Effect of Coated Urea with Humic-Calcium on Transformation of Nitrogen in Coastal Sandy Soil: A Soil Column Method

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ABSTRACT

Effect of Coated Urea with Humic-Calcium on Transformation of Nitrogen in Coastal Sandy Soil: A Soil Column Method (Sulakhudin, A Syukur, D Shiddieq and T Yuwono): In coastal sandy soil, mainly nitrogen losses due to leaching resulted to low fertilizer efficiency. Slow-release N fertilizers are proposed to minimize these losses, and humic-calcium coated urea has been examined. A soil column method was used to compare the effects of coated urea with humic-calcium on transformation and leaching loss of N in coastal sandy soil. The experiment aid to compare two kinds sources of humic substances (cow manure and peat) which mixed with calcium as coated urea on transformation, vertical distribution and leaching N in coastal sandy soil. The concentration of humic-calcium coated urea *i.e.*1%, 5% and 10% based on their weight. The results showed that urea coated with humic-calcium from cow manure (UCHM) and humic-calcium from peat (UCHP) increased the N total and available N in the soil and decreased leaching loss of N from the soil column. Compared to UCHP, UCHM in all concentration showed N-nitrate higher than N-ammonium on incubation length 2, 4 and 6 weeks. The N leached from a costal sandy soil with application coated urea with UCHM ranged from 21.18% to 23.72% of the total N added as fertilizer, for coated urea with UCHP they ranged between 21.44% and 23.25%, whereas for urea (control) reached 29.48%. Leaching losses of mineral N were lower when urea coated with UCHM compared to urea coated with UCHP or urea fertilizer. The study concluded that the UCHM is better than UCHP in decreasing N leached from coastal sandy soil.

Keywords: Coastal sandy soil, coated urea, humic-calcium, nitrogen

INTRODUCTION

Nitrogen is the most limiting nutrient for crop production in many regions of the world (Fageria 2009), especially in arid and semiarid regions (Sharifi *et al.* 1988). So it is very important to increase the growth of plants and their quality with improving nitrogen fertilizer. In addition, nitrogen fertilizers worldwide is estimated to be 9.09 × 107 Mg yr^{-1} (International Fertilizer Industry Association 2006). Urea (U) is the predominant source of inorganic N fertilizer in agriculture throughout the world, accounting for 50% of the total world fertilizer N consumption (Cobena *et al.* 2008). Urea, when applied to soil, is hydrolyzed by urease to form NH_4^+ and is subsequently converted to nitrate by the action of nitrifying bacteria (Kiran and Patra 2003), which can be leached or denitrified (Patra *et al.* 2009). About 16.2% to 30.4% of the N leached from the sandy loam soil originated from the urea-N fertilizer (Zhou *et al.* 2006).

The excessive loss of N due to NO^-_3 leaching causes not only large economic and resource losses but also very serious environmental pollution (Wu and Liu 2008). One method of reducing fertilizer nutrients losses involves the use of slow- or controlled-release fertilizers (Wu *et al.* 2008). The control of fertilizer release keeps the fertilizer concentration at effective levels in the soil solution and releases the fertilizer when the plant most needs it (Al-Zahrani 1999). These fertilizers can be physically prepared by coating granules of

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conventional fertilizers with various materials that reduce their dissolution rate (Tomaszewska *et al.* 2002). The release and dissolution rates of water-soluble fertilizers depend on the coating materials. The membrane materials developed can be divided into two main varieties, inorganic mineral and organic polymer (Zou *et al.* 2009).

Humic substances (Hs), as one of the organic macromolecule compounds, were made for membrane material. It can incorporate nitrogen into their structure either directly through chemical reactions or indirectly through microbial activities and subsequent decomposition of microbial biomass (Clinton *et al.* 1995). Humic acid made from low grade coal, such as lignite, has a long history of use as a fertilizer in combination with urea. It has been shown that lignite humic acid can increase crop yields and plant N use efficiency relative to urea-only treatments (Ahmed *et al.* 2006; Zheng 1991).

