



**UNIVERSITI PUTRA MALAYSIA**

***EFFECTS OF Cu AND Zn COATED UREA ON RICE PRODUCTION IN  
ACIDIC AND ALKALINE SOILS***

**SAIMA KALSOOM BABAR**

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ACIDIC AND ALKALINE SOILS**

**By**

**SAIMA KALSOOM BABAR**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra  
Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of  
Philosophy**

**July 2016**

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in  
fulfilment of the requirement for the degree of Doctor of Philosophy

## **EFFECTS OF Cu AND Zn COATED UREA ON RICE PRODUCTION IN ACIDIC AND ALKALINE SOILS**

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**SAIMA KALSOOM BABAR**

**July 2016**

**Chairman : Prof. Mohd Khanif bin Yusop, PhD**  
**Faculty : Agriculture**

Acidic soils of Malaysia and alkaline soils of Pakistan are in incidence of micronutrient insufficiency. Despite of that urea is considered as the most broadly used nitrogen (N) fertilizer. Unfortunately, its application is associated with losses such as emissions of ammonia ( $\text{NH}_3$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ) gases. In couple to the economic loss, such N losses may threaten atmospheric quality and results in poor plant synchrony. Application of both urease and nitrification inhibitors is encouraged as an approach to mitigate these gaseous losses. The rate of urea hydrolysis is accelerated as it remains in conventional form and about 70% of applied urea losses. Ammonia volatilization ( $\text{NH}_3$ ) is a substantial loss of urea. Therefore, to minimize  $\text{NH}_3$  volatilization and to supply the adequate Cu and Zn was the major aim of this research. Copper and Zn status were evaluated in selected paddy soils of Malaysia and Pakistan. Based on the results, Kuala Kedah and Chempaka soil series were below the critical level (Cu 0.1-1.0  $\text{mg kg}^{-1}$  and Zn 0.5-3.0  $\text{mg kg}^{-1}$ ) according to the method Mehlich-I in Malaysia, whereas in Pakistan Rustum soil series was below the critical level on Zn ( AB-DTPA 0.5  $\text{mg kg}^{-1}$ ). Soils deficient in Cu and Zn were selected for this current study. The research was based on trials conducted at: (1) laboratory; (2) glass house; and (3) field conditions. Copper and Zn coated urea was prepared manually, where micronutrient fertilizer sources copper sulphate (3 and 5  $\text{kg ha}^{-1}$ ) and zinc sulphate (7 and 10  $\text{kg ha}^{-1}$ ) were used. Palm stearin was used as coating material to overlap Cu and Zn on urea. The specific aims of this study were to evaluate the effect of Cu and Zn coated urea on: (1)  $\text{NH}_3$  volatilization loss; (2) yield components of rice under acidic and alkaline soils; and (3) fluctuation of soil Eh and pH. In this regard a laboratory study was conducted on two acidic soil series of Malaysia. Results revealed that 50% less  $\text{NH}_3$  volatilization loss was observed under Cu and Zn coated urea treated soils as compared to common urea. After the positive results found in laboratory testing of Cu and Zn coated urea, a glass house study was designed to evaluate its effect on rice and Cu and Zn availability. Copper (3 and 5  $\text{kg ha}^{-1}$ ) and Zn (7 and 10  $\text{kg ha}^{-1}$ ) either alone or in combinations were applied as surface application or coated with urea followed by recommended doses of P and K (70  $\text{kg ha}^{-1}$ ). Results manifested that Cu and Zn coated urea controlled fluctuating pH, Eh and

facilitated Cu and Zn availability. The Cu and Zn had positive effect on growth, yield and nutrients concentration in rice plants. There was 40.9% yield increment over control under acidic soils. To confirm the results of glass house, a filed study was conducted on alkaline soils of Pakistan. Copper and Zn were applied all in coated form either alone or in the combinations (Cu3, Cu5, Zn10 and Zn15 kg ha<sup>-1</sup>) followed by the recommended doses of P (70 kg ha<sup>-1</sup>) and K (50 kg ha<sup>-1</sup>). Copper and Zn coated urea showed the positive response on the growth and yield of rice (50% grain yield increment was obtained over control). Coated urea increased the Cu, Zn and N contents in soil and plants.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia  
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

