

## Ammonia Volatilization Loss From Surface Placed Urea-treated POME Pellets

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### ABSTRAK

Ammonia yang hilang melalui pemeruapan dari baja urea yang digunakan pada tanah pendalaman Malaysia boleh mencapai 50% dari N yang diberi. pH yang tinggi terbentuk di kawasan-mikro bila urea terhidrolisis membuat  $\text{NH}_4^+$  tidak stabil dan  $\text{NH}_3$  teruap. Dalam kajian ini urea dimatrikan dengan POME (palm oil mill effluent) terasid dan dimampatkan bertujuan merendahkan pH kawasan-mikro bila urea terhidrolisis. Keupayaan pertukaran kation (KPK) POME yang tinggi akan meningkatkan daya tampan H dan kawasab herao  $\text{NH}_4^+$ . Kajian menunjukkan urea-30% POME terasid dapat merendahkan  $\text{NH}_3$  teruap ke paras 8% dari 30% pada until urea-sahaja. Penurunan  $\text{NH}_3$  teruap selari dengan peningkatan POME dalam until urea-POME, peningkatan POME merendahkan  $\text{NH}_3$  teruap. KPK dan daya tampan adalah sifat POME yang merendahkan  $\text{NH}_3$  teruap dari urea. KPK dan daya tampan adalah sifat POME yang merendahkan  $\text{NH}_3$  teruap dari urea. KPK yang tinggi menjerap  $\text{NH}_4^+$  terhasil dari hidrolisis urea dan daya tampan H merendahkan pH kawasan -mikro.

### ABSTRACT

Ammonia volatilization loss from urea applied to inland Malaysian soils can be as high as 50% of the nitrogen (N) applied. The high pH of the microsities developed upon urea hydrolysis results in  $\text{NH}_4^+$  being unstable leading to ( $\text{NH}_3$ ) volatilizing. In this study acidified POME (palm oil mill effluent) was matrixed with urea and pelletized with the objective of providing lower pH of the microsite during urea hydrolysis. The high cation exchange capacity (CEC) of the POME could also increase the H-buffering and sites for  $\text{NH}_4^+$  adsorption. Results show that urea-30% POME acidified was able to reduce  $\text{NH}_3$  volatilization loss to 8% compared with 30% of the urea-only pellets. Reduction in  $\text{NH}_3$  volatilization loss was directly correlated with increase in the POME content in pellets. The higher the POME, the lower  $\text{NH}_3$  volatilized. CEC and H-buffering are properties of POME that help reduce  $\text{NH}_3$  volatilization loss. The high CEC adsorps  $\text{NH}_4^+$  from the hydrolysis of urea and the H-buffering reduces the pH of the microsities.

### INTRODUCTION

Ammonia volatilization loss from surface-placed urea in inland Malaysian soils can be as high as 50 percent (Pushparajah, 1982; Chan and Chew, 1984). The high  $\text{NH}_3$  losses are due to the low H-buffering and low organic matter content of the soil coupled with favourable environmental conditions for volatilization to occur. Due to the high N loss from fertilizer urea, most oil palm and rubber plantations in Malaysia are fertilized with ammonium sulphate [ $(\text{NH}_4)_2\text{SO}_4$ ] for the

N source. Urea in soil undergoes hydrolysis resulting in high pH in the area surrounding the urea granules (microsites) and often exceeds 8.5 (Fenn and Richards, 1986). Instability of ammonium at high pH results in it being volatilized (Vlek and Carter, 1983). Ammonia volatilization loss can be controlled by reducing microsite pH with acidic materials (Stumpe *et al.*, 1984). Increase in H-buffering of soils decreases  $\text{NH}_3$  volatilization loss (Fenn and Kissel, 1976; Ferguson *et al.*, 1984). Ammonium,

the product of urea hydrolysis could be adsorped on exchange sites, thus soils with high cation exchange capacity (CEC) have lower  $\text{NH}_3$  volatilization loss from urea applied (Fenn and Kissel, 1976; Fenn *et al.*, 1982). Our hypothesis is that POME (an agricultural waste material produced in abundance and which has high a CEC value) could, when modified to have a low pH and matrixed with urea, reduce  $\text{NH}_3$  volatilization loss.

