

*Full Length Research Paper*

# Ammonia loss reduction, exchangeable ammonium and available nitrate retention in soil treated with urea mixed with humic acid and acid sulphate soil

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Exchangeable ammonium ( $\text{NH}_4^+$ ) could be recovered in soil by the application of humic acid (HA) and acid sulphate soil. The ability of humic acids to retain  $\text{NH}_4^+$  has been demonstrated in our previous study. In that study, the effect of both acids on soil exchangeable  $\text{NH}_4^+$ , dry matter production and available nitrate ( $\text{NO}_3^-$ ) was investigated. This laboratory study compared the effect of enhancing urea mixtures with HA and acid sulphate soil on  $\text{NH}_3$  loss, and soil ammonium and nitrate contents, with loss from surface applied urea and to study the appropriate application ratio. HA, acid sulphate soil, and the mineral soil Nyalau Series (*Typic paleudults*) used in the incubation studies were characterized prior to the experiment. A closed-dynamic air flow system was used to evaluate the treatments effects with 3 replications in a completely randomized design (CRD). The data obtained were analyzed using Duncan's test with Statistical Analysis System (SAS) version 9.2. Application of urea amended with various amounts of HA and acid sulphate soil and urea with HA alone did not minimize ammonia loss especially at higher amounts ( $T_5$ ,  $T_9$  and  $T_{10}$ ). The application of urea amended with acid sulphate soil however did not reduce ammonia loss even though it delayed the ammonia loss at higher amounts ( $T_{13}$  and  $T_{14}$ ). The application of acid sulphate-urea-HA mixture ( $T_5$ ) and urea-HA mixtures ( $T_9$  and  $T_{10}$ ) reduced  $\text{NH}_3$  loss in acid soil by improving ammonium retention. This study can contribute to improving urea N use efficiency as well as reducing environmental pollution in agriculture and forestry.

**Key words:** Humic acids, acid sulphate soils, urea, ammonium, nitrate, ammonia loss.

## INTRODUCTION

Urea is noted for being the most widely used N fertilizer in agriculture because of its high N and low price. Ammonia loss due to rapid hydrolysis of urea in soil following surface application can be substantial (Ahmed et al., 2010; Latifah et al., 2010; Cai et al., 2002; Preasertsak et al., 2001). An approach to solve this problem involves control of the dissolution and hydrolysis of urea-N availability by reducing the microsite pH with acid materials such as acid phosphates and phosphoric acid (Latifah et al., 2011a, b, c; Ahmed et al., 2010, 2006; Fan and Mackenzie, 1993; Siva et al., 1999).

The cost of amendments, however, prohibits their use. Any effective, low-cost and readily available amendments would encourage their application. Urea-phosphate, which is a mixture of urea and phosphoric acid, has been reported to reduce  $\text{NH}_3$  volatilization from urea and reduces seedling damage (Fenn and Richards, 1989; Shamsuddin, 2006; Ahmed et al., 2006, 2008). However, these mixtures are corrosive and require special precautions in handling and storage.

Considering the low pH (usually less than 3.5) and low cost of acid sulphate soil and humic acids from peat soils, a paradigm approach could be the use of little amount of these soils to amend urea before soil application. This could be of great benefit to Malaysia and elsewhere because an alternative such as this encourages the

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**Table 1.** Treatments details.

Treatment	Caption
T <sub>1</sub>	Soil without treatment
T <sub>2</sub>	2.02 g urea
T <sub>3</sub>	2.02 g urea + 0.25 g HA + 0.25 g ASS
T <sub>4</sub>	2.02 g urea + 0.50 g HA + 0.50 g ASS
T <sub>5</sub>	2.02 g urea + 0.75 g HA + 0.75 g ASS
T <sub>6</sub>	2.02 g urea + 1.00 g HA + 1.00 g ASS
T <sub>7</sub>	2.02 g urea + 0.25 g HA
T <sub>8</sub>	2.02 g urea + 0.50 g HA
T <sub>9</sub>	2.02 g urea + 0.75 g HA
T <sub>10</sub>	2.02 g urea + 1.00 g HA
T <sub>11</sub>	2.02 g urea + 0.25 g ASS
T <sub>12</sub>	2.02 g urea + 0.50 g ASS
T <sub>13</sub>	2.02 g urea + 0.75 g ASS
T <sub>14</sub>	2.02 g urea + 1.00 g ASS