In general, negative charge in Hs is originated from dissociation of ion H from functional groups especially carboxyl and phenol. Approximately 85 to 90% negative charged are derived from those groups. The carboxyl and phenol from Hs, having similar negative charged, are not able to bond ion nitrate; therefore become easier subject to leaching. In order to bond the nitrate from urea with Hs, the process needs cation, *i.e.* calcium to bridge functional humic group and ion nitrate. Existence of Ca in between humic and nitrate will create *out sphere* complex.

The cation Ca is selected because it has two positively charged and the bonding energy weaker but has strong bond not to be leach by irrigation. One of Ca positively charged aims to bond NO_3^-, while the other positively charged will be bonded to oxygen of humic (Oviasogie and Okolo 2008). According to Huang and Schnitzer (1997), the bonding between Ca and Oxygen is 839 kcal mol^{-1} smaller than that of Al^{3+}, Fe^{3+} and Mg^{2+} respectively are 1,793; 919; dan 912 kcal mol^{-1}. The study in coastal sandy soil was performed to examine the effect of coated urea with several humic-calcium (hucalci) to transformation and reduction of leaching N.

MATERIALS AND METHODS

Study Site and Soil Preparation

Surface soil samples (0 – 40 cm) were sampled from the Bugel coastal area in Panjatan Subdistrict, Kulon Progo District, Yogyakarta Special Province. It is classified as a Typic Udicpsamment in the USDA system (USDA 2003). The collected samples were air-dried, crushed, and passed through a 2-mm sieve and preserved for analysis. The cow manure derived from veterinarian in Bugel, whilst peat from lake rawa pening in Ungaran. Selected physical and chemical properties of soil were determined using standard procedures. The soil texture was carried out using the International Pipette method. Particle density (Dp) was measured using Pycnometer. Bulk density (Db) was determined using Clod Saturation Method. Hydraulic conductivity was determined using Constant Head Permeameter Method. Distribution of soil pores was estimated using Pressure Plate Method and calculated based on pF value (pF 0, 2.0, 2.54, 4.0, and 7.0). Porosity was estimated mathematically using equation (=1-(Db/Dp)) (Sarkar and Haldar 2005).

The pH of soil determined in a 1:2.5 soil: distilled water suspension and KCl using a glass electrode. Soil organic carbon was determined using Walkley and Black method. Soil CEC was determined by leaching 1 *M* ammonium acetate buffer adjusted to pH 7.0 followed by steam distillation (Pansu and Jacques 2006). Soil available phosphorus was extracted with NaHCO3 (0.5 *M*) at pH 8.5 and determined colorimetrically after treating with ammonium molybdate and stannous chloride at a wavelength of 660 nm. Extraction of exchangeable K, and Ca was done by the double acid method (Tan 1996). After extraction, the cations were measured using atomic absorption spectrophotometry (AA-6200 SHIMADZU). The HS extraction was carried out by the methods of Rocha *et al.* (1998). Carboxylic-COOH, phenolic-OH and total acidity of HS were determined using the method described by Pansu and Jacques (2006).

The Production of Slow Released Urea

To obtain Hs, manure and peat was air dried and added with 20 ml KOH 0.5 N. Hucalci gained from Hs plus $CaCl_2$ 0.5 M is filtered used whatman 42. The oven dry hucalci is powdered and mixed with starch at the rate of 1% (low), 5% (moderate) and 10% (high) concentration to obtain 6 combination of hucalci used as coating material of urea. The coating material was spread to the urea particles until the surface was cover homogeneously. Then the coated urea was dried. The N content of each coated was analyzed and the result is in Table 1.

Table 1. The N content and rates of UCHM, UCHP and urea fertilizer.