## **KESAN UREA BERSALUT Cu DAN Zn TERHADAP PENGHASILAN PADI DI TANAH BERASID DAN ALKALI**

Oleh

**SAIMA KALSOOM BABAR**

**Julai 2016**

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Tanah berasid Malaysia dan tanah alkali Pakistan berada dalam insiden mikronutrien kekurangan. Walaupun urea yang dianggap sebagai baja nitrogen paling meluas digunakan (N). Malangnya, permohonan dikaitkan dengan kerugian seperti pelepasan ammonia ( $\text{NH}_3$ ) dan nitrus oksida ( $\text{N}_2\text{O}$ ) gas. Dalam beberapa kepada kerugian ekonomi, kerugian N itu boleh mengancam kualiti atmosfera dan menyebabkan synchrony tumbuhan miskin. Permohonan kedua-dua urease dan penitritan perencat digalakkan sebagai satu pendekatan untuk mengurangkan ini kerugian gas. Kadar urea hidrolisis dipercepatkan kerana ia masih dalam bentuk konvensional dan kira-kira 70% daripada kerugian urea digunakan. Pemeruapan ammonia ( $\text{NH}_3$ ) adalah satu kehilangan besar urea. Oleh itu, untuk mengurangkan  $\text{NH}_3$  pemeruapan dan untuk membekalkan Cu mencukupi dan Zn adalah matlamat utama kajian ini. Dan menyediakan Cu dan Zn yang cukup adalah matlamat utama kajian ini. Kuprum dan Zn status di analisa pada tanah padi di Malaysia dan Pakistan. Berdasarkan keputusan, tanah siri Kuala Kedah dan Chempaka adalah di bawah paras krikital (Cu  $0.1\text{-}1.0 \text{ mg kg}^{-1}$  dan Zn  $0.5\text{-}3.0 \text{ mg kg}^{-1}$ ) berdasarkan kaedah Mehlich-1 di Malaysia manakala tanah siri Pakistan Rustum berada di bawah paras kritikal untuk Zn (AB-DTPA  $0.5 \text{ mg kg}^{-1}$ ). Tanah yang kekurangan Cu dan Zn dipilih untuk kajian ini. Kajian ini berdasarkan percubaan pada: (1) makmal; (2) rumah kaca; (3) ladang. Urea bersalut disediakan secara manual. Di mana baja miknonutrien sebagai sumber Kuprum sulfat (3 dan  $5 \text{ kg ha}^{-1}$ ) dan zink sulfat (7 dan  $10 \text{ kg ha}^{-1}$ ) digunakan. Stearin kelapa sawit digunakan sebagai bahan penyalut untuk melekatkan Cu dan Zn pada urea. Matlamat spesifik kajian ini adalah untuk menganalisa kesan urea bersalut Cu dan Zn terhadap: (1) penguapan  $\text{NH}_3$ ; (2) komponen hasil padi pada tanah berasid dan beralkali; dan (3) turun naik Eh dan pH tanah. Berdasarkan matlamat di atas, kajian makmal dijalankan pada dua siri tanah berasid Malaysia. Keputusan menunjukkan kurang 50% kehilangan penguapan ammonia ditunjukkan pada tanah yang dirawat oleh urea bersalut Cu dan Zn berbanding urea biasa. Selepas keputusan yang positif diperoleh di makmal pada urea bersalut Cu dan Zn, kajian di rumah kaca dibuat untuk menilai kesan pada padi dan keberadaan Cu dan Zn. Kuprum ( $3 \text{ dan } 5 \text{ kg ha}^{-1}$ ) dan Zn ( $7 \text{ dan } 10 \text{ kg ha}^{-1}$ )

Samada Cu dan Zn sahaja atau gabungan keduanya digunakan pada aplikasi permukaan atau bersalut urea diikuti dengan dos yang P dan K yang dicadangkan ( $70 \text{ kg ha}^{-1}$ ). Keputusan membuktikan urea bersalut Cu dan Zn mengawal turun naik pH, Eh dan memudahkan keberadaan Cu dan Zn. Cu dan Zn mempunyai kesan positif terhadap pertumbuhan, hasil dan kepekatan nutrient di dalam padi. 40.9% peningkatan hasil berbanding rawatan kawalan pada tanah berasid. Untuk memastikan lagi keputusan yang diperoleh dari rumah kaca, kajian di ladang dilakukan pada tanah beralkali Pakistan. Kuprum dan Zn disalurkan pada semua samada Cu dan Zn sahaja atau gabungan kedua-duanya ( $\text{Cu}_3$ ,  $\text{Cu}_5$ ,  $\text{Zn}_{10}$  dan  $\text{Zn}_{15} \text{ kg ha}^{-1}$ ) diikuti oleh dos P ( $70 \text{ kg ha}^{-1}$ ) dan K ( $50 \text{ kg ha}^{-1}$ ) yang disyorkan. Urea bersalut Cu dan Zn menunjukkan respon positif terhadap tumbesaran dan hasil padi (50% peningkatan hasil padi berbanding rawatan kawalan). Urea bersalut meningkatkan kandungan Cu, Zn dan N di dalam tanah dan tumbuhan.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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## LIST OF ABBREVIATIONS