HA, humic acid; ASS, acid sulphate soil.

appropriate use of acid sulphate and peat soils in the country where these soils have been estimated to be 0.5 million ha (Shamsuddin, 2006) and 2.5 million ha (Andriess, 1988), respectively. At the moment, Malaysia imports HA based fertilizers from China and Australia at a high cost.

The new approach to reduce NH<sub>3</sub> loss and at the same time increase N use efficiency in agriculture is worth investigating because the cultivation of crops such as oil palm, coconut, rice has not been successful on acid sulphate and peat soils in Malaysia (Shamsuddin, 2006). Thus, in this study, the effects of mixing urea with HA and acid sulphate soil on NH<sub>3</sub> loss, exchangeable ammonium, and available nitrate under laboratory conditions were investigated.

## MATERIALS AND METHODS

The study was conducted in laboratory conditions to test the effectiveness of the urea mixtures using a Closed-Dynamic airflow system described by Siva et al. (1999) in a completely randomized design (CRD) with 3 replications. All the 12 treatments listed in Table 1 (T<sub>3</sub> to T<sub>14</sub>) including 2 controls (T<sub>1</sub> and T<sub>2</sub>) were tested on a 250 g Nyalau Series (*Typic paleudults*) placed in an incubation chamber. The amount of urea used was calculated based on the standard recommendation for mature oil palm.

The fertilizer mixtures were prepared based on the method described by Ahmed et al. (2004) with some modification where the materials were weighed separately based on the treatments before mixing them in a plastic vial by using reciprocal mechanical shaker (200 rpm). The HA was isolated from a tropical peat soil using the method described by Rosliza et al. (2009). The acid sulphate soil was collected from Telaga Air Mangrove and Rempagi in Kuching, Sarawak.

Prior to the incubation study, all the materials used were characterized. The HA was analysed for the humification level by the E<sub>4</sub>/E<sub>6</sub> method (Stevenson, 1994), total acidity using the method

described by Inbar et al. (1990). The yield of HA was expressed in percentage (%). The selected characteristics of the Nyalau Series and the acid sulphate soil were carried out using standard procedures for total nitrogen (Bremner, 1965), soil cations exchange capacity (CEC) (Tan, 2005), soil pH (Brady and Weil, 2002), inorganic nitrogen (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) (Keeney and Nelson, 1982), soil texture (Tan, 2005), total C (Tan, 2005), exchangeable K, Ca, Mg and Na (Tan, 2005), and available P (Murphy and Riley, 1962).

Analysis of variance was used to test for treatments effect and means were compared using Duncan's new multiple range test (DNMRT) (SAS, 2007). The Statistical Analysis Software version 9.2 was used for the statistical analysis.

## RESULTS AND DISCUSSION

The selected physico-chemical properties of Nyalau Series, HA and acid sulfate soil are presented in Table 2. The chemical properties of the acid sulphate soil are similar to those reported by Shamsuddin (2006) and similar observations were also found for the HA characterization as reported by Tan (2003). The soil physico-chemical properties of the used in the incubation study were also comparable with those reported by Paramanathan (2000).

Daily loss of NH<sub>3</sub> over 22 days of incubation are presented in Figures 1 to 3. All the mixtures of urea with HA and acid sulphate soil (T<sub>3</sub> to T<sub>6</sub>) effectively delayed NH<sub>3</sub> loss compared with urea alone (T<sub>2</sub>) from day 3 to day 4 (T<sub>3</sub> and T<sub>4</sub>) and day 7 (T<sub>5</sub> and T<sub>6</sub>). The highest loss was recorded for treatments T<sub>3</sub>, T<sub>4</sub>, T<sub>5</sub>, and T<sub>6</sub> but the losses were also lower compared with T<sub>2</sub>.

