



**UNIVERSITI PUTRA MALAYSIA**

**USE OF PALM OIL MILL EFFLUENT (POME)  
AND PEAT TO REDUCE AMMONIA  
VOLATILISATION FROM  
FERTILISER UREA**

**SIVA KUMAR BALASUNDRAM**

**FP 1997 6**

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AMMONIA VOLATILISATION FROM FERTILISER UREA**

By

**SIVA KUMAR BALASUNDRAM**

Thesis Submitted in Fulfilment of the Requirements for the  
Degree of Master of Agricultural Science in the  
Faculty of Agriculture, Universiti Putra Malaysia.

May 1997



*Dedicated to*

*'the estimable nucleus in my life who championed my struggle'*

*Thank you Mother dearest*



## ACKNOWLEDGEMENTS

Foremost, I extend my ingenuous gratitude to Assoc. Prof. Dr. Aminuddin Hussin, Dr. Ahmad Husni Mohd. Hanif and Dr. Abdul Rahman Manas for the direction they navigated me to through their adept supervision.

Noteworthy appreciation is due to Dr. Anuar Abd. Rahim for his statistical input, Dr. Che Fauziah Ishak, Dr. Radziah Othman and Assoc. Prof. Dr. Mohd. Khanif Yusop for their technical convictions, Dr. Tan Wee Tee (Dept. of Chemistry, UPM) for granting liberty on the use of his polarograph instrument, Dr. Norhayati Morris and Dr. Zainab Hamzah (both from RRI) for their resourceful counsel on Experiment 2a, and staff members from the Dept. of Soil Science (Mazuki, Sarimah, Rosnah, Nasir, Junaidi, Zulkapli, Yeni and Fuzi) for their contributions in making my analytical and sampling tasks surmountable. Special thanks to Ibrahim (Jab. Pertanian Temerloh, Pahang) for being a propitious coursemate and a caring friend, and to Tong Viet Thinh (RRI, Vietnam) for his company during my tedious hours in the laboratory.

I am indebted to Assoc. Prof. Dr. A. Rajan for the motivation he gave me in pursuing postgraduate work. I wish to also record my appreciation to Mr. M. Sabapathy (Klang, Selangor) and Dr. K. Paramanathan (Kuantan, Pahang), the former for his inspirational words of wisdom and the latter for his strong encouragement and financial support during crucial moments which together made me see the light at the end of the tunnel.

Last but not least, I thank my mother for being the pillar who inculcated the academic perseverance in me, family members who showed deep insight on the mundane nature of my work and Chubs for her never-ending forbearance which eased my endeavour through this challenging passage of life.



## TABLE OF CONTENTS

|                             |   |       |
|-----------------------------|---|-------|
| ACKNOWLEDGEMENTS .....      |   | iii   |
| LIST OF TABLES .....        |   | vii   |
| LIST OF FIGURES .....       |   | viii  |
| LIST OF APPENDICES .....    |   | xi    |
| LIST OF ABBREVIATIONS ..... |   | xiii  |
| ABSTRACT .....              |   | xv    |
| ABSTRAK .....               |   | xviii |
| <b>CHAPTER</b>              |   |       |
| <b>I</b>                    | INTRODUCTION.....   | 1     |
| <b>II</b>                   | REVIEW OF LITERATURE.....   | 4     |
|                             | Urea.....   | 4     |
|                             | Mechanism of NH <sub>3</sub> volatilisation.....  | 5     |
|                             | Factors influencing NH <sub>3</sub> volatilisation.....   | 6     |
|                             | Inherent soil properties.....   | 6     |
|                             | Interacting processes.....  | 11    |
|                             | Environmental factors.....  | 14    |
|                             | Agronomic factors.....  | 18    |
|                             | Methods and strategies to reduce NH <sub>3</sub> volatilisation.....                                      | 19    |
|                             | Acids.....  | 20    |
|                             | Urease inhibitors.....  | 21    |
|                             | Soluble salts.....  | 22    |
|                             | Coatings and matrices.....  | 23    |
|                             | Palm oil mill effluent (POME).....  | 25    |
|                             | Peat.....   | 28    |
|                             | Humic substances (HS).....  | 31    |
|                             | Analytical and structural characteristics of HS.....  | 32    |
|                             | Chemical interactions of HS.....  | 33    |
|                             | Current uses of HS.....   | 34    |
| <b>III</b>                  | MATERIALS AND METHODS.....  | 35    |
|                             | Experiment 1.....   | 35    |
|                             | Soils and organic materials.....  | 35    |
|                             | Analytical procedures.....  | 36    |
|                             | Urea matrix preparation.....  | 37    |
|                             | Estimation of volatilised NH <sub>3</sub> , pH change and<br>recovered NH <sub>4</sub> <sup>+</sup> ..... | 38    |



