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Effect of Organic Based N Fertilizer on Dry Matter (*Zea mays L.*), Ammonium and Nitrate Recovery in an Acid Soil of Sarawak, Malaysia

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Abstract: Problem statement: Exchangeable ammonium (NH_4^+) could be recovered by humic and fulvic acids from humic substances. The ability of these acids in fixing or retaining NH_4^+ has been demonstrated in many findings and reports. Both acids could affect the plant growth, nutrients uptake by enhancing photosynthesis rate and root growth among others. Thus, in this study, the effect of both acids (in liquid form) on soil exchangeable NH_4^+, dry matter production and available nitrate (NO_3^-) was investigated. **Approach:** Humic molecules were isolated using standard procedures, followed by liquid organic N fertilizers formulation. Organic based N fertilizers were applied to soil in pots at 10 Days After Planting (DAP) and 28 DAP. Treated soils and plant parts were sampled at 54 DAP or at tasselling stage. Soil samples were analyzed for pH, ammonium and nitrate content. The plant samples were weighed to assess dry matter production. **Results:** Under acid condition, organic based liquid N fertilizers (fulvic acid or both, humic and fulvic acids) increased accumulation of NH_4^+in soil. The presence of carboxylic groups in humic molecules increased NH_4^+ retention with increasing soil's stock labile carbon. However, low percentage of these acids reduced their full effect on dry matter production. The availability of nitrate was not statistically different for all treatments. Low soil pH could had reduced nitrification processes and simultaneously soil NO_3^- content. **Conclusion:** Liquid form of humic and/or fulvic acids could play an important role in enhancing urea efficiency. However, their contribution needs to be studied in detail in relation to humic molecules characteristics. This study had a potential in the development of liquid and foliar organic fertilizers.

Key words: Humic acid, fulvic acid, nitrogen fertilizer, liquid fertilizer, ammonium, nitrate, maize

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INTRODUCTION

In recent times, judicious use of fertilizers *vis a vis* food safety and environmental pollution is of paramount concern. For instance, unbalanced used of urea (the most commonly used nitrogen fertilizer in agriculture) has created a global environmental issue such as ammonia (NH_3) volatilization upon surface application[1,2]. Thus, a new approach is needed to reduce NH_3 loss while improving or increasing Urea-N use efficiency in agriculture.

Ammonia loss is governed by soil factors such as pH, Cation Exchange Capacity (CEC), temperature and moisture[3-5]. The amount of N loss ranges from 10-60% of the total N applied[6]. With the ever growing concern about the polluting effect of excessive use of nitrogen fertilizers on the environment, improvement of urea-N use efficiency in agriculture cannot be over emphasized. One of the approaches that could be used to improve urea-N use efficiency is to mix it with acidic organic materials such as humic and fulvic acids which have the ability to retain NH_4^+ ions from urea during hydrolysis and at the same time reducing urea pH during hydrolysis. Some studies have shown positive results regarding the mixture of organic and mineral fertilizers. Increase in total organic carbon and total nitrogen was noted when compost was mixed with mineral fertilizers such as NPK fertilizer. This mixture increased the stock of labile organic carbon[7]. Labile organic carbon is known to play an important role in

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providing plant nutrients as well as interfering in aggregate stability under favorable conditions[8]. Organic substances also have a good effect in controlling N loss from urea, even in small quantities, thus this attempt was made to evaluate its effectiveness on maize. A previous study showed that Humic Acid (HA) has a great effect in reducing N loss. For instance the use of 0.75 $g\ kg^{-1}$ HA together with zeolite reduced N loss up to 60%[9].

Besides being good at controlling N loss, HA promote plant growth by increasing nutrients (most essential macro and micro nutrients) uptake[10,11]. Whilst, humate could give a direct effect to plant photosynthesis, chlorophyll density and plant root respiration, which simultaneously affect and promote plant growth[12].

The objective of this study was to investigate the effect of liquid HA, fulvic acid (FA) and urea mixtures on soil exchangeable NH_4^+, available NO_3^- and dry matter of maize (*Zea mays*) on Nyalau series *(Typic Paleudults).*

MATERIALS AND METHODS

Well decomposed peat (*Saprist*) soil was sampled (0-25 cm) from Kuala Tatau, Sarawak, Malaysia whilst the mineral soil used in this study was taken from an undisturbed area of University Putra Malaysia Bintulu Campus, Sarawak at a depth of 0-25 cm. Both soils were air dried and sieved to pass through 2 mm sieve for further analysis and glasshouse study. Prior to chemical analysis, the peat samples were oven dried at 60°C for 24 h. The mineral soil was analyzed for pH (water and KCl) at a ratio of 1:2.5 using glass electrode, CEC by leaching with 1 N ammonium acetate (adjusted to pH 7) followed with steam distillation technique[13], exchangeable cations (K, Ca and Mg) by atomic absorption spectrophotometry (A Analyst 800, Perkin Elmer Instruments, Norwalk, CT), total N by the Micro-kjeldahl method, organic matter and total organic carbon by combustion method[14] and bulk density was determined using standard procedures[15].