No.	Type of fertilizer	N content of fertilizer (%)	Rate/column (g)	Total N/column (%)
1	UCHM 1 %	43.92	0.38	0.62
2	UCHM 5 %	45.42	0.37	0.62
3	UCHM 10 %	41.10	0.41	0.62
4	UCHP 1 %	43.17	0.39	0.62
5	UCHP 5 %	42.39	0.40	0.62
6	UCHP 10 %	43.32	0.39	0.62
7	Urea	44.54	0.38	0.62

Experimental Design

Completely randomized design (CRD) was performed to examine the effects of hucalci coated with urea (UCH) on soil dynamic and leaching N. The treatments consist of 6 kinds of UCH, plus non coated urea as control, with three replications. The study was conducted in a greenhouse at 25 ± 3°C using soil packed in a polyvinyl chloride (PVC) pipe (50 cm long by 6 cm *i.d.*). The pipe was split longitudinally into three pipes *i.e.* 0 – 10 cm, 10 – 30 cm and 30 – 50 cm. The three pipes were joined and taped to form a column. A nylon mesh was fixed at the bottom of each PVC tube. The soil was air-dried and passed through a 2-mm sieve. Then, each tube was packed with 2.8 kg sandy soil having a bulk density of 1.31 g cm^{-3}, and the PVC tubes were fixed in a pot to collect the drainage water during irrigation. Each UCH fertilizer with the rates follows Table 1, were applied on the 5 cm soil surface and incubated for 2, 4, and 6 week length. In every three days, the columns were given with aquadest on the level between the field capacity and saturated condition. Three kinds of UCH consists of urea (U), urea coated with hucalci from cow manure (UCHM) and urea coated with hucalci from peat (UCHP). At the end of each incubation periods soil was sampled to measure total N (0 – 50 cm); avaibility N (NH_4^+ and NO_3^- : 0 – 10 cm, 10 – 30 cm and 30 – 50 cm); N leached on drainage water. Analysis of variance (ANOVA) was used to test treatment effects whilst means of treatments were compared using Duncan's test.

RESULTS AND DISCUSSION

The Characteristic of Coastal Sandy Soil and Hs

Table 2 shows that the texture is sandy (97.31% sand), and the bulk density (1.89 g cm^{-3}) is considered high (Hazelton and Murphy 2007). Consequently porosity is high at 32.03% with drainage pore is also high (29.12%). The capability of the coastal sandy soil to retain water is low the percentage of water fill pores very small (0.66%). The water velocity of this soil is very fast appearing from the rate of soil hydraulic conductivity is very high (134.7 cm $hour^{-1}$). Therefore the available water capacity (AWC) is very low 2.10%.

The initial soil analysis showed that macro and micro nutrients are very low. The availability of nitrogen is dominated by nitrate (4.26 ppm) form. The ammonium was only 0.7 ppm. The level of cation exchange capacity (CEC) is very low (1.91 cmol (+) kg^{-1}). The soil reaction is considered neutral (soil pH 7.76). Although this soil is located in coastal area, it is not considered a sodic soil.

The high sand particles, porosity, drainage pores, and permeability with the low CEC of in this coastal sandy soil could support N leaching. Generally NO_3^- leached more rapidly from sandy than silt and clay soils. An average annual leaching rate of 63 kg NO_3^--N ha^{-1} was estimated for sandy soils as compared to 16 kg NO_3^--N ha^{-1} for heavier arable soils developed in loess (Neinder and Benbi 2008).

Table 3 shows that the Hs material extracted from cow manure (26.23%) are not significantly

Table 2. Some physical and chemical properties of the experimental soil at the beginning of the experiment.

Soil properties	Value	Level
Soil fractions (%)		
clay	0.90	-
silt	1.79	-
sand	97.31	-
Texture class	sand	
pH H_2O	6.67	Neutral*
pH KCl	5.69	Medium acid*
EC (mS)	0.20	
Total organic C (%)	0.08	Very low*
Organic matter (%)	0.13	Very low*
Total N (%)	0.02	Very low*
N-NO_3^- (ppm)	4.26	Very low*
N-NH_4^+ (ppm)	0.70	Very low*
C/N	8.00	low*
Available P (ppm)	9.67	Very low*
Exchangeable K (cmol (+) kg^{-1})	0.17	low*
Exchangeable Ca (cmol (+) kg^{-1})	0.88	Very low*
CEC (cmol (+) kg^{-1})	1.91	Very low*
Bulk density (D_b) (g cm^{-3})	1.89	-
Particle density (Dp) (g cm^{-3})	2.78	-
Porosity (%)	32.03	Very high*
Hydraulic conductivity (cm $hour^{-1}$)	134.7	Very quick*
Distribution of soil pores		
Total soil pores (%)	31.85	-
Useless soil pores (%)	2.07	-
Usefull soil pores (%)	29.78	-
Water hold pores (%)	0.66	-
Drainage pores (%)	29.12	-
Slow drainage pores (%)	1.71	-
Rapid drainage pores (%)	27.41	-