|  |           |
|--|-----------|
| Experiment 2a.....   | 40        |
| Extraction and separation of HS.....   | 40        |
| Purification of HA and FA.....   | 41        |
| Characterisation techniques.....   | 42        |
| Experiment 2b.....   | 43        |
| Urea matrix preparation, and estimation of volatilised NH <sub>3</sub> ,<br>pH change and recovered NH <sub>4</sub> <sup>+</sup> ..... | 43        |
| Statistical analysis.....  | 45        |
| <b>IV RESULTS AND DISCUSSION.....</b>  | <b>46</b> |
| Soil and material analysis.....  | 46        |
| Experiment 1.....  | 48        |
| Extent of NH <sub>3</sub> volatilisation.....  | 48        |
| Effect of matrixing agents and influence of<br>pre-treatment on NH <sub>3</sub> volatilisation.....                                    | 50        |
| Effect of differing matrixing ratios (rates) on<br>NH <sub>3</sub> volatilisation.....   | 53        |
| Extent of NH <sub>4</sub> <sup>+</sup> recovery.....   | 53        |
| Effect of matrixing agents and influence of<br>pre-treatment on NH <sub>4</sub> <sup>+</sup> recovery.....                             | 57        |
| Effect of differing matrixing ratios (rates) on<br>NH <sub>4</sub> <sup>+</sup> recovery.....  | 62        |
| Extent of pH change.....   | 64        |
| Effect of matrixing agents and influence of<br>pre-treatment on pH change.....   | 67        |
| Effect of differing matrixing ratios (rates) on<br>pH change.....  | 70        |
| Pattern of cumulative NH <sub>3</sub> volatilisation.....  | 70        |
| Correlation between parameters.....  | 75        |
| Experiment 2a.....   | 77        |
| Yield of humic fractions.....  | 77        |
| Loss on ignition.....  | 79        |
| Elemental composition.....   | 79        |
| Functional group analysis.....   | 80        |
| Optical density.....   | 81        |
| Spectral characteristics.....  | 82        |
| Experiment 2b.....   | 87        |
| Extent of NH <sub>3</sub> volatilisation.....  | 87        |
| Effect of humic fractions from differing sources<br>on NH <sub>3</sub> volatilisation.....   | 89        |
| Effect of differing rates of humic fractions<br>on NH <sub>3</sub> volatilisation.....   | 91        |
| Extent of NH <sub>4</sub> <sup>+</sup> recovery.....   | 91        |
| Effect of humic fractions from differing sources<br>on NH <sub>4</sub> <sup>+</sup> recovery.....                                      | 96        |
| Effect of differing rates of humic fractions<br>on NH <sub>4</sub> <sup>+</sup> recovery.....  | 96        |

|   |            |
|---|------------|
| on pH change.....   | 105        |
| Pattern of cumulative NH <sub>3</sub> volatilisation..... | 110        |
| Correlation between parameters.....                       | 113        |
| General discussion.....                                   | 115        |
| <b>V    CONCLUSION.....</b>                               | <b>118</b> |
| <b>BIBLIOGRAPHY.....</b>                                  | <b>120</b> |
| <b>APPENDICES.....</b>                                    | <b>138</b> |
| <b>VITA.....</b>  | <b>152</b> |



## LIST OF TABLES

| Table |   |     |
|-------|---|-----|
| 1     | Treatments employed in Experiment 1.....  | 39  |
| 2     | Treatments employed in Experiment 2b.....   | 44  |
| 3     | Selected properties of soils and materials under study.....                                 | 47  |
| 4     | Matrix of simple correlation coefficients (r) between parameters studied<br>in Exp. 1.....  | 76  |
| 5     | Chemical attributes of humic substances derived from POME and peat.....                     | 78  |
| 6     | Matrix of simple correlation coefficients (r) between parameters studied<br>in Exp. 2b..... | 114 |





