

UNIVERSITI PUTRA MALAYSIA

AMMONIA VOLATILIZATION AND PHOSPHATE RELEASE FROM COMPACTED MIXED FERTILIZERS IN PURE SYSTEM AND IN AN ACID SOIL

SUSILAWATI BINTI KASIM

FP 2003 25



AMMONIA VOLATILIZATION AND PHOSPHATE RELEASE FROM COMPACTED MIXED FERTILIZERS IN PURE SYSTEM AND IN AN ACID SOIL

SUSILAWATI BINTI KASIM

MASTER OF AGRICULTURAL SCIENCE UNIVERSITI PUTRA MALAYSIA 2003



AMMONIA VOLATILIZATION AND PHOSPHATE RELEASE FROM COMPACTED MIXED FERTILIZERS IN PURE SYSTEM AND IN AN ACID SOIL

Ву

SUSILAWATI BINTI KASIM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Agricultural Science

July 2003



Dedicated to.....

All my family members especially my mother, father and siblings who have supported me along my way to success.....

I love you all.....



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in Fulfilment of the requirements for the degree of Master of Agricultural Science

AMMONIA VOLATILIZATION AND PHOSPHATE RELEASE FROM COMPACTED MIXED FERTILIZERS IN PURE SYSTEM AND IN AN ACID SOIL

By

SUSILAWATI BINTI KASIM

July 2003

Chairman : Associate Professor Aminuddin Bin Hussin, Ph.D.

Faculty : Agriculture

Urea and phosphate rock (PR) have been widely used in Malaysian agriculture. However, ammonia (NH₃) volatilization and slow release of P are two major problems encountered when urea and PR fertilizers were used. High pH, Al and Fe oxides content and low cation exchange capacity (CEC) have been identified as causing these problems in soil. Peat and triple superphosphate (TSP) may be mixed to supply humic substances from peat to reduce P fixation, N loss and proton (H⁺) from TSP to solubilize PR in water and soil. Thus, a study was initiated to investigate the effect of these mixed fertilizers on NH₃ volatilization and dissolution of PR in a pure system and in an acid soil. Various combinations of urea, TSP, CIPR fertilizers and peat were compacted and studied in the two systems in the laboratory. In pure system, the N loss following addition of peat (5.09%) is better than TSP (28.15%). Four combinations of fertilizers gave the second highest P



dissolution (70.53%) at day one and day 10 (71.15%) based on changes in P released (ΔP) method after urea plus TSP and peat. Almost 40% of changes in Ca released (Δ Ca) was detected in solution when any combination of TSP and Christmas Island Phosphate Rock (CIPR) was used in the mixture after 10 days. This is due to the production of phosphoric acid by TSP. Surface application of compacted mixed fertilizer on the soil showed that urea plus TSP and CIPR and urea plus TSP and peat managed to decrease the loss of N by nearly 50% compared to only urea. This is due to the production of Ca²⁺ by P sources and additional CEC by peat. Delay in the peak N loss differed with fertilizer combinations: urea + TSP +CIPR (3 days), urea + TSP + CIPR + peat (7 days), urea + TSP + peat (7 days) and urea + peat (5 days). The CIPR and peat mixture showed the highest ΔP value (394.66 mg kg⁻¹) after 90 days of incubation in soil. On a verage, the highest (310.98 mg kg⁻¹) P dissolution as measured by ΔP method was obtained using urea plus TSP, CIPR and peat. This was attributed to the protons supplied by TSP and Casink from peat which promoted the dissolution of PR in mixed fertilizer. Thus, compacted mixed fertilizer is an effective way to decrease NH₃ volatilization and increase ΔP in soil and pure system. However, this depends on the combination of the fertilizers used.



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

PEMERUAPAN AMONIA DAN PELEPASAN FOSFAT DARI CAMPURAN BAJA DALAM SISTEM TULEN DAN DALAM TANAH BERASID

Oleh

SUSILAWATI BINTI KASIM

Julai 2003

Pengerusi : Profesor Madya Aminuddin Bin Hussin, Ph.D.

