^{-1}, respectively. They were lower than those reported by Serna et al [11], which k values were 0.089 to 0.883 week^{-1}. The increasing of sludge application rate could increase k value. Thus the highest k value was found at application rate 30 ton/ha. A study of Lindermann et al [14] also reported that mean k values were increasing with sludge addition. The application of sewage sludge gave lower N_o but higher in k value than that of the septage sludge. A study of Deng et al [13] explained that the N_o and k values of soils tested had significantly negatively correlated (r = -0.72). However, Lindermann et al [14] pointed out that the k values were significantly difference between soils but the tendencies were not clearly observed for the difference types of sludge.

When N_o was multiplied by the first-order kinetic (k), the product obtained could be used as an index of nitrogen availability. It is the amount of nitrogen potentially mineralizable in one week under optimum soil temperature and moisture conditions [11]. From the studied results, the application of septage sludge 30 ton/ha without lime addition had the highest N_ok value (16.06) while application of 10 ton/ha with lime addition had the lowest N_ok value (8.24). These results supported the suitability of N_ok value as a reliable index of nitrogen availability because they had close relationship with the cumulative amounts of available nitrogen. Beside this, an application of sewage sludge also gave a similar direction result.

Phosphorus mineralization

The phosphorus mineralization had been observed after applied the sludges. The total phosphorus in the treatments applied with septage sludge and sewage sludge were ranged from 10.91 to 30.64 mg/kg and 8.62 to 64.58 mg/kg, respectively. The decreasing of total phosphorus was very fast in the first two weeks.

Thereafter, they were slowly decreased until week 4 which caused by the change of organic phosphorus forms to inorganic phosphorus forms. And then they were increased at week 6, which caused by the utilization of available from the dead cell [1]. A study of Thompson et al [15] suggested that there is a fraction of changing for organic phosphorus in soil that soon disappears under cultivation. As the remaining organic phosphorus is changed much more, it is slowly changed after this fraction is gone. Thus the lowest concentration of total phosphorus was found at week 4 of incubation period. On opposite for available phosphorus, it was increased the concentration during first four weeks and decreased afterward. The decreasing of available phosphorus was due to the utilization of available phosphorus by soil microbes [1, 15]. The process of mineralization and immobilization occurs with nitrogen and phosphorus in a similar way and will determine the amount of nutrients available for plant uptake [16].

Most of phosphorus mineralization rates increased with increasing of sludge application. Ahn [8] indicated that a high organic content and good rate of organic matter mineralization should ensure a rate of release of phosphate ions adequate for crop production. However, the addition of lime could increase the phosphorus mineralization rate up to 8-12%. The mineralization of organic phosphorus is enhanced by pH values that are conductive to general microbial actions [7]. The mean phosphorus mineralization rate (49.82) was higher than that of the nitrogen mineralization rate (21.78) since phosphorus mineralization is partly dependent on the availability of nitrogen and a small amount of nitrogen included in a phosphorus fertilizer makes it more effective [15]. The cumulative amount of phosphorus mineralization in soil applied with sewage sludge was higher than that of the septage sludge. However, there was not much different between phosphorus mineralization rates of the soil applied with septage sludge (48%) and sewage sludge (51%). The C/P ratio is one of the factor which be considered for the phosphorus mineralization rate. Microbiologists agreed that a net rate of phosphorus mineralization will occur when C/P ratio in plant residues less than 200:1 [7]. Such this reason, the C/P ratio of studied septage sludge was 31:1 while that of sewage sludge was 13:1. It can imply that the phosphorus mineralization could occur very well in both soil applied with septage sludge and sewage sludge.

Factors influencing nitrogen mineralization

There are many factors influencing organic nitrogen mineralization in soil applied with sludge such as soil type, soil pH, temperature, aeration, moisture, rate of sludge, type of sludge and rainfall [11,12]. From the analyzed results, factors influencing nitrogen mineralization were in this order; incubation time, addition of lime and sludge application rate. Increasing the incubation time could increase cumulative amount of nitrogen mineralization. The incubation time has affects on microbial activities and nutrients transformation. Regarding to addition of lime, without addition of lime could help increasing the nitrogen mineralization rates. It might due to the treatment without addition of lime had higher amount of total nitrogen than that of the treatment with lime addition. A study of Epstein et al [17] indicated that lime addition generally reduces the level of soluble nitrogen and total nitrogen. Although the treatments without lime addition gave higher nitrogen mineralization rates, however, it can not clearly explain since it was a short-term incubation time and there was not enough time for the lime to react in the soil. Generally, lime should be applied 3-6 months ahead of planting the crop especially on very acid soils [18]. Concerning sludge application rate, it could increase nitrogen mineralization rates, cumulative amounts of nitrogen mineralization, N_o values and N_ok values. The amounts of ammonium and nitrate nitrogen were highest in the soil applied with sludge 30 ton/ha. It was agreed with a study of Wong et al [1], who found that increasing sludge amendment rate caused an increasing of nitrogen mineralization. In addition, Serna et al [11] reported that increasing sludge application rate could increase cumulative amount of nitrogen mineralization, N_o values and N_ok values.