## LIST OF FIGURES

| Figure |   |    |
|--------|---|----|
| 1      | NH <sub>3</sub> volatilisation from treated urea as compared to untreated control in soil A: (a)unacidified matrices, (b)acidified matrices, and in soil B: (c)unacidified matrices, (d)acidified matrices.....                                   | 49 |
| 2      | Effect of matrixing agents (OM) on NH <sub>3</sub> volatilisation in relation to pre-treatment in soil A: (a)unacidified matrices, (b)acidified matrices, and in soil B:  | 51 |
| 3      | Effect of pre-treatment on NH <sub>3</sub> volatilisation in relation to matrixing agents in soil A: (a)UDPOME, (b)DPOME, (c)peat, and in soil B: (d)UDPOME, (e)DPOME, (f)peat.....   | 52 |
| 4      | Effect of matrixing ratio on NH <sub>3</sub> volatilisation in relation to treatments employed in (a)soil A, (b)soil B.....   | 54 |
| 5      | NH <sub>4</sub> <sup>+</sup> -N recovery from the microsite region of treated urea as compared to untreated control in soil A: (a)unacidified matrices, (b)acidified matrices, and in soil B: (c)unacidified matrices, (d)acidified matrices..... | 55 |
| 6      | NH <sub>4</sub> <sup>+</sup> -N recovery from the outersite region of treated urea as compared to untreated control in soil A: (a)unacidified matrices, (b)acidified matrices, and in soil B: (c)unacidified matrices, (d)acidified matrices..... | 56 |
| 7      | Effect of matrixing agents (OM) on NH <sub>4</sub> <sup>+</sup> -N recovery in relation to pre-treatment in soil A at microsite: (a)unacidified OM, (b)acidified OM, and at outersite: (c)unacidified OM, (d)acidified OM.....                    | 58 |
| 8.     | Effect of matrixing agents (OM) on NH <sub>4</sub> <sup>+</sup> -N recovery in relation to pre-treatment in soil B at microsite: (a)unacidified OM, (b)acidified OM, and at outersite: (c)unacidified OM, (d)acidified OM.....                    | 59 |
| 9      | Effect of pre-treatment on NH <sub>4</sub> <sup>+</sup> -N recovery in relation to matrixing agents in soil A at microsite: (a)UDPOME, (b)DPOME, (c)peat, and at outersite: (d)UDPOME, (e)DPOME, (f)peat.....                                     | 60 |
| 10     | Effect of pre-treatment on NH <sub>4</sub> <sup>+</sup> -N recovery in relation to matrixing agents in soil B at microsite: (a)UDPOME, (b)DPOME, (c)peat, and at outersite: (d)UDPOME, (e)DPOME, (f)peat.....                                     | 61 |
| 11     | Effect of matrixing ratio on NH <sub>4</sub> <sup>+</sup> -N recovery in relation to treatments employed in soil A: (a)microsite, (b)outersite, and soil B: (d)outersite.....   | 63 |