Treatment seven (T<sub>7</sub>) not effectively controlled NH<sub>3</sub> loss compared with T<sub>2</sub>, even though both started releasing NH<sub>3</sub> gas at 3 day of incubation. Treatments T<sub>8</sub>, T<sub>9</sub>, and T<sub>10</sub> effectively minimized NH<sub>3</sub> loss from urea especially

**Table 2.** Selected physio-chemical characteristics of HA, ASS, and soil (Nyalau Series).

Property	HA	ASS	Soil
pH (water)	nd	3.45	4.85
pH (1 M KCl)	nd	nd	3.65
Total organic carbon (%)	55.59	nd	nd
CEC (cmol kg <sup>-1</sup> )	<sup>a</sup>	40.50	21.25
Carboxylic group (cmol kg <sup>-1</sup> )	300	nd	nd
Phenolic group (cmol kg <sup>-1</sup> )	220	nd	nd
Total acidity <sup>a</sup> (cmol kg <sup>-1</sup> )	520	nd	nd
Total N	nd	nd	0.4132
Exchangeable K (cmol kg <sup>-1</sup> )	nd	nd	0.8016
Exchangeable Mg (cmol kg <sup>-1</sup> )	nd	nd	0.0177
Exchangeable Ca (cmol kg <sup>-1</sup> )	nd	nd	0.0001
Exchangeable Na (cmol kg <sup>-1</sup> )	nd	nd	0.0280
Exchangeable NH <sub>4</sub> <sup>+</sup>	nd	nd	0.1540
Available NO <sub>3</sub> <sup>-</sup>	nd	nd	0.1243
Field capacity (%)	nd	nd	75.57
Texture	nd	nd	SCL

CEC, Cation exchange capacity; SCL, sandy clay loam; nd, not determined; <sup>a</sup> CEC of humic acid = total acidity.

**Table 3.** Total amount of ammonia loss and soil pH over 22 days of incubations.

Treatment	NH <sub>3</sub> loss	pH <sub>water</sub>	pH <sub>acid</sub>
T <sub>1</sub>	0.00 <sup>d</sup>	4.57 <sup>b</sup>	3.68 <sup>b</sup>
T <sub>2</sub>	48.76 <sup>a</sup>	7.23 <sup>a</sup>	6.29 <sup>a</sup>
T <sub>3</sub>	44.57 <sup>ab</sup>	7.60 <sup>a</sup>	6.37 <sup>a</sup>
T <sub>4</sub>	44.71 <sup>ab</sup>	7.42 <sup>a</sup>	6.39 <sup>a</sup>
T <sub>5</sub>	30.45 <sup>c</sup>	7.67 <sup>a</sup>	6.37 <sup>a</sup>
T <sub>6</sub>	37.45 <sup>b</sup>	7.31 <sup>a</sup>	6.36 <sup>a</sup>
T <sub>7</sub>	35.39 <sup>ab</sup>	7.29 <sup>a</sup>	6.31 <sup>a</sup>
T <sub>8</sub>	46.09 <sup>ab</sup>	7.73 <sup>a</sup>	6.39 <sup>a</sup>
T <sub>9</sub>	26.75 <sup>c</sup>	7.67 <sup>a</sup>	6.37 <sup>a</sup>
T <sub>10</sub>	36.72 <sup>c</sup>	7.39 <sup>a</sup>	6.41 <sup>a</sup>
T <sub>11</sub>	49.72 <sup>a</sup>	7.23 <sup>a</sup>	6.36 <sup>a</sup>
T <sub>12</sub>	49.58 <sup>a</sup>	7.19 <sup>a</sup>	6.35 <sup>a</sup>
T <sub>13</sub>	38.82 <sup>ab</sup>	7.50 <sup>a</sup>	6.36 <sup>a</sup>
T <sub>14</sub>	35.96 <sup>ab</sup>	7.15 <sup>a</sup>	6.35 <sup>a</sup>

Note: Means within a column with different alphabets indicate significant difference between treatments by Duncan's New Multiple range Test (DNMRT) at  $p \leq 0.05$ .