Fakulti : Pertanian

Urea dan batuan fosfat (PR) telah digunakan dengan meluas dalam pertanian di Malaysia. Walaubagaimanapun, pemeruapan ammonia (NH₃) dan pelepasan phosphorus (P) yang perlahan merupakan dua masalah utama apabila kedua-dua baja ini digunakan. Nilai pH serta kandungan oksida Al dan Fe yang tinggi dan keupayaan pertukaran kation (KPK) yang rendah telah dikenalpasti sebagai punca masalah ini. Gambut dan baja triple supersphosphate (TSP) boleh dicampur untuk membekalkan bahan humik bagi mengurangkan pengikatan P dan kehilangan N, dan punca proton (H⁺) bagi merangsang pelarutan PR. Oleh itu, satu kajian telah dijalankan untuk menyelidik kesan campuran baja ini terhadap pemeruapan NH₃ dan pelarutan PR dalam sistem tulen dan tanah berasid (Siri Munchong). Beberapa kombinasi baja urea, TSP, CIPR dan gambut telah dipadatkan untuk kajian dalam sistem tulen dan pengeraman dengan tanah yang dilakukan di makmal. Dalam sistem tulen, kehilangan N oleh urea dengan



penambahan gambut (5.09%) adalah lebih baik dari TSP (28.15%). Kombinasi e mpat j enis baja memberikan p elarutan P k edua tertinggi p ada hari pertama (70.53%) dan 10 (71.15%) selepas campuran urea, TSP dan gambut. Hampir 40% p erubahan Ca (ΔCa) t elah d ikesan di d alam larutan apabila TSP dan Christmas Island Phosphate Rock (CIPR) digunakan sebagai sebahagian daripada campuran baja selepas 10 hari. Ini disebabkan oleh penghasilan asid fosforik oleh TSP. Pemberian baja di permukaan tanah menunjukkan, kombinasi urea dengan TSP dan CIPR dan urea dengan TSP dan gambut menurunkan kehilangan N hampir 50%. Ini disebabkan oleh penghasilan Ca²⁺ dari sumber P dan penambahan KPK dari gambut. Perlambatan nilai tertinggi kehilangan N berbeza mengikut kombinasi baja: urea + TSP + CIPR (3 hari), urea + TSP + CIPR + gambut (7 hari), urea + TSP + gambut (7 hari) dan urea + gambut (5 hari). Campuran gambut dan CIPR memberikan ΔP tertinggi (394.66 mg kg⁻¹- hari ke 90). Secara puratanya, nilai tertinggi (310.98 mg kg⁻¹) pelarutan sumber P, diukur berdasarkan ΔP diberikan oleh urea, TSP, CIPR dan gambut. Ini disebabkan oleh penambahan proton (H⁺) dari TSP dan takungan Ca (Ca-sink) dari gambut telah merangsang pelarutan sumber P dalam campuran baja. Maka, campuran baja merupakan cara yang efektif untuk mengurangkan pemeruapan NH₃ dan meningkat ΔP dalam tanah dan sistem tulen. Walaubagaimanapun, ianya bergantung kepada kombinasi baja yang digunakan.



ACKNOWLEDGEMENTS

Alhamdulillah, I pray to Allah that gave me strength in finishing my research and thesis. First of all, I would like to convey my gratitude to my supervisor (Assoc. Prof. Dr. Aminuddin Bin Hussin) who has given me the opportunity, advice and strong encouragement in my research. I am proud to be supervised by him and hopefully this will guide me to success. Appreciation also goes to Assoc. Prof. Dr. Mohd Khanif Bin Yusop and Assoc. Prof. Dr. Mohd Hanafi Bin Musa for being my supervisory committee members and for their guidance, cooperation and support in my study.

I am grateful to my beloved parent and family members for their support and understanding in what ever situation. They are always beside me. Special appreciation to Kak Nah, Kak Fid, Kak Umi, Kak Farid, Kak Shima, En. Rahim, Wak, Kak Ogy and Kak Sarimah from Department of Land Management for their technical assist.

I also record my special gratitude to Nor Diana Mohd Idris (Kolej Shah Putra, Pekan) for her motivation, inspirational words of wisdom and being a caring friend. I really appreciate what she had done for me. Lastly, special thanks to my friends Lin, Muryaty and Wan for their assistance in the laboratory and data analysis. All of you will always be in my mind.