|    |  |    |
|----|--|----|
| 12 | Changes in pH from the microsite region of treated urea as compared to untreated control in soil A: (a)unacidified matrices, (b)acidified matrices, and in soil B: (c)unacidified matrices, (d)acidified matrices..... | 65 |
| 13 | Changes in pH from the outersite region of treated urea as compared to untreated control in soil A: (a)unacidified matrices, (b)acidified matrices, and in soil B: (c)unacidified matrices, (d)acidified matrices..... | 66 |
| 14 | Effect of matrixing agents (OM) on pH change in relation to pre-treatment in soil A at microsite: (a)unacidified OM, (b)acidified OM, and at outersite: (c)unacidified OM, (d)acidified OM.....                        | 68 |
| 15 | Effect of matrixing agents (OM) on pH change in relation to pre-treatment in soil B at microsite: (a)unacidified OM, (b)acidified OM, and at outersite: (c)unacidified OM, (d)acidified OM.....                        | 69 |
| 16 | Effect of matrixing ratio on pH change in relation to treatments employed in soil A: (a)microsite, (b)outersite, and soil B: (c)microsite, (d)outersite.....   | 71 |
| 17 | Trend of NH <sub>3</sub> volatilisation in soil A: unacidified (a)UDPOME, (b)DPOME, (c)peat, and acidified (d)UDPOME, (e)DPOME, (f)peat.....   | 73 |
| 18 | Trend of NH <sub>3</sub> volatilisation in soil A: unacidified (a)UDPOME, (b)DPOME, (c)peat, and acidified (d)UDPOME, (e)DPOME, (f)peat.....   | 74 |
| 19 | FTIR spectra of humic fractions derived from UDPOME: (a)humic acid, (b)humic.....  | 83 |
| 20 | FTIR spectra of humic fractions derived from DPOME: (a)humic acid, (b)humic.....   | 84 |
| 21 | FTIR spectra of humic fractions derived from peat: (a)humic acid, (b)humic.....  | 85 |
| 22 | Effect of humic substances, matrixed with urea, on NH <sub>3</sub> volatilisation as compared to untreated control in soil A: (a)HA, (b)H, and soil B: (c)HA, (d)H.....  | 88 |
| 23 | Effect of HS source on NH <sub>3</sub> volatilisation in relation to matrixing ratio in soil A: (a)HA, (b)H, and soil B: (c)HA, (d)H.....  | 90 |
| 24 | Effect of matrixing ratio on NH <sub>3</sub> volatilisation in relation to HS source in soil A: (a)HA, (b)H, and soil B: (c)HA, (d)H.....  | 92 |
| 25 | Effect of humic substances, matrixed with urea, on NH <sub>4</sub> <sup>+</sup> -N recovery as compared to untreated control in soil A at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H.....                   | 94 |



|    |   |     |
|----|---|-----|
| 26 | Effect of humic substances, matrixed with urea, on $\text{NH}_4^+$ -N recovery as compared to untreated control in soil B at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H..... | 95  |
| 27 | Effect of HS source on $\text{NH}_4^+$ -N recovery in relation to matrixing ratio in soil A at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H.....                               | 97  |
| 28 | Effect of HS source on $\text{NH}_4^+$ -N recovery in relation to matrixing ratio in soil B at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H.....                               | 98  |
| 29 | Effect of matrixing ratio on $\text{NH}_4^+$ -N recovery in relation to HS source in soil A at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H.....                               | 100 |
| 30 | Effect of matrixing ratio on $\text{NH}_4^+$ -N recovery in relation to HS source in soil B at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H.....                               | 101 |
| 31 | Effect of humic substances, matrixed with urea, on pH change as compared to untreated control in soil A at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H.....                   | 102 |
| 32 | Effect of humic substances, matrixed with urea, on pH change as compared to untreated control in soil B at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H.....                   | 104 |
| 33 | Effect of HS source on pH change in relation to matrixing ratio in soil A at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H.....   | 106 |
| 34 | Effect of HS source on pH change in relation to matrixing ratio in soil B at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H.....   | 107 |
| 35 | Effect of matrixing ratio on pH change in relation to HS source in soil A at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H.....   | 108 |
| 36 | Effect of matrixing ratio on pH change in relation to HS source in soil B at microsite: (a)HA, (b)H, and at outersite: (c)HA, (d)H.....   | 109 |
| 37 | Trend of $\text{NH}_3$ volatilisation from HA treatments in soil A: (a) HAUD, (b) HAD, (c) HAP, and in soil B:  | 111 |
| 38 | Trend of $\text{NH}_3$ volatilisation from H treatments in soil A: (a) HUD, (b) HD, (c) HP, and in soil B: (d) HUD, (e) HD, (f) HP.....   | 112 |