Source *: Hazelton and Murphy (2007).

different than that of peat (23.77%). In comparison with similar method Hs from cow manure and peat is higher than that from vermicompos and Cananeia island soil which contains 9.12% and 10.28% (Rocha *et al*. 1998). The result also showed that total acidity, functional carbolic and phenolic and the AWC of Hs from cow manure is not significantly different than those of peat.

Transformation of Urea in Soil after Fertilization

The Change in the distribution of NH_4^+-N and NO_3^--N in the soil columns after several periods of 2, 4, and 6 weeks of incubation is presented in Figure 1 and 2. For NH_4^+-N (Figure 1), the distribution of NH_4^+-N in various layers of the soil column under all type of fertilizer treatments at 2 weeks incubation was different with those at 4 and 6 weeks incubation periods. NH_4^+-N in the upper layer (0 – 10 cm) of the soil column at 2 weeks incubation was lower than that in the deeper layers (30 – 50 cm), indicating higher proportion of the downward movement of NH_4^+-N ions in the sandy soil. At 4 and 6 weeks incubation periods, the amount of NH_4^+-N in all layers soil column was low (Figure 1), suggesting the high leaching loss of NH_4^+-N from the sandy soil. Zhou *et al*. (2006) also found that about 16.2% of the total ammonium fertilizer applied to the soil column was leached from the sandy loam soil. It suggested that although soil colloids could adsorb NH_4^+ ions, high concentrations of NH_4^+ ion cation could overload the adsorption capacity of this soil. The adsorption capacity in sandy soil was very low (1.91 cmol (+) kg^{-1}, Table 2), due to the result that NH_4^+ ions could be easily leached into the deeper layers of the sandy soil.

Compared to the control (U) with application of non coated urea, there was a trend of increasing in NH_4^+-N in the soil column (Figure 1) on the 6 weeks incubation, especially treatment UCHM. Figure 1 shows also that to compare with other treatments the ammonium content is highest (3.15) on 2 weeks incubation period of 10% HCUM. This is probably because not all portion functional groups of Hs negatively charged bounded the calcium. The rest portion bounded the positively charged of anion. Those functional groups like phenolic-OH and carboxylic-COOH were able to capture and retain NH_4^+. This positively charged NH_4^+ is in turn adsorbed to the negatively charged sites of phenolic-OH and carboxylic-COOH compounds (Reeza *et al*. 2009). After 2 weeks incubation, NH_4^+-N in the soil was significantly reduced, and NO_3^--N still high (Figure 2), suggesting the occurrence of the nitrification.

Table 3. ANOVAs result of Hs extracted from cow manure and peat.

No.	Material	Total Acidity (cmol (+) kg^{-1})	-COOH (cmol (+) kg^{-1})	-OH (cmol (+) kg^{-1})	AWC (%)	Weight (gram)	Percentage (%)
1.	Cow manure	5.45 a	0.72 a	4.73 a	3.34 a	2.63 a	26.32 a
2.	Peat	3.45 a	0.67 a	2.78 a	2.53 a	2.38 a	23.77 a

Note: Values with similar letter are not significantly different ($\alpha \leq 0.05$).