## MATERIALS AND METHOD

### *Urea-POME Pellets*

Urea-treated POME pellets were prepared by mixing 0.52 g ground urea with HCl-treated POME and pelletized at 3 tons using a hydraulic press. The HCl-treated POME was made by reacting 1 M HCl  $\text{kg}^{-1}$  POME. The urea-treated POME pellets had a diameter of 12 mm and thickness varied according to the POME content in the pellet. Levels of POME used were 10, 20 and 30% (w/w). Three treatments, urea-only, POME-only, and urea-20% POME unacidified pellets were tested. Each treatment had three replicates. Acidified POME has a CEC of 73  $\text{cmol}(+) \text{kg}^{-1}$  and a pH of 2.92, whereas unacidified POME has a pH of 6.58.

### *Ammonia Volatilization Loss Measurement*

Volatilized  $\text{NH}_3$  was measured using the method of Fenn and Kissel (1973). A Buchner flask was used as the air exchange chamber. Air was pumped through the exchange chamber at the rate of 20 chamber's volume  $\text{min}^{-1}$  and subsequently through an Erlenmeyer flask containing boric acid mixed indicator to trap  $\text{NH}_3$  released. Volatilized  $\text{NH}_3$  was determined daily by titrating the boric acid containing the trapped  $\text{NH}_3$  with 0.01M HCl. Urea-treated POME pellets were placed in a nylon sieve pouch (30 mm sieve size, 5 cm L and 2 cm W) in the exchange chamber with 300 g soil (Munchong series, Isotropeptic Haplorthox, pH 4.36, N - 0.34%, C - 3.11%, clay - 51% CEC - 13.7  $\text{cmol kg}^{-1}$  soil). The moisture content of the soil was maintained at 80% field capacity. Ammonia volatilization loss measurement was carried out for 7 days. At the end of Day 7, the pouch was retrieved and remains of the pellet and 10 g of soil surrounding it were analysed for pH and exchangeable  $\text{NH}_4$  (KCl extractable, Bremner, 1965). This soil was considered as the microsite

region. A sample from the remaining soil was also taken and similarly analysed. This soil was considered as the outer soil region.

## RESULTS AND DISCUSSION

N loss through volatilization of the urea-only pellet was 29.3% and from the POME-only pellet was negligible (Table 1). The level of acidified POME content in the urea-POME pellets was found to influence the extent of  $\text{NH}_3$  volatilized, the higher the POME content the less  $\text{NH}_3$  volatilized. Ammonia volatilization was reduced to 18, 12 and 8% when 10, 20 and 30% acidified POME respectively was matrixed with urea. Urea-20% POME unacidified had 17.9% N loss, indicating acidification of the POME had reduced N loss by 5.8%. The ability of the microsite to resist increase in pH during urea hydrolysis influenced the amount of  $\text{NH}_3$  volatilized. POME has high CEC and its acidification creates high H-ions buffering of the microsite thus resisting the pH increase during urea hydrolysis. The influence of microsite acidification on  $\text{NH}_3$  loss has been reported by Fenn *et al.* (1990) and Bremner and Douglas (1971) in studies where phosphoric acid was mixed with urea. This mixture, however, has the disadvantage of being corrosive and needs special care in handling. The influence of CEC of POME in reducing  $\text{NH}_3$  volatilization loss can be deduced from the urea-20% POME pellets that are acidified and unacidified. Reduction in  $\text{NH}_3$  volatilization loss due to the CEC was 12.1% and 5.8% was due to acidity. Ammonium from urea hydrolysis could be adsorped on the adsorptive sites of POME. Influence of CEC on reducing  $\text{NH}_3$  volatilization loss has been reported (Du Plessis and Kroontje, 1964; Fenn *et al.*, 1982). Ammonia loss peaked on Day 2 for the urea-only pellet, Day 3 for the 10%, and Day 4 for the 20 and 30% POME content respectively. When acidified POME was compared with unacidified POME, acidification delayed the peak by one day. Delay in peak  $\text{NH}_3$  loss resulted in an overall lowering in the cumulative  $\text{NH}_3$  loss from pellets which could be due to lower urease activity (Delaune and Patrick, 1970).