## LIST OF APPENDICES

### Appendix

|   |   |     |
|---|---|-----|
| 1 | Additional figure   |     |
|   | Figure 39. Schematic representation of POME extraction and separation.....  | 139 |
| 2 | Analytical procedures   |     |
|   | A. Determination of carboxyl groups.....  | 140 |
|   | B. Determination of phenolic-OH groups.....   | 141 |
|   | C. Determination of quinonoid C=O groups.....   | 142 |
| 3 | Additional tables   |     |
|   | Table 7. ANOVA showing the effect of experimental variables studied in<br>Exp. 1 on % NH <sub>3</sub> volatilized in (a) soil A, (b) soil B.....  | 143 |
|   | Table 8. ANOVA showing the effect of experimental variables studied in<br>Exp. 1 on recovery of NH <sub>4</sub> <sup>+</sup> -N volatilized in (a) soil A at microsite,<br>(b) soil A at outersite, (c) soil B at microsite, (d) soil B at outersite.....                                 | 144 |
|   | Table 9. ANOVA showing the effect of experimental variables studied in<br>Exp. 1 on pH change occurring in (a) soil A at microsite, (b) soil A at<br>outersite, (c) soil B at microsite, (d) soil B at outersite.....   | 145 |
|   | Table 10. ANOVA showing the effect of experimental variables studied in<br>Exp. 2b, using <i>humic acid</i> , on % NH <sub>3</sub> volatilized in (a) soil A, (b) soil B.....   | 146 |
|   | Table 11. ANOVA showing the effect of experimental variables studied in<br>Exp. 2b, using <i>humic acid</i> , on recovery of NH <sub>4</sub> <sup>+</sup> -N volatilized in<br>(a) soil A at microsite, (b) soil A at outersite, (c) soil B at microsite,<br>(d) soil B at outersite..... | 147 |
|   | Table 12. ANOVA showing the effect of experimental variables studied in<br>Exp. 2b, using <i>humic acid</i> , on pH change occurring in (a) soil A at microsite,<br>(b) soil A at outersite, (c) soil B at microsite, (d) soil B at outersite.....  | 148 |



|   |     |
|---|-----|
| Table 13. ANOVA showing the effect of experimental variables studied in Exp. 2b, using <i>humin</i> , on % NH <sub>3</sub> volatilized in (a) soil A, (b) soil B.....   | 149 |
| Table 14. ANOVA showing the effect of experimental variables studied in Exp. 2b, using <i>humin</i> , on recovery of NH <sub>4</sub> <sup>+</sup> -N volatilized in (a) soil A at microsite, (b) soil A at outersite, (c) soil B at microsite, (d) soil B at outersite. | 150 |
| Table 15. ANOVA showing the effect of experimental variables studied in Exp. 2b, using <i>humin</i> , on pH change occurring in (a) soil A at microsite, (b) soil A at outersite, (c) soil B at microsite, (d) soil B at outersite.....                                 | 151 |



## LIST OF ABBREVIATIONS

### Non symbolic

|        |   |
|--------|---|
| ANOVA  | Analysis of Variance                    |
| ATS    | Ammonium thiosulfate                    |
| BOD    | Biochemical Oxygen Demand               |
| BTPT   | N-butyl thiophosphoric triamide         |
| CRD    | Completely Randomised Design            |
| DMRT   | Duncan's Multiple Range Test            |
| DPOME  | Decomposed Palm Oil Mill Effluent       |
| FTIR   | Fourier Transform Infra-Red             |
| H      | Humic acid                              |
| HA     | Humic Acid                              |
| HAD    | Humic acid derived from decomposed POME |
| HAP    | Humic acid derived from peat            |
| HAUD   | Humic acid derived from clarified POME  |
| HD     | Humic acid derived from decomposed POME |
| HP     | Humic acid derived from peat            |
| HUD    | Humic acid derived from clarified POME  |
| NMR    | Nuclear Magnetic Resonance              |
| PPDA   | Phenylphosphorodiamidate                |
| SCU    | Sulfur-coated urea                      |
| Soil A | Alkali soil                             |
| Soil B | Acid soil                               |
| TEA    | Triethanolamine                         |
| UAN    | Urea-Ammonium nitrate                   |
| UDPOME | Clarified Palm Oil Mill Effluent        |
| UP     | Urea-Phosphate                          |