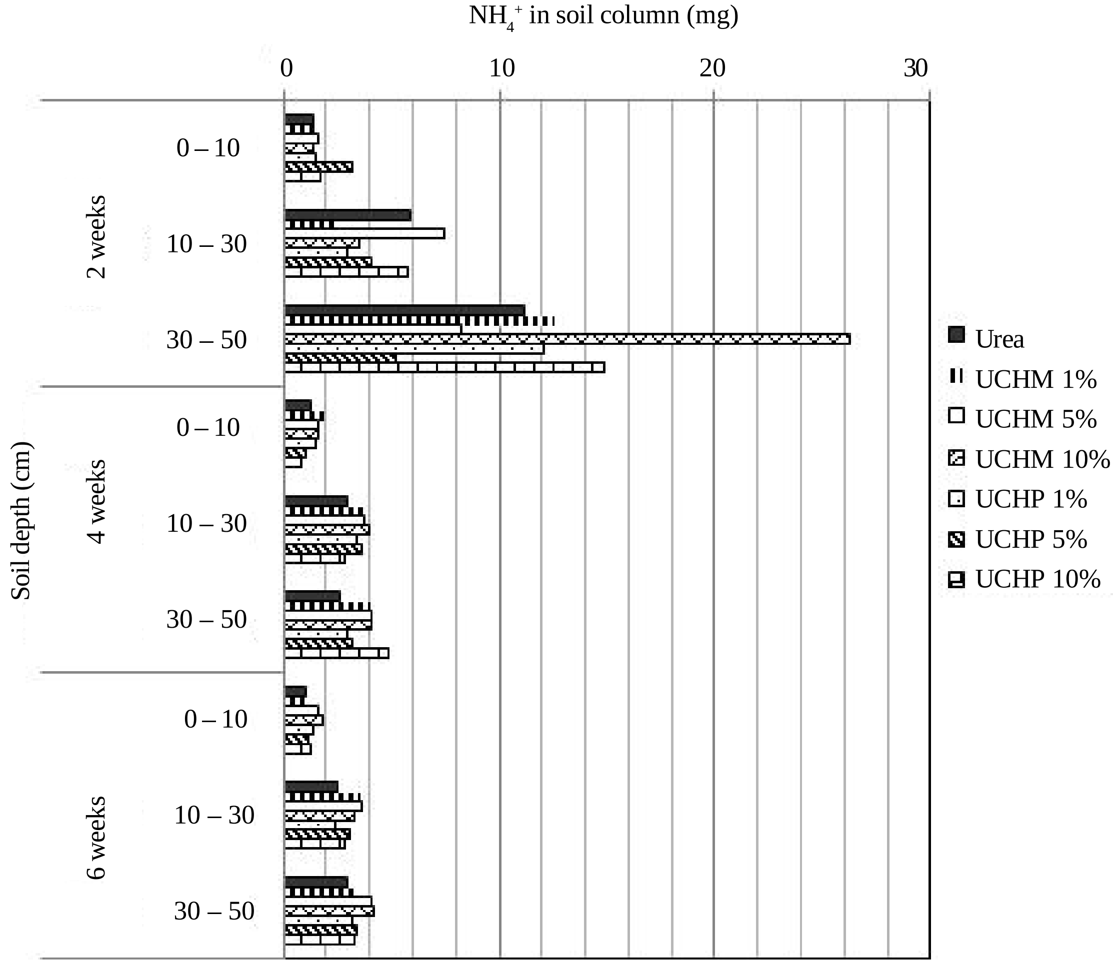

Figure 1. Distribution of NH_4^+-N in soil column at 2, 4 and 6 incubation periods.

The distribution of NO_3^--N in all layers of the soil column under type of fertilizer treatments was similar at all incubation periods, but amount NO_3^--N was higher than NH_4^+-N. It indicated the leaching loss of NO_3^--N from soil column was lower than NH_4^+-N. At 6 weeks incubation period, it is shown that treatment UCHM 10% has content of NO_3^--N in 0 – 10 cm and 10-30 cm layers higher than other treatment. This suggests that UCHM 10% was slower leach than other fertilizers.

The highest nitrate content form is the nitrate from UCHM on 5% concentration in 30 – 50 cm depth on 6 weeks incubation period. Vertical distribution (Figure 2) shows that nitrate content of urea coated with UCHM 10% is relatively higher than the other treatment. The nitrates content found on 0 – 10 cm depth, 10 – 30 cm depth and 30 – 50 cm depth respectively 6.55, 14.50 and 23.66 mg. This is a favorable condition for seasonal crop because their shallow root is able to reach and take N from soil.