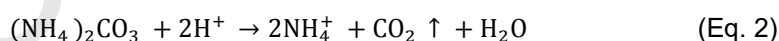
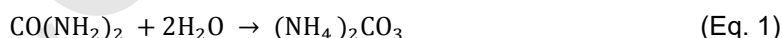
AAS	Atomic Absorption Spectrophotometer
AB-DTPA	Ammonium Bicarbonate Di ethylene Tri Amine Penta Acetic Acid
ANOVA	Analysis of Variance
ARI	Agriculture Research Institute
CEC	Cation Exchange Capacity
CRF	Controlled Released Fertilizer
Contr.	Contrast
CU	Coated Urea
Cu	Copper
dSm <sup>-1</sup>	deciSiemens per meter
EDTA	Ethylene Diamine Tetra acetic Acid
Eh	Redox Potential
Fe <sup>2+</sup>	Ferrous Ion
Fe <sup>3+</sup>	Ferric Ion
H <sup>+</sup> /OH <sup>-</sup> ions	Hydrogen and Hydroxide Ion
HSD	Honest Significant Difference
MADA	Muda Agricultural Development Authority
mV	Millivolt
NIA	Nuclear Institute of Agriculture
NS	Not Significant
RCBD	Randomized Complete Block Design
rpm	Revolutions Per Minute
SE	Standard Error
SD	Standard Deviation
SPAD	Special Products Analysis Division
UCU	Un-Coated Urea
YEL	Youngest Fully Expanded Leaf
Zn	Zinc

## CHAPTER 1

### INTRODUCTION

The chemistry of the rice soils is different as compared to the normal soils. Normally rice requires 10-15 cm of stagnant water thorough out its life cycle. Submergence in paddy causes the oxygen eradication. This anaerobic soil condition eventually affected the nutrients availability in rhizosphere (Fageria et al., 2011). Generally, in flooded paddy soils (acidic or alkaline) two scenarios occur 1) some of the nutrients like Fe and Mn become more soluble, whereas; 2) some of the nutrients get adsorbed or lost from the soils reservoir such as N, Cu and Zn (Dobermann and Fairhurst, 2000).

Copper availability under rice soils decreases. The formation of insoluble Cu sulfides and Cu ferrite ( $\text{Cu}_2 \text{Fe}_2 \text{O}_4$ ) and complexes with organic matter came into existence. The Zn accessibility reduces under the flooded rice soils. The calcareous soil reduces the Zn solubility with the formation of  $\text{ZnS}$  and it also getting adsorbed on  $\text{CaCO}_3$  or  $\text{MgCO}_3$  along with the oxides of Zn and Mn (Dobermann and Fairhurst, 2000). Therefore, to apply Cu and Zn fertilizers in rice soils with an appropriate method at controlled condition is important. Nitrogen losses from agricultural fields are commonly observed particularly from urea. The rate of urea hydrolysis is accelerated as it remains in the conventional form and about 70% of the applied urea losses in different forms to the atmosphere. Ammonia volatilization is persuasive loss among all the losses from urea (Fenn and Miyamoto, 1981). The N-use efficiency (NUE) markedly influences if the urea applied as surface application. The environmental deterioration chances are more under conventional urea (Khanif, 1992). The only source of the high concentration of nitrogen (46%) is urea therefore; to enhance its aptitude is required. Controlled release urea is the solution, as it assumes to improve crop yield by minimizing the hazardous emission of  $\text{NH}_3$  and  $\text{N}_2\text{O}$  gases from the fertilizers (Shaviv, 2005). Upon the application in soil, the urea is hydrolyzed rapidly and form ammonium carbonate  $[(\text{NH}_4)_2\text{CO}_3]$  (Eq. 1), later on it dissociates in ammonium hydroxides ( $\text{NH}_4 \text{OH}$ ) and carbon dioxide ( $\text{CO}_2$ ) (Eq. 2). The after effect of hydrolysis is high pH which rises at the urea microsite, is because of the formation of hydroxyl ions ( $\text{OH}^-$ ) (Eq. 3)



This favors to release a significant amount of gaseous ammonia in the soil for a few days following the surface application of urea (Kissel et al., 1988). The alternate to reduce the rate of urea hydrolysis is coating. There is an important need of selecting such material which is not only used as coating layer, but can also provide the essential micronutrients to the soil. The micronutrients can

serve as urease inhibitors and reduces the ammonia volatilization loss. The Cu and B as inhibitors were supportive in minimizing the ammonia loss from urea (Reddy and Sharma, 2000). Besides being active in reducing  $\text{NH}_3$  volatilization, the Cu and