## Symbolic

|  |                           |
|--|---------------------------|
| $(\text{NH}_4)_2 \text{CO}_3 \cdot \text{H}_2\text{O}$ | Ammonium carbonate        |
| $(\text{NH}_4)_2 \text{SO}_4$                          | Ammonium sulfate          |
| B  | Boron                     |
| C  | Carbon                    |
| $\text{Ca}(\text{OAc})_2$                              | Calcium acetate           |
| $\text{Ca}^{2+}$                                       | Calcium ion               |
| $\text{CaCl}_2$  | Calcium chloride          |
| $\text{CaCO}_3$  | Calcium carbonate         |
| $\text{CO}(\text{NH}_2)_2$                             | Urea                      |
| $\text{CO}_2$  | Carbon dioxide            |
| $\text{CO}_3^{2-}$                                     | Carbonate ion             |
| Cu   | Copper                    |
| H  | Hydrogen                  |
| $\text{H}_2\text{O}$                                   | Water                     |
| $\text{H}_2\text{SO}_4$                                | Hydrogen sulfate          |
| HCl  | Hydrogen chloride         |
| HF   | Hydrogen fluoride         |
| K  | Potassium                 |
| KBr  | Potassium bromide         |
| KCl  | Potassium chloride        |
| $\text{Mg}^{2+}$                                       | Magnesium ion             |
| Mn   | Manganese                 |
| N  | Nitrogen                  |
| $\text{NaHCO}_3$                                       | Sodium hydrogen carbonate |
| NaOH   | Sodium hydroxide          |
| $\text{NH}_4\text{NO}_3$                               | Ammonium nitrate          |
| OH   | Hydroxyl ion              |
| P  | Phosphorus                |
| $\text{SO}_4^{2-}$                                     | Sulfate ion               |



Abstract of the thesis submitted to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the Degree of Master of Agricultural Science.

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By

**SIVA KUMAR BALASUNDRAM**

May, 1997

Chairman : Assoc. Prof. Dr. Aminuddin Hussin

Faculty : Agriculture

Ammonia (NH<sub>3</sub>) volatilization is a major pathway of nitrogen loss which limits the efficiency of urea as a fertilizer when surface-applied to soils. High pH and low cation exchange capacity in soils have been identified as the principal causes of NH<sub>3</sub> volatilization from urea. The several approaches proposed to correct such inefficiency in urea, thus far, were fundamentally based upon delay of urea dissolution and impedance of urea hydrolysis.





An attempt was made to establish a preferred environment within the urea-soil reaction zone (microsite) using palm oil mill effluent (POME) and peat. Both POME and peat are organic matter-rich, and contain humic substances across their respective organic matrix. Humic substances have been shown to interact with ammoniacal compounds and urea. As such, a study was engaged to explore the effects of POME and peat, and their respective humic derivatives on  $\text{NH}_3$  volatilization from urea surface-applied to two Malaysian soils of contrasting pH values.

The organic materials and their humic derivatives were separately matrixed with urea into pelletised form and evaluated under laboratory regimes for %  $\text{NH}_3$  volatilization, pH change and  $\text{NH}_4^+$ -N recovery. Estimation of  $\text{NH}_3$  volatilization was carried out using a closed-dynamic air-flow system. Determination of the chemical and physical attributes of soils and materials, and measurement of the parameters studied were done using standard procedures. Characterisation of the POME- and peat-derived humic substances was performed using chemical and spectral methods.

Results showed that reduction in  $\text{NH}_3$  volatilisation by peat-treated urea was more pronounced than that of POME in both soils. Such reduction was accompanied by a corresponding increase in  $\text{NH}_4^+$  recovery and decrease in pH, particularly at the microsite. The use of differing matrixing ratios did not yield significant variation in the performance of matrixing agents. Acidification of POME and peat resulted in impedance of urea movement from microsite to outersite.

However, with humic substances, particularly humic acid, reduction in volatilisation was not accompanied by a corresponding increase in  $\text{NH}_4^+$  recovery.

Generally, results indicated that the mechanism governing the ability of peat and POME to reduce  $\text{NH}_3$  volatilisation from urea was  $\text{NH}_4^+$  adsorption. With humic substances, there appeared to be possible involvement of other mechanisms, i.e. urease inhibition, urea absorption and  $\text{NH}_3$  fixation. The chemical and spectral attributes of humic acids and humins closely corresponded with those reported elsewhere. Nevertheless, higher functional group values were obtained from the fractions under study.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains Pertanian.