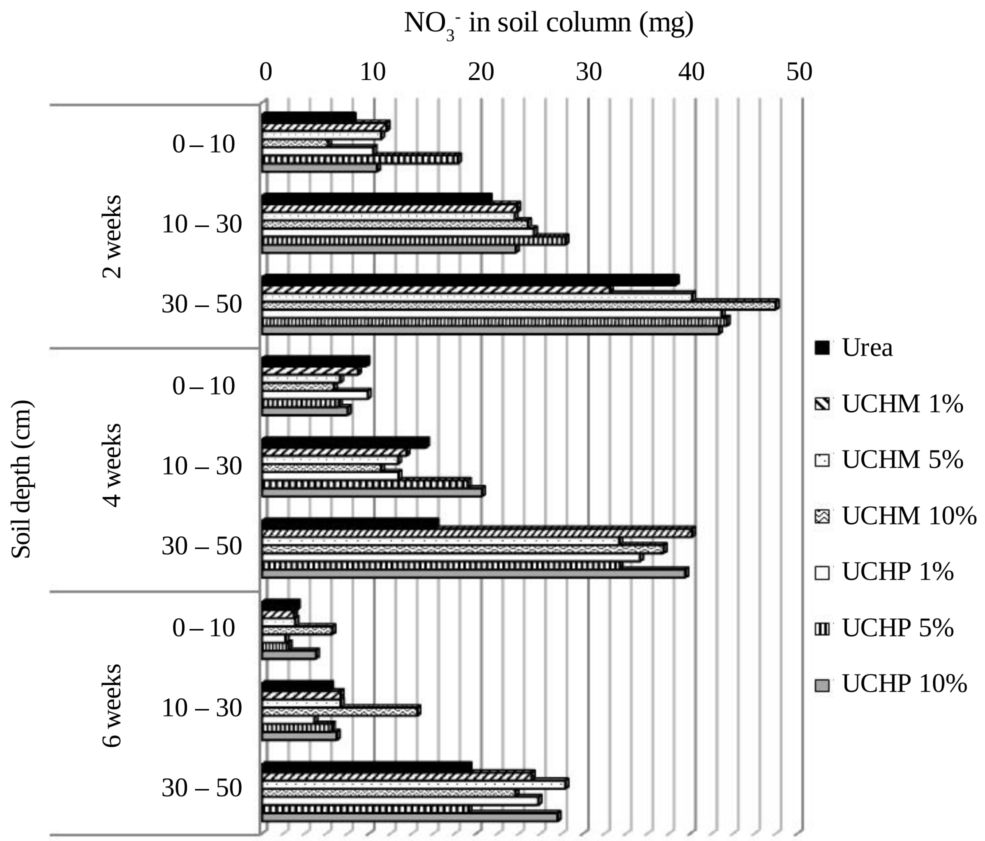

Figure 2. Distribution of NH_4^+-N in soil column at 2, 4 and 6 incubation periods.

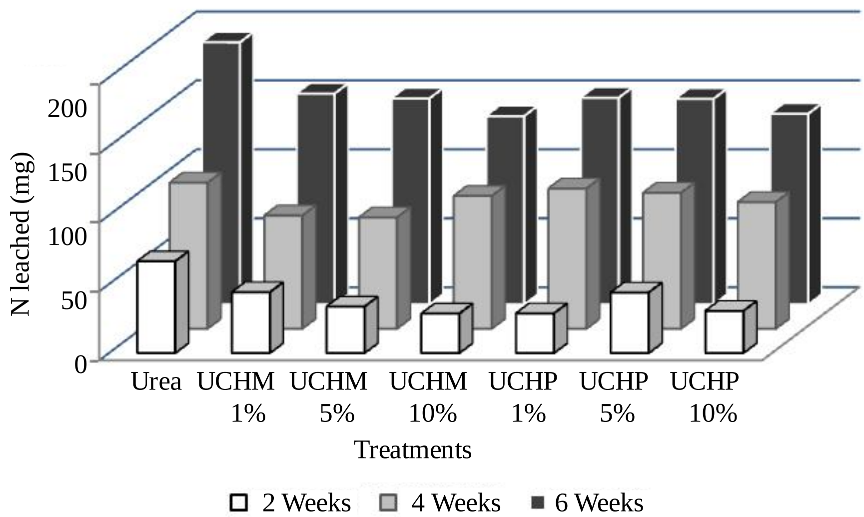

Figure 3. Effects of treatments on N leached from coastal sandy soil after 2, 4, and 6 weeks of incubation.