TABLE OF CONTENTS

		Page
DEDICATION		iii v vii viii x xiv
СНА	PTER	
1	INTRODUCTION	1.1
2	LITERATURE REVIEW 2.1 Soil Phosphorus 2.2 Reactions of Phosphate Fertilizers in Soils 2.3 Phosphorus Retention 2.3.1 Soil Properties 2.3.1.1 Clay Content 2.3.1.2 pH 2.3.1.3 Hydrous Oxides of Fe and Al 2.4 Phosphate Rock 2.5 Phosphate Mineralogy 2.6 Factor Affecting Released and Available P in Soil 2.6.1 Soil Factor 2.6.1.1 Acidity 2.6.1.2 Soil Moisture 2.6.1.3 Ca Sink 2.6.1.4 P Sink 2.6.1.5 Organic Matter 2.7 Soil Nitrogen 2.8 Urea 2.9 Ammonia Volatilization 2.10 Factors Affecting Losses of Ammonia	2.12.32.42.42.52.72.82.92.102.102.112.12
	2.10.1 Soil Factor	2.15 2.16
	2.10.1.3 Cation Exchange Capacity	



	2.10.2.1 Soil Moisture	2.17
	2.10.2.2 Temperature	
	2.11 Control of Ammonia Volatilization	
	2.11.1 Coating	2.18
	2.11.2 Urease Inhibitors	
	2.11.3 Altering the N Fertilizer Microsite	
	2.12 Peat	
	2.13 Mixed Fertilizer	
	2.13.1 Mixture of PR with Urea	
	2.13.2 Mixture of PR with Soluble Phosphate Fertilizer	
	2.13.3 Mixture of Soluble Phosphate Fertilizer with Urea	
	2.13.4 Mixture of PR with Organic Matter	
	2.13.5 Mixture of Organic Matter with Urea	2.25
	2.14 Interaction of N and P Fertilizer	
	2.15 Summary	2.26
3	MATERIAL C AND METHODS	2.4
3	MATERIALS AND METHODS	
	3.1 Soils and Peat	. O. I
	3.1.2 Soil and Peat Sampling	3.1 3.1
	·	
	3.1.3 Soil and Peat Analyses	
	3.2.1 Description of P Sources	
	3.2.2 Preparation of P Sources	
	3.2.3 Solubility of P Fertilizer	
	3.2.4 Total Ca and P in PR and TSP	
	3.3 Preparation of Fertilizer Pellet	
	3.4 Ammonia Volatilization and PR Dissolution in Pure	5.5
	System	3.5
	3.5 Ammonia Volatilization in Soil	3.7
	3.5.1 Estimation of Ammonia Volatilization	
	3.6 Phosphate Rock Dissolution in Soil	
	3.6.1 Soil Analysis	
	3.7 Statistical Analysis.	
	,	
4	RESULTS AND DISCUSSION	4.1
	4.1 Physical and Chemical Characteristic of Soil and Peat	4.1
	4.2 Chemical Characteristic of the P Sources	
	4.3 Ammonia Volatilization and PR Dissolution in Pure	
	System	4.3
	4.3.1 Losses of N	4.3
	4.3.2 Urea-N and Ammonium-N Recovery	4.11
	4.3.3 Dissolution of PR	4.18
	4 2 2 1 AD	1 10



	4,3.3.2 ΔCa	4.23	
	4.4 Effect of Compacted Mixture Fertilizer Placement on		
	Ammonia Volatilization in Soil	4.27	
	4.4.1 Surface Application	4.27	
	4.4.2 Mixed Method		
	4.5 Phosphate Rock Dissolution in Soil	4.35	
	4.5.1 Dissolution of PR Measured by ΔP	4.35	
	4.5.2 Dissolution of PR Measured by ΔCa	4.45	
5	CONCLUSIONS	5.1	
REFERENCES		R.1	
VITA		V.1	



LIST OF TABLES

Table		Page
3.1	Treatment used in NH ₃ Volatilization and PR Dissolution in Pure System	3.7
3.2	Treatment used in Ammonia Volatilization in Soil	3.9
3.3	Treatment used in PR Dissolution in Soil	3.11
4.1	Chemical and Physical Properties of the Soil and Peat used in the Laboratory Experiment	4.2
4.2	Solubility of P Fertilizer and Total P and Ca	4.4
4.3	Effect of Compacted Mixture Fertilizer on Losses of N at Day Ten	
4.4	Changes in Pure System pH in Urea plus Peat Mixture	4.8
4.5	The IP Value and Status of (NH ₄)H ₂ PO ₄	4.10
4.6	Changes in Pure System pH in Urea plus TSP Mixture	4.11
4.7	Effect of Compacted Mixture Fertilizer on Urea-N and NH ₄ ⁺ -Recovery at Day Ten	
4.8	ΔP Measured in Pure System at Day One	4.19
4.9	ΔP Measured in Pure System at Day Ten	4.20
4.10	ΔCa Measured in Pure System at Day One	4.24
4.11	ΔCa Measured in Pure System at Day Ten	4.25
4.12	Cumulative of N Loss in All Treatments at the End of Incubation.	4.31
4.13	Comparison of pH, P, Ca and NH ₄ ⁺ ion in Different Treatments	4.31