**PENGGUNAAN EFFLUEN KILANG KELAPA SAWIT (POME) DAN  
GAMBUT UNTUK MENGURANGKAN PEMERUAPAN AMONIA DARI BAJA  
UREA.**

Oleh

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May, 1997

Pengerusi : Prof. Madya. Dr. Aminuddin Hussin

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Pemeruapan amonia ( $\text{NH}_3$ ) merupakan mekanisme utama kehilangan unsur nitrogen yang menghadkan kecekapan baja urea, khasnya apabila ditabur atas permukaan tanah. Ketinggian nilai pH dan keupayaan pertukaran kation yang rendah dalam tanah telah dikenalpasti sebagai punca utama pemeruapan  $\text{NH}_3$  dari urea. Setakat ini, pendekatan yang telah diutarakan untuk mencegah pemeruapan  $\text{NH}_3$  berlandaskan penangguhan pelarutan urea serta halangan proses hidrolisis urea.



Percubaan telah dijalankan menggunakan effluen kilang kelapa sawit (POME) dan gambut untuk mewujudkan persekitaran kimia yang sesuai di zon reaksi urea-tanah (kawasan mikro). Penggunaan POME dan gambut didorong oleh ketinggian kandungan bahan organik serta kehadiran bahan humik dalam matrik organik tersebut. Justeru itu, kajian berikut dikendalikan untuk menyelidik kesan POME dan gambut bersama dengan bahan humik masing-masing terhadap pemeruapan  $\text{NH}_3$  dari baja urea yang ditabur pada dua jenis tanah di Malaysia yang berbeza nilai pH.

Baja urea dirawat secara berasingan dengan POME/gambut dan bahan humik yang diekstrak, dijadikan matrik dalam bentuk pelet dan dinilai dari segi % pemeruapan  $\text{NH}_3$ , perubahan pH serta kepadatan  $\text{NH}_4^+$  dalam rejim makmal. Anggaran pemeruapan  $\text{NH}_3$  telah dibuat menggunakan kaedah sistem pengaliran udara dinamik pada keadaan tertutup. Penentuan sifat fizikal dan kimia tanah dan bahan organik serta pengukuran parameter kajian dibuat menggunakan kaedah piawai. Pencirian bahan humik berdasarkan kaedah kimia dan spektroskopi.

Keputusan menunjukkan penurunan dalam pemeruapan  $\text{NH}_3$  dari rawatan urea-gambut lebih ketara daripada rawatan urea-POME pada kedua jenis tanah. Penurunan  $\text{NH}_3$  teruap selari dengan peningkatan kepadatan  $\text{NH}_4^+$  dan pengurangan nilai pH, terutamanya di kawasan mikro. Penggunaan nisbah rawatan tidak menunjukkan perbezaan yang bermakna terhadap prestasi agen rawatan. Pengasidan POME dan gambut telah menghalang pergerakan urea dari kawasan mikro. Namun, rawatan menggunakan bahan

humik, khasnya asid humik, tidak menghasilkan penurunan  $\text{NH}_3$  teruap yang selari dengan peningkatan dalam kepadatan  $\text{NH}_4^+$ .

Secara keseluruhan, keputusan mengimplicasikan bahawa penyerapan  $\text{NH}_4^+$  merupakan mekanisme yang beroperasi dalam penurunan  $\text{NH}_3$  teruap pada rawatan urea-POME dan urea-gambut. Bagi rawatan urea-bahan humik, adalah disyaki mekanisme lain seperti perencatan enzim 'urease', penyerapan urea dan pengikatan  $\text{NH}_3$  beroperasi secara serentak. Sifat kimia dan spektroskopi bahan humik yang dikaji didapati selaras dengan hasil kajian lain yang telah dilaporkan. Walaubagaimanapun, analisa kumpulan berfungsi bahan humik yang dikaji menunjukkan nilai yang lebih tinggi.

## CHAPTER I

### INTRODUCTION

Nitrogen (N) is the most common and widely used fertiliser nutrient. Produced primarily as ammonia, it can be applied as such or further processed into a variety of liquid or solid N fertilisers. Among solid N fertilisers, urea is most popular because of its low handling, storage and transportation costs, low energy consumption and less pollution during manufacture, and high N analysis (46%). Urea is suitable to be applied in solution, as solids, foliar spray, components of high analysis compound fertiliser and bulk blends (Nayan, 1982).

Although urea is equivalent to other nitrogenous fertilisers (Van Lierop and Tran, 1980) poor crop responses to urea have frequently been observed. A number of studies have identified ammonia ( $\text{NH}_3$ ) volatilisation as the major cause of low N efficiency in urea (Mikkelsen *et al.*, 1978; Fillery *et al.*, 1984) where as much as 80% of the applied urea-N may be lost within 2-3 weeks of application (Torello *et al.*, 1983; Hargrove and Kissel, 1979). As the major pathway of N loss in urea,  $\text{NH}_3$  volatilisation not only reduces N turnover in agricultural systems but also causes environmental pollution.