T<sub>9</sub> and T<sub>10</sub> compared with T<sub>2</sub> (Table 3).

The effects of urea amended with different levels of acid sulphate soil on NH<sub>3</sub> loss are presented in Figure 3. Treatments T<sub>11</sub> and T<sub>12</sub> were inefficient in controlling NH<sub>3</sub> loss compared with T<sub>2</sub>. Soil (Nyalau Series) without urea (T<sub>1</sub>) did not contribute to NH<sub>3</sub> loss over 22 days of incubation. The ability of the aforementioned treatments (T<sub>3</sub>, T<sub>4</sub>, T<sub>5</sub>, T<sub>6</sub>, T<sub>8</sub>, T<sub>9</sub>, T<sub>10</sub>, T<sub>13</sub>, and T<sub>14</sub>) to delay urea

hydrolysis may be partly attributed to the addition of the acidic materials (HA and acid sulphate soil) which might have caused temporary acidic conditions to the soil microsite pH and affected the soil NH<sub>3</sub> - NH<sub>4</sub><sup>+</sup> equilibrium. Ahmed et al. (2006) and Siva et al. (1999) also reported similar findings when urea was mixed with HA or triple superphosphate (TSP).

The statistically insignificant effect of T<sub>3</sub>, T<sub>4</sub>, T<sub>7</sub>, T<sub>8</sub>, T<sub>11</sub>,

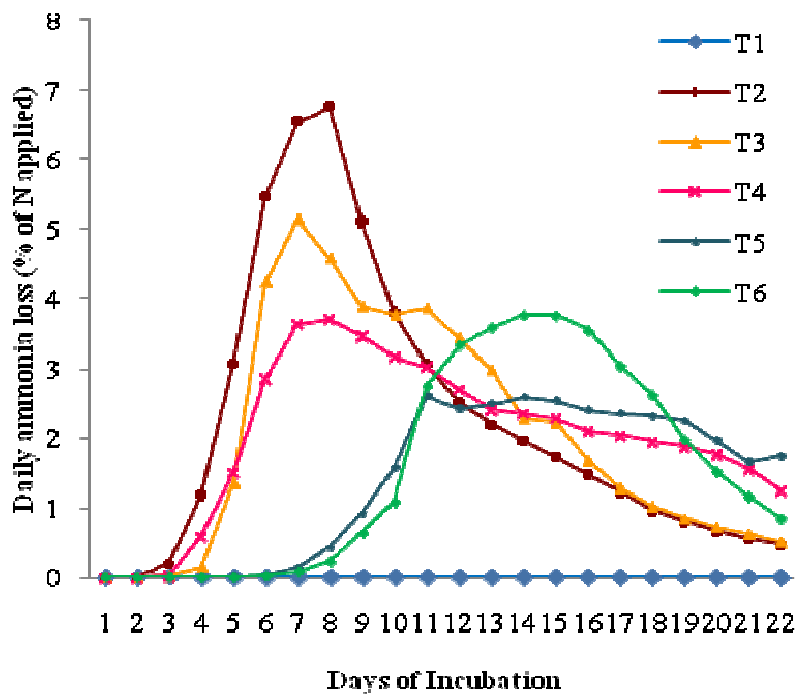


Figure 1. Comparison of the daily loss of ammonia of T<sub>1</sub> and T<sub>2</sub> with T<sub>3</sub>, T<sub>4</sub>, T<sub>5</sub> and T<sub>6</sub> over 22 days of incubation.