### *Ammonium Adsorption*

Table 2 shows the amount of ammonium adsorped on exchange sites of pellets and soils. No ammonium was recorded from the urea-only pellet as all had hydrolysed and nothing was left



TABLE 1  
Ammonia volatilization loss (% of applied N) from urea-POME pellets

Pellets	Day							Total
	1	2	3	4	5	6	7	
urea	4.2 <sup>a</sup>	15.4 <sup>a</sup>	4.7 <sup>b</sup>	2.3 <sup>c</sup>	1.5 <sup>d</sup>	1.0 <sup>e</sup>	0.9 <sup>c</sup>	30.0 <sup>a</sup>
100% POME	0 <sup>b</sup>	0 <sup>c</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>e</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>e</sup>
10% acid POME	0.1 <sup>b</sup>	2.1 <sup>b</sup>	5.4 <sup>a</sup>	4.4 <sup>a</sup>	2.6 <sup>a</sup>	2.0 <sup>b</sup>	1.7 <sup>a</sup>	18.3 <sup>b</sup>
20% acid POME	0.2 <sup>b</sup>	1.0 <sup>bc</sup>	1.9 <sup>c</sup>	3.8 <sup>b</sup>	2.1 <sup>bc</sup>	1.7 <sup>c</sup>	1.4 <sup>b</sup>	12.1 <sup>c</sup>
30% acid POME	0 <sup>b</sup>	0.4 <sup>c</sup>	1.6 <sup>c</sup>	2.2 <sup>c</sup>	1.7 <sup>cd</sup>	1.2 <sup>d</sup>	1.0 <sup>c</sup>	8.1 <sup>d</sup>
20% POME	0.2 <sup>b</sup>	2.0 <sup>b</sup>	5.1 <sup>ab</sup>	4.4 <sup>b</sup>	2.3 <sup>ab</sup>	2.2 <sup>a</sup>	1.6 <sup>ab</sup>	17.9 <sup>b</sup>
CV (%)	59.3	19.8	9.5	5.9	12.5	5.7	13.3	6.2

Means followed by the same letter in a column are not significantly different at P=0.05 using DMRT

TABLE 2  
Amount of ammonium adsorped on urea-POME pellet, microsite and outer soil

Treatments	Pellet (mg)	Microsite (mg g <sup>-1</sup> )	Outer soil (mg g <sup>-1</sup> )
urea	-	639.3 <sup>c</sup>	494.7 <sup>b</sup>
100% acid POME	175.0 <sup>d</sup>	58.3 <sup>d</sup>	84.0 <sup>c</sup>
10% acid POME	408.3 <sup>c</sup>	704.7 <sup>b</sup>	457.3 <sup>b</sup>
20% acid POME	781.7 <sup>b</sup>	704.7 <sup>b</sup>	485.3 <sup>b</sup>
30% acid POME	1201.7 <sup>a</sup>	765.3 <sup>a</sup>	711.7 <sup>a</sup>
20% POME	513.3 <sup>c</sup>	704.7 <sup>b</sup>	539.0 <sup>b</sup>
CV(%)	20.7	4.2	13.6

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the product of urea hydrolysis could be adsorbed on exchange sites, thus soils with high cation exchange capacity (CEC) have lower  $\text{NH}_3$  volatilization loss from urea applied (Fenn and Kissel, 1976; Fenn *et al.*, 1982). Our hypothesis is that POME (an agricultural waste material produced in abundance and which has high a CEC value) could, when modified to have a low pH and matrixed with urea, reduce  $\text{NH}_3$  volatilization loss.