In soil, urea is first molecularly diffused and then hydrolysed to ammonium bicarbonate by the microbially-produced enzyme urease under favourable conditions. The

resultant high pH, often exceeding 8.5 (Fenn and Richards, 1986), within the area surrounding urea granules renders instability to ammonium ions ( $\text{NH}_4^+$ ) thus promoting  $\text{NH}_3$  volatilisation. The magnitude of  $\text{NH}_3$  volatilisation can be ascribed to soil properties, external factors and agrotechnical procedures which operate interactively in dimensions not easily perceptible. Remedial efforts to address the problem of  $\text{NH}_3$  volatilisation have accentuated over the years yielding potential control methods such as urease inhibitors, urea coatings, slow-release urea polymers, and addition of neutral salts and mineral acids. These approaches have principally dealt with either impedance of urea hydrolysis or delaying dissolution of urea.

Numerous findings have attributed  $\text{NH}_3$  volatilisation to high pH and low cation exchange capacity (CEC) in soil (Whitehead and Rainstrick, 1990, 1993; Santra *et al.*, 1988) while a few have elucidated in terms of soil hydrogen buffering capacity (HBC) (Ferguson *et al.*, 1984; Hargrove, 1988). In general, soil pH, CEC and HBC are factors that interact reciprocally, whereby high pH catalyses an increase in CEC resulting in a decline in HBC. Urea inefficiency due to  $\text{NH}_3$  volatilisation has been demonstrated on relatively low pH-tropical soils (Khanif, 1992), which was attributed to sufficient increase in pH at the urea-soil reaction zone (microsite). This concept sanctioned the search for a material that could introduce a preferred environment within the microsite. One such material has been the palm oil mill effluent (POME) (Aminuddin, 1994), while the other being peat (Aminuddin *et al.*, 1994). In both studies,  $\text{NH}_3$  volatilisation was successfully reduced to 8% and 4% of the applied N, respectively. Palm oil mill effluent and peat, both

rich in organic matter, are believed to contain varying amounts of humic substances across their respective organic matrix.

As bulk constituents of organic matter, humic substances have been reported to interact with ammoniacal compounds (Banerjee and Basak, 1978; Thorn and Mikita, 1992) *via* adsorption and fixation mechanisms respectively, and urea (Patti *et al.*, 1992) through inhibition of nitrification. Structural explication of humic substances have indicated presence of quinones (Schnitzer, 1982), a widely documented class of urease inhibitors, in fractional amounts. Thus, there appears to be a potential for humic substances, derived either from POME or peat, to address the problem of NH<sub>3</sub> volatilisation. At present, there is no published reports which have elucidated the effect of POME or peat-derived humic substances on urea *per se* which leads to alleviating NH<sub>3</sub> volatilisation.

As such, a study was engaged with the following objectives:

- i) to investigate the effects of POME and peat on NH<sub>3</sub> volatilisation
- ii) to characterise humic substances derived from POME and peat, and to study their effect on NH<sub>3</sub> volatilisation
- iii) to elucidate the chemistry between humic substances and urea, in retarding NH<sub>3</sub> volatilisation.



## CHAPTER II

### REVIEW OF LITERATURE

#### Urea

In the past, ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) was widely available as a non-volatile N source but economics of production now favour urea. The new generation of urea production facilities have the advantage of the latest technology and economies of size. Hence, the proportion of urea procurable in the fertiliser market is rapidly increasing.

Despite being the cheapest dry N fertiliser available to agriculture, use of urea is plagued by the problem of  $\text{NH}_3$  volatilisation. An upsurge of interest in  $\text{NH}_3$  volatilisation has occurred over the years due to evidence from agronomic nitrogen-balance studies that generally showed an unexplained 10-80% loss of applied fertiliser nitrogen (Hargrove and Kissel, 1979; Legg and Meisinger, 1982; Torello *et al.*, 1983). Various efforts have been undertaken to address the problem, however, the problem still persists to an extent which significantly limits urea efficiency.