4.14	Effect of Mixing of Fertilizer with Soil on NH ₄ ⁻ -N Recovery	4.34
4.15	ΔP and pH Value Measured at Day One	4.38
4.16	ΔP and ΔpH Measured in Urea plus CIPR and Peat Mixture	4.39
4.17	ΔP Measured from Compacted Mixture Fertilizer	4.42
4.18	ΔP Measured at Day 90	4.42
4.19	ΔP Measured in 90 Days	4.45
4.20	ΔCa Measured at Day One	4.47
4.21	ΔCa Measured at Day 90	4.49
4.22	Relationship between ΔCa Measured and the Ca-sink Size of Mixed Fertilizer Incubated with Munchong Soil at 90 Days	4.53



LIST OF FIGURES

Figure	F	age
4.1 (A)	Daily N Loss in Pure System	4.5
4.1 (B)	Daily N Loss in Pure System	4.6
4.2 (A)	Daily Urea-N Recovery in Pure System	4.13
4.2 (B)	Daily Urea-N Recovery in Pure System	4.14
4.3 (A)	Daily NH ₄ ⁺ -N Recovery in Pure System	4.16
4.3 (B)	Daily NH ₄ ⁺ -N Recovery in Pure System	4.17
4.4	Relationship between pH and NH ₄ ⁺ -N Recovery	4.19
4.5	Effect of Compacted Mixture Fertilizer on mean PR Dissolution	4.22
4.6	Effect of Compacted Mixture Fertilizer on Dissolution PR Measured by ΔP Method	
4.7	Effect of Compacted Mixture Fertilizer on Dissolution of PR Measured by ΔCa Method	4.25
4.8	Effect of Compacted Mixture Fertilizer on ΔCa	4.27
4.9	Daily NH ₃ Volatilization Loss from Surface Applied Mixed Fertilizers	4.28
4.10	Cumulative NH ₃ Volatilization Loss from Surface Appl Mixed Fertilizers	
4.11	The Dissolution of P Sources as Measured by ΔP in 90 Days Incubation Period	4.36
4.12	Relationship between ΔP and ΔpH in Urea plus CIPR	4.40
4.13	Relationship between ΔP and ΔpH in CIPR	4.41



4.14	in 90 Days Incubation Period	4.46
4.15	Effect of Compacted Mixture Fertilizer on ΔCa Measured in 90 Days	4.51
4.16	Relationship between % ΔP and % ΔCa from Compacted Mixture Fertilizer	4.54



LIST OF ABBREVIATIONS

Non Symbolic

UPR Udaipur phosphate rock

CIPR Christmas island phosphate rock

CEC Cation exchange capacity

FC Field capacity

UPM University Putra Malaysia

AAS Atomic absorption spectrophotometer

CRD Completely randomised design

AA Auto analyser

ANOVA Analysis of variance

DMRT Duncan's multiple range test

DCPD Dicalciumphosphate dehydrate

NaOH Sodium hydroxide

TSP Triple superphosphate

SSP Single superphosphate

PR Phosphate rock

MAP Monoammonium phosphate

WSP Water-soluble phosphate

NH₃ Ammonia

IP Ion Product

K_{sp} Solubility Product

SE Standard Error



Symbolic

OH $^{-}$ Hydroxyl ion NH $_{4}$ $^{+}$ Ammonium ion Hidrogen ion

 $(NH_4)H_2PO_4$ ammonium phosphate $Ca(H_2PO_4)_2$ monocalcium phosphate

KCI Potassium chloride

H₂SO₄ Sulfuric acid

 $K_2Cr_2O_7$ Potassium dikromat H_3PO_4 Orthophosphoric acid

 $C_{12}H_{10}NH$ Diphenylamine Na_2SO_4 Sodium sulphate $HCIO_4$ Perchloric acid

KOH Potassium hydroxide

NaOAc Sodium acetate

 NO_2 Nitrite NO_3 Nitrate

NO Nitric oxide

N₂ Nitrogen gas



CHAPTER 1

INTRODUCTION

The use of fertilizer has been the forefront in the struggle to increase world food production. Over the past two-and-a-half decades, the aggregate consumption of fertilizers has increased substantially. Malaysian fertilizer consumption has steadily increased with time and the fertilizer application rate is relatively high at about 111 kg of nutrient per ha (Maene *et al.*, 1988). Total fertilizer consumption in Malaysia increased from 964,000 Mt (1992) to 1,130,717 Mt (2001) and the use of phosphate fertilizer in 2001 is 158,800 Mt (FAO, 2003). According to Malaysia Agricultural Directory and Index 1999 - 2000, changes in Malaysian agriculture increased the fertilizer consumption.