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100% POME	0 <sup>b</sup>	0 <sup>c</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>e</sup>	0 <sup>d</sup>	0 <sup>d</sup>	0 <sup>e</sup>
10% acid POME	0.1 <sup>b</sup>	2.1 <sup>b</sup>	5.4 <sup>a</sup>	4.4 <sup>a</sup>	2.6 <sup>a</sup>	2.0 <sup>b</sup>	1.7 <sup>a</sup>	18.3 <sup>b</sup>
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20% POME	0.2 <sup>b</sup>	2.0 <sup>b</sup>	5.1 <sup>ab</sup>	4.4 <sup>b</sup>	2.3 <sup>ab</sup>	2.2 <sup>a</sup>	1.6 <sup>ab</sup>	17.9 <sup>b</sup>
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of the pellet. Adsorbed  $\text{NH}_4^+$  increased with the levels of POME in the pellets. This was due to the increase in the CEC of the pellets. Acidification of the POME significantly increased  $\text{NH}_4^+$  adsorption compared with normal POME. The lowering of pH in the microsite had probably reduced the amount of  $\text{NH}_4^+$  converted to  $\text{NH}_3$  resulting in more  $\text{NH}_4^+$  being adsorbed on exchange sites. The amount of  $\text{NH}_4^+$  adsorbed approximately doubled for every 10% increase in POME content in the pellet. Ammonium adsorbed by microsites was similar for all levels of POME incorporated except for the highest POME level. The outer soil region had less  $\text{NH}_4^+$  adsorbed compared with the microsites. The reduction in  $\text{NH}_3$  volatilization from urea-POME pellets had resulted in more  $\text{NH}_4^+$  being adsorbed on the pellets.

#### *pH of Pellets and Soils*

The pH of urea-POME pellets seven days after urea application was similar irrespective of the POME content (Table 3.). Ammonium released upon urea hydrolysis had increased the pH of the urea-POME pellets as compared with the POME-only pellet, which had a pH of 4.85. The microsite pH was lower and the outer soil region had the lowest pH compared with the pellets. The influence of site distance from fertilizer

granule and time after fertilizer application on pH of soil was reported by Fan and MacKenzie (1993). They found that the sphere of influence of urea fertilizer on soil pH increases with time and was effective to 35 mm distance from fertilizer granule. In our experiment, the influence of microsite distance extends up to 15 mm and the outer soil up to 16-45 mm from the pellets. Since we only monitored the pH at Day 7, the daily pH is not known.

#### CONCLUSION

Pelletizing urea with acidified POME (30%) reduced  $\text{NH}_3$  loss through volatilization from 30% to 8%. This reduction is explained by the increase in  $\text{NH}_4^+$  adsorbed on the pellets, microsites and the outer soil of the urea-POME pellets. This in turn was due to the increase in the CEC of pellets by the presence of POME. Low pH and high H-buffering of the urea-POME pellet was observed when urea-acidified POME had higher  $\text{NH}_4^+$  adsorbed on the pellets than for the urea-unacidified POME. Investigation on the effects of urea-POME pellets on plant N uptake efficiency under field conditions needs to be carried out in order to realise the potential of the pellets as a fertilizer N source.

TABLE 3  
The pH of urea-POME pellets, microsite and outer soil at Day 7 after application

Treatments	Pellet	Microsite	Outer soil
urea	-	6.57 <sup>b</sup>	6.33 <sup>c</sup>
100% acid POME	4.85 <sup>b</sup>	5.04 <sup>c</sup>	5.03 <sup>d</sup>
10% acid POME	7.87 <sup>a</sup>	7.57 <sup>a</sup>	7.25 <sup>a</sup>
20% acid POME	7.98 <sup>a</sup>	7.49 <sup>a</sup>	6.94 <sup>b</sup>
30% acid POME	7.97 <sup>a</sup>	7.41 <sup>a</sup>	6.92 <sup>b</sup>
20% POME	8.02 <sup>a</sup>	7.46 <sup>a</sup>	6.97 <sup>b</sup>
CV(%)	1.44	1.6	1.54

Means followed by the same letter in a column are not significantly different at  $P=0.05$  using DMRT