A modified method by Susilawati *et al*.[16] was used to isolate HA and FA of peat for fertilizer formulation. Since HA isolation involves acidification processes to separate humic and fulvic acids using 6N HCl, two types of mixtures were made and they were acidified and unacidified mixtures. Both mixtures contained humic and fulvic acids.

A glasshouse study was conducted using a completely randomized block design with 3 replications. There were 8 treatments selected for testing in this study. The treatments evaluated were: Liquid urea (T_1), solid urea (T_2), urea + liquid HA (T_3), urea + liquid FA (T_4), urea + liquid mixture of acidified HA + FA (T_5), urea + liquid mixture of unacidified HA + FA (T_6), liquid ammonium sulphate [$(NH_4)_2SO_4$] (T_7) and control (soil without any treatments) (T_0). A total of 7.5 kg soil (based on the bulk density of the soil) was weighed into each plastic pots measuring 27×18 cm.

The fertilizer requirement of the maize crop (330.4 $kg\ ha^{-1}$ urea; 121.6 $kg\ ha^{-1}$ TSP; 107.2 $kg\ ha^{-1}$ MOP) was scaled down to per pot basis equivalent to: Urea (4.13 $g\ pot^{-1}$), triple superphosphate (TSP) (1.52 $g\ pot^{-1}$) and Murate Of Potash (MOP) (1.34 $g\ pot^{-1}$). These fertilizers were surface applied ten days after planting (DAP) and 28 DAP. The plants were monitored up to tassel stage (54 DAP) before harvest, because tassel stage is the maximum growth stage the plant can achieve before it goes to productive stage. The shoots of the plants were harvested and partitioned into leaf and stem. The remaining roots in the soil were collected by washing the soil from the roots using tap water. The plant parts were oven dried at 60°C to constant weight and weighed using a digital balance. Prior to harvesting, soil samples were taken from the pots and analyzed for pH, exchangeable NH_4^+ and available NO_3^- using standard method.

Analysis of variance was used to test treatment effects while means of treatments were compared using Duncan's New Multiple Range Test (DNMRT)[17].

RESULTS

The soil used in this study was acidic, in both water and KCl (Table 1). The CEC of the soil was consistent with that reported for Nyalau series by Paramanathan[18] (Table 1). Nitrogen content in this soil was low but those of organic matter and total organic carbon were relatively high (Table 1). The bulk density of the soil was 1.548.

Table 1: Physico-chemical characteristics of Nyalau series

Property	Value obtained (0-25 cm)	Standard data range* (0-35 cm)
pH_w	4.290	4.7-4.8
pH_{KCl}	3.570	4.0-4.2
Exchangeable K^+ ($cmoL\ kg^{-1}$)	0.180	0.09*
Exchangeable Ca^{2+} ($cmoL\ kg^{-1}$)	2.260	0.05*
Exchangeable Mg^{2+} ($cmoL\ kg^{-1}$)	2.980	<0.01*
CEC ($cmoL\ kg^{-1}$)	24.500	24.6-53.5
Total nitrogen (%)	0.340	0.03-0.06*
Total organic carbon (%)	3.350	0.69-1.30*
Organic matter (%)	5.780	1.12-2.24*
C/N ratio	9.850	22-23*
Bulk density	1.548	nd
Clay (%)	22.840	11-14*
Sand (%)	58.520	78-81*
Silt (%)	21.000	8*

*: Subject to the soil development, standard data range by Paramananthan[18]

Table 2: Effect of treatments on soil pH at 54 DAP

Label	Treatment	pH_w	pH_{KCl}
T_0	Control (without urea fertilizer)	4.47^b	3.65^b
T_1	Liquid urea	4.58^{ab}	3.68^{ab}
T_2	Solid urea	4.63^{ab}	3.66^{ab}
T_3	Urea + liquid HA	4.44^b	3.60^b
T_4	Urea + liquid FA	$4.63a^b$	3.72^{ab}
T_5	Urea + liquid of HA + FA (acidified)	4.70^a	3.78^a
	Urea + liquid of HA + FA (unacidified)		
T_6	Liquid $(NH_4)_2SO_4$	$4.56a^b$	3.68^{ab}
T_7		4.13^c	3.60^b