Nitrogen (N) is the major nutrient used in the fertilization of crops. More than 75% of the total fertilizer N use in Asia is in the form of urea (Mikkelsen, 1987). It is the leading N fertilizer used in the world agriculture with an N content of approximately 46%; has the edge in terms of price per unit N, storage space and transportation costs over other N sources (Harre and Bridges, 1988). Usage of urea in Malaysia in 2001 is 134,000 Mt (FAO, 2003).



Although urea has been the choice fertilizer used in supplying N, the efficiency of this fertilizer is low. One major problem encountered in using urea is loss through volatilization. Eighty percent of applied urea-N may be lost within 2 - 3 weeks after application (Torella *et al.*, 1983). In flooded condition, increased in pH and ammonium ion (NH₄^T) concentration occurred especially when the fertilizer is broadcast and when the water level is low (Vlek and Stumpe, 1978). It is common for farmers to loose 70% of the applied urea (Wetselaar *et al.*, 1984; Pasandaran *et al.*, 1999).

Surface application of urea often resulted in high ammonia (NH₃) volatilization. High urease activity and excessive increase in microsite pH that occurred during urea hydrolysis gave significant losses of N through volatilization (Khanif and Pancras, 1988). Previous research in this area suggests that the efficiency of urea can be improved by correct time of applications, deep placement, slow release, or the use of biological inhibitors (Craswell, 1988).

Another approach in reducing NH₃ volatilization is applying urea together with acidic phosphatic fertilizer. Combining urea with phosphate fertilizer offer several advantages; simultaneous and uniform application of several nutrients and save on distribution costs (Fan *et al.*, 1996). The agronomic efficiency of urea can be improved when combined in an intimate



mixture with triple superphosphate (TSP) or monoammonium phosphate (MAP), while urea hydrolysis rate in acid soils could be reduced with addition of TSP (Fan and MacKenzie, 1993^a, Fan and MacKenzie, 1994, Fan et al., 1996)

Generally, the amount of plant available phosphorus (P) in Malaysian soils is low. This is due to high soil acidity and high fixation of P by Fe and Al oxides and hydroxides (Havlin et al., 1999). Water soluble-P fertilizers, such as TSP and single superphosphate (SSP) have normally been used to fulfill the P requirement of plants. In developing countries, used of these fertilizers are limited primarily by their higher costs. To reduce production and capital cost, the use of phosphate rock (PR) as direct application has been suggested (Chien et al., 1996).

Although direct application of PR may be a cost effective mean to supply P, PRs with low and medium reactivity often do not perform as well as soluble P fertilizers (Chien et al., 1990, Chien and Friesen, 1992) Mixing PR with soluble P fertilizer (TSP) significantly increased the available P and solubility of PR (Chien et al., 1996)

In some developing countries, there is a growing interest in the use of mixtures of PR with N fertilizer for direct application (Chien, 1978). Nitrogen



fertilizer increases the availability of P from PR to the plants, whilst Ca content in P fertilizer influences NH₃ volatilization (Fenn *et al.*, 1981).

There are some good advantages offered when organic matter was mixed together with urea and P fertilizer. Hydrolysis of urea which was occurred as soon as it was introduced into the soil leads to dissolved organic matter due to the increase in pH and NH₄⁺. Dissolution of this organic matter could increase the transport of P in soils (Qualls and Haines, 1991), decrease P fixation and improve P availability (Chien *et al.*, 1987). However, humic and fulvic acids from organic matter would form soluble salt with NH₄⁺ (Stevenson, 1982). These two beneficial processes make P and N available in soil solution.

Addition of acidic phosphate fertilizer to this mixture may result in reactions that will influence the solubility of PR and availability of NH₄⁺ in soil. Hence, the general objective of the present research was to investigate the effect of fertilizer mixture consisting of urea, P and organic matter on the NH₃ volatilization and dissolution of PR in pure system and in an acid soil. The specific objectives were to determine and compare the effect of various mixture fertilizers on NH₃ volatilization and PR dissolution in pure system and in an acid soil.