The alteration in the vertical distribution of NH_4^+-N and NO_3^--N in the soil column after fertilization reflects not only the movement of soil N, but also the transformation of N fertilizer. The sum of NH_4^+-N and NO_3^--N in soil column suggested the levels of mineral N in the soil. It seems that the mineral N in the soil decreased during the 6 weeks incubation period after applying urea and UCH. The decreasing in NH_4^+-

Table 3. Total N leaching over 2, 4 and 6 weeks of incubation and the reduction in N loss in comparison with the loss in urea (control).

Treatments	Nitrate leached (mg)			Reduction in total nitrogen leaching as compared to urea (%)		
	2 weeks	4 weeks	6 weeks	2 weeks	4 weeks	6 weeks
Urea	66.56 a	105.95 a	190.11 a	None	None	None
UCHM 1%	44.19 b	82.09 a	152.94 b	33.62	22.52	19.55
UCHM 5%	33.76 b	80.74 a	149.38 b	49.28	23.80	21.42
UCHM 10%	28.65 b	96.30 a	136.56 b	56.97	9.11	28.17
UCHP 1%	28.85 b	101.75 a	149.91 b	56.67	3.97	21.14
UCHP 5%	43.97 b	98.63 a	149.06 b	33.94	6.91	21.59
UCHP 10%	30.61 b	91.86 a	138.27 b	54.02	13.30	27.27

Note: Mean values with different letters are significantly different between treatments at $P \leq 0.05$ using DMRT test.

N did not equal to an increasing in the amount of NO_3^--N in the soil which indicating the probable loss of NH_4^+-N from the soil column. Rosliza *et al*. (2009) found that ammonia loss from N fertilizer could occur in soil pH was 6.2. Since the pH of the sandy soils used in this research was 6.7, N may have been lost from the soil due to volatilization.

Leaching Loss of Fertilizer Nitrogen

The effects of fertilizer type on N losses due to leaching during incubation in coastal sandy soil are shown in Figure 3. N leached from HCUM and HCUP was much lower compared to the urea (Figure l). Incubation periods also had a strong effect on N lost due to leaching.

The total amount of N lost at the end of the study is shown in Table 3. All the treatments with UCHM and UCHP in significantly reduced N loss compared to urea alone. Nonetheless, UCHM 100% was less pronounced in reducing N leaching compared to other treatments. As a result, the total N loss was effectively reduced to 28.17% compared to the total loss in urea (Table 3).

The effect of urea coated with hucalci from several humic material on N leached can be seen in Table 3. In Table 3 shows that on 2 and 6 weeks incubation period, N leached on urea coated with hucalci both from manure and peat are significant different with non coated urea. The study found that the smallest N leached (136.56 mg) on 6 weeks incubation period is in the column of urea coated with hucalci this result possible because humic – calcium complex of UCHM is higher that UCHP, consequently the nitrate hold is much higher. In this case, calcium acts as Cation Bridge because of the two positive charges; one charge hold in Hs and the other charge hold nitrate. According to Marinsky *et al*. (1999), calcium ion binding to fulvic acid is modeled assuming formation of a monodentate carboxlate complex. Essington (2004) also found that Ca complexation by Hs formed a monodentate aliphatic carboxylate weak outersphere metal.

CONCLUSIONS

Based on the results of our experiment, it can be concluded that N leached in coastal sandy soil can be reduced with the application of accurate fertilizers. The study found that the urea coated humic-calcium from cow manure (UCHM) is better than urea coated humic-calcium from peat in decreasing N leached from coastal sandy soil.

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