Factors influencing phosphorus mineralization

The factors influencing phosphorus mineralization are ranged in this order; sludge application rate, type of sludge (sewage sludge) and incubation time. In case of sludge application rate, the sludge application rate 30 ton/ha gave highest phosphorus mineralizartion rate and cumulative amount of phosphorus mineralizartion. Wong et al [1] found that the phosphorus mineralization increased as the sludge amendment increasing. Regarding to type of sludge, the sewage sludge gave higher cumulative amount of phosphorus mineralization than that of septage sludge. The lower pH of septage sludge (6.37) might inhibit the soil microbe activities than the more neutral pH (6.69) of sewage sludge. Concerning incubation time, the cumulative amount of phosphorus was increased with a short-term of incubation time (week 4) and it was decreased thereafter. It might due to the utilization of available phosphorus by the bacteria and the decrease in easily degradable organic phosphorus. Wong et al [1] also found the similar result. However, incubation time is one of factor influencing phosphorus mineralizartion since increasing incubation time could increase phosphorus mineralizartion rates as a whole.

Such these results, the factors influencing both nitrogen and phosphorus mineralization were incubation time and sludge application rate. The longer incubation time and higher sludge application rate could enhance greater nutrient mineralization. However, increasing of sludge application rate must be considered in order to increase the mineralization efficiency but an excessive sludge amendment could also give higher metals in sludge applied soil as well.

Change of sludge applied soil characteristics

The pH of most soil applied with sludges was nearly seven at the end of operation and within the appropriate range for plant growth. It is an important factor affecting microbial growth and the high pH could help decreasing of heavy metals availability in the soil [19, 20]. Organic matter (OM) was increased with increasing sludge application rate. The soil applied with septage sludge had higher OM than soil applied with sewage sludge since OM contents in the septage sludge were two times more than the sewage sludge. The amount of OM at the end of incubation time was higher than that of the first week of experiment. It might result from a changing of materials by soil microorganism for their growth.

The amounts of total heavy metals in the soil applied with sludges were increased than the soil. However, they were lower than an acceptable range for agricultural utilization as reported in many countries. Most sludge applied soil with lime addition had lower available heavy metals than those of without lime addition. When soil pH is raised up from sludge amendment, most heavy metals were partitioned into sparingly mobile pools [21]. The amount of available heavy metals was increased with increasing sludge application rate. At the end of operation, however, they were under the phytotoxic threshold concentrations of plant growth [18].

CONCLUSION

The sewage sludge and septage sludge had large amount of plant nutrients and appropriate pH range for plant growth. They could be used as soil conditioner since the Rangsit soil had poor characteristics for agricultural purpose.

Application of sludge caused significant increasing of plant nutrients in the soil. The amount of organic nitrogen and phosphorus forms were lowest at week 4 of incubation times. On opposite, at this period, the content of inorganic nitrogen and available phosphorus were the highest. At the end of experiment (6 weeks), nitrogen mineralization rates in the soil applied with septage sludge and sewage sludge were 26% (21% to 31%) and 17% (10% to 22%), respectively. Phosphorus mineralization rates in the soil applied with septage sludge and sewage sludge were 48% (29% to 63%) and 51% (42% to 65%), respectively.

There was a curvilinear relationship between cumulative amount of nitrogen mineralization and incubation time. It indicated that the nitrogen mineralization can be approximately explained by the first-order kinetics using a nonlinear regression technique that described [5]. The amount of nitrogen potentially mineralizable in one week under optimum soil temperature and moisture conditions ($N_o k$) was then estimated. The application of septage sludge gave a potentially mineralizable nitrogen (N_o) 247 mg N/kg soil with mineralization rate constant 0.046 week^{-1}. The sewage sludge gave a bit lower potentially mineralizable nitrogen (N_o) 213 mg N/kg soil with mineralization rate constant 0.052 week^{-1}. These obtained data could be use as an index of nitrogen availability for sludge application to acid soil.

The nitrogen and phosphorus mineralization rates increased with an increasing sludge application and incubation time. Application of 30 ton/ha of sludge to the soil caused a maximum mineralization rate. Other factor influencing nitrogen mineralization was lime addition, without lime addition gave a higher mineralization. Type of sludge also affect phosphorus mineralization, soil applied with sewage sludge had higher mineralization rate than that of the septage sludge.

After six weeks of incubation, the soil pH became neutral (pH 7) and the organic matter content was around 3-4%. It had significant increasing of both plant nutrients and heavy metals. The available and total heavy metals were under the allowable metals concentrations and phytotoxic threshold for plant growth. It is recommended for agricultural utilization of sludge that the amendment rate should be considered in order to increasing the mineralization ability while minimizing the toxic effects of the amendment at the same time.

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