Different letters indicate significant difference between means using Duncan's New Multiple Range Test (DNMRT) at p = 0.05

Table 3: pH values of formulated liquid organic-urea mixture fertilizer

		pH	
Code	Treatment	Without urea	With urea
F_1	Urea (liquid)	Nd	8.14
F_2	HA	1.89	9.04
F_3	FA	1.02	1.64
F_4	HA + FA (acidified)	0.98	1.60
F_5	HA + FA (unacidified)	6.56	6.89

Table 4: Effect of treatments on dry matter production of maize at 54 DAP

Label	Treatment	Total dry weight (g)
T_0	Control (without urea fertilizer)	12.92^b
T_1	Liquid urea	123.75^a
T_2	Solid urea	125.67^a
T_3	Urea + liquid HA	107.59^a
T_4	Urea + liquid FA	110.42^a
T_5	Urea + liquid of HA + FA (acidified)	106.94^a
T_6	Urea + liquid of HA + FA (unacidified)	117.47^a
T_7	Liquid $(NH_4)_2SO_4$	34.57^b

Different letters indicate significant difference between means using Duncan's New Multiple Range Test (DNMRT) at p = 0.05

Except for T_5 and T_7 (pH_w) and T_5 (pH_{KCl}), the pH of the treatments were not statistically different from T_0 (control) at 54 DAP (Table 2). This suggests that soil treated with urea, or mixture of urea with liquid organic materials does not significantly change pH values. As expected, the lowest pH was recorded from T_7 treatment. As shown in Table 2, application of high pH fertilizer (Table 3) for some of the treatments did not show any significant effect on pH (water and KCl).

The dry matter production of the test crop was superior for the treatment with liquid organic fertilizer (T_3-T_6) and urea (T_1 and T_2), compared to $(NH_4)_2SO_4$ (T_7) and control (T_0) (Table 4). Even though, the HA containing fertilizers recorded highest pH as compared to other treatments (Table 3), the dry matter production under this treatment was not statistically different from others. This observation is particularly consistent with the result of T6, whose pH was 6.89.

Ammonium sulphate $[(NH_4)_2SO_4]$ is also an important N fertilizer in agriculture. However, in this study it failed to improve dry matter production compared to the other treatments although the concentration of NH_4^+ under this treatment was the highest (Fig. 1).

In terms of NH_4^+ accumulation, T_4 and T_5 were more effective (Fig. 1) compared to the other treatments except for T_7. Generally, soil available NO_3^- was the same for all the treatments applied, except for T_7 and T_0 (Fig. 2).

DISCUSSION

The difference in exchangeable cations (K, Ca and Mg), clay, sand and silt contents were probably due to differences in soil horizon. The presence of either cambic (unclear horizon with some changes in physical and chemical properties) or argillic (accumulation of clay silicate and present of clay in pad surface) horizon leads to different results in certain soil properties of Nyalau series. However, a comparison could not be made due to lack of information for the Nyalau series data with cambic, instead of argillic (reported in Paramananthan[18].

The liquid form of fertilizer applied could be one of the reasons for the low pH. High mobility of fertilizer fractions would enhance fertilizer loss, through water or air movement and hence less effect on pH. In this study, the fertilizers could not give long term effect on pH. The low pH of the soil treated with organic based N fertilizers (F_1-F_5) does not necessarily suggest that those treatments did not increase or decrease the pH of the soil. Their effect could be temporary as reported by Ahmed *et al.*[19] where a short term effect of urea mixed with acidic materials temporarily reduced soil pH.

The tendency of HA to react with NH_3, released by urea, was high in the formulated fertilizers consisting HA. Hydrolysis of urea, which increased the surrounding pH could promote the reaction to occur. The presence of high NH_3 due to continuos hydrolysis of urea and overload of NH_4^+ could enhance fixation processes[20].

The acidic nature of $(NH_4)_2SO_4$ reduced its effect on dry matter production. This acidity without liming may cause poor plant growth and development. The sulfur, in the form of sulphate (SO_4^{2-}) reduces soil pH and affects NH_3 volatilization[21]. Thus, $(NH_4)_2SO_4$ seems not suitable for use in acid soils.