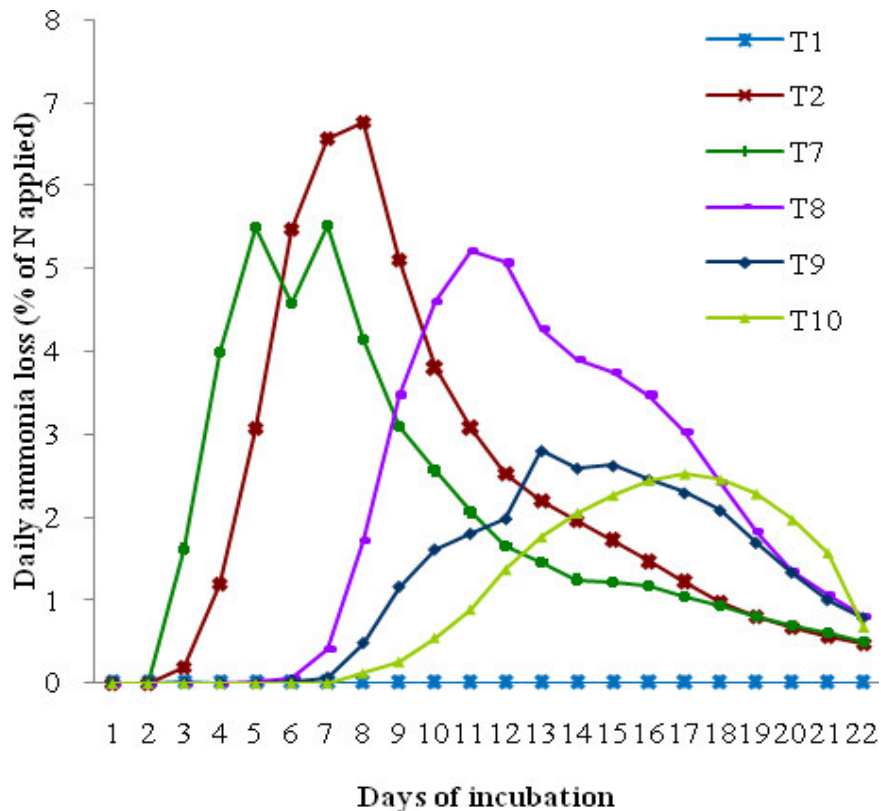
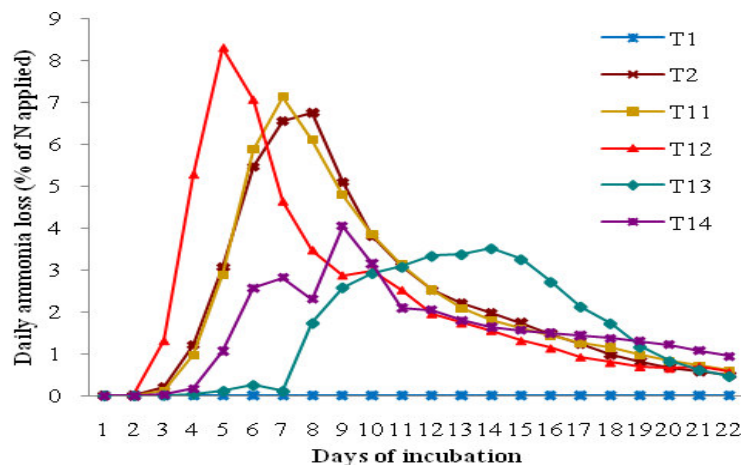


Figure 2. Comparison of the daily loss of ammonia of T<sub>1</sub> and T<sub>2</sub> with T<sub>7</sub>, T<sub>8</sub>, T<sub>9</sub> and T<sub>10</sub> over 22 days of incubation.



**Figure 3.** Comparison of the daily loss of ammonia of T<sub>1</sub> and T<sub>2</sub> with T<sub>11</sub>, T<sub>12</sub>, T<sub>13</sub> and T<sub>14</sub> over 22 days of incubation.