Functional groups present in humic molecules together with its characteristics produced a lot of effects on NH_4^+ recovery. Less oxygen containing functional groups present in HA as compared to FA reduced soil exchangeable NH_4^+ in T_4. The ability of carboxylic groups to dissociate their protons at pH 3[22] however, may have enabled the humic molecules (especially FA) to retain more NH_4^+ at this low pH. Hence, this partly explains why T_5 recorded more NH_4^+ in soil at 54 DAP. The low cation exchange capacity (total acidity) of HA could be one of the reasons for inefficiency of HA. According to Tan[22], the total acidity of HA varies from 6-8.9 meq g^{-1} while that of FA, ranges between 10 and 12.3 meq g^{-1}. Thus, FA could perform better in acid soil to enhance urea efficiency through NH_4^+ retention.

The formulated fertilizers, T_4 and T_5 were acidic (Table 3: F_3 and F_4). Treated soil with T_4 and T_5 may cause soil to be acidic hence reduction of N loss through volatilization. Thus, in this study, these treatments recorded more exchangeable NH_4^+ as compared to others. Similar results have been reported by Fan *et al*.[23], where they found that the use of TSP (more acidic) reduced NH_3 volatilization from urea as compared to monoammonium phosphate (MAP).

Basically, total N and C:N ratio values could indicate NH_4^+ fixation by soils. For instance, total N of 0.29% with C: N ratio of 10.4 could fix 125 µg g^{-1} of NH_4^+ in soils[20]. The possibility of these processes to occur was high in treated soil with total N of 0.34% and C: N ratio of 9.85. However, its contribution could not be significant between treatments because the soils in this study received the same amount of N due to this process. This is clearly demonstrated in Fig. 1 and 2 and dry matter production (Table 3).

Inefficiency of HA in enhancing N recovery and dry matter production was recorded in this study. The low amount of HA used in fertilizer formulation could be a significant factor. The HA used was much lower as compared to the soil (0.16 g HA used/7.5 kg soil). Since, humic substances are believed to contain a very small amount of permanent charges which are responsible for CEC development with 10% estimation from its total negative charges[24,25], its contribution to cations retention would be subjective and relying on its quantity used. However, at this small percentage, HA still showed significant difference (p = 0.05) of soil exchangeable NH_4^+ as compared to T1 and T2.

Insignificant difference in NO_3^- content could probably be due to low soil pH, which reduces nitrification processes. Based on a previous report, the optimum pH for this process to take place is 8.5[3]. At the pH range of this study, this process could not progressively occur thus, causing low soil NO_3^- content.

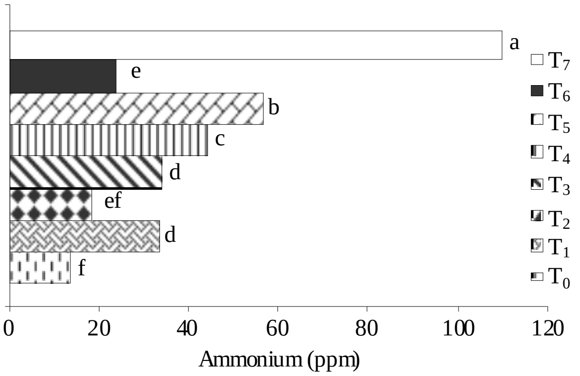

Fig. 1: Effect of treatments on soil exchangeable ammonium at 54 DAP. (Different letter indicate significant difference between means using Duncan's New Multiple Range Test (DNMRT) at p = 0.05)

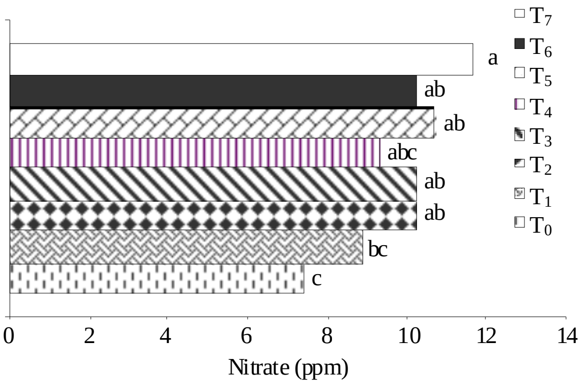

Fig. 2: Effect of treatments on soil available nitrate at 54 DAP. (Different letter indicate significant difference between means using Duncan's New Multiple Range Test (DNMRT) at p = 0.05)

CONCLUSION

Liquid form of humic and/or fulvic acids could play an important role in enhancing urea efficiency. However, their contribution needs to be studied in detail in relation to humic molecule characteristics. The amount or rate of humic molecules to enhance NH_4^+ and NO_3^- recovery in soil which can indirectly promote plant growth needs detail investigation. This study has the potential to be advanced especially in terms of liquid organic fertilizer development. Liquid organic fertilizer has a big potential to be used as foliar fertilizer in the future.

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