**Table 4.** Effect of treatments on exchangeable ammonium and nitrate accumulation.

Treatment	Available NO <sub>3</sub> (mg kg <sup>-1</sup> )	Exchangeable NH <sub>4</sub> (mg kg <sup>-1</sup> )
T <sub>1</sub>	14.02 <sup>a</sup>	28.03 <sup>h</sup>
T <sub>2</sub>	21.02 <sup>a</sup>	994.71 <sup>ab</sup>
T <sub>3</sub>	24.52 <sup>a</sup>	802.08 <sup>cd</sup>
T <sub>4</sub>	10.51 <sup>a</sup>	224.16 <sup>g</sup>
T <sub>5</sub>	21.02 <sup>a</sup>	693.50 <sup>de</sup>
T <sub>6</sub>	21.02 <sup>a</sup>	994.71 <sup>ab</sup>
T <sub>7</sub>	21.02 <sup>a</sup>	595.43 <sup>ef</sup>
T <sub>8</sub>	14.01 <sup>a</sup>	861.62 <sup>bc</sup>
T <sub>9</sub>	21.02 <sup>a</sup>	697.00 <sup>de</sup>
T <sub>10</sub>	14.01 <sup>a</sup>	1099.79 <sup>a</sup>
T <sub>11</sub>	14.01 <sup>a</sup>	518.38 <sup>f</sup>
T <sub>12</sub>	10.51 <sup>a</sup>	919.99 <sup>bc</sup>
T <sub>13</sub>	21.02 <sup>a</sup>	950.35 <sup>abc</sup>
T <sub>14</sub>	24.52 <sup>a</sup>	882.63 <sup>bc</sup>

Means within a column with different alphabets indicate significant difference between treatments by Duncan's new multiple range test (DNMRT) at  $p \leq 0.05$ .

T<sub>12</sub>, T<sub>13</sub>, and T<sub>14</sub> on the total NH<sub>3</sub> loss compared with urea alone (T<sub>2</sub>) was because of the low amounts of HA and acid sulphate soil used to enhance ammonium retention and as well as reducing microsite pH. The increase in the soil pH was due to poor or reduced buffering capacity of the soil. The statistically insignificant effect of T<sub>1</sub> to T<sub>14</sub> on soil total acidity and active acidity is related to more hydrogen ion consumption. The insignificant effect of T<sub>6</sub>, T<sub>8</sub>, T<sub>10</sub>, T<sub>12</sub>, T<sub>13</sub>, and T<sub>14</sub> compared with T<sub>2</sub> was because of the high amount of exchangeable NH<sub>4</sub><sup>+</sup> inside the soil solution as the performance of all the treatments were similar at the end of 22 days of the incubation study.

Lack of significant difference in available NO<sub>3</sub><sup>-</sup>

regardless of treatment (Table 4) suggests favorable formation of exchangeable NH<sub>4</sub><sup>+</sup> over nitrate as the concentrations of NH<sub>4</sub><sup>+</sup> were generally higher for all the treatments.

The insignificant effect of all the treatments on available NO<sub>3</sub> was probably because N from urea was volatilized and the nitrified NH<sub>4</sub> ion in soil solutions was not influenced by the application of urea based fertilizers. It was found that the application of acid sulphate soil did not have significant effect on controlling NH<sub>3</sub> volatilization even though some of the mixtures (T<sub>13</sub> and T<sub>14</sub>) delayed urea hydrolysis (Figure 3). The application of acid sulphate soil can also retard the potential use of HA in

retaining  $\text{NH}_4$  ion from the oxidation of Fe and Al in this soil (Shamsuddin, 2006).

## Conclusion

The application of acid sulphate-urea-HA mixture ( $T_5$ ) and urea-HA mixtures ( $T_9$  and  $T_{10}$ ) can reduce  $\text{NH}_3$  loss in acid soil by improving ammonium retention. This study can contribute to improving urea N use efficiency as well as reducing environmental pollution in agriculture and forestry. To consolidate these findings a similar investigation on organic soils is suggested. Both greenhouse and field experiments using test crop such as *Zea mays* if retention of ammonium ion observed in the laboratory experiment will result in improved urea-N use efficiency and yield.

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**Abbreviations:** **HA**, Humic acid; **CRD**, completely randomized design; **SAS**, statistical analysis system; **CEC**, cations exchange capacity; **DNMRT**, Duncan's New Multiple range Test; **TSP**, triple superphosphate.

**Nomenclatures:**  $\text{NH}_4^+$ , Ammonium;  $\text{NO}_3^-$ , nitrate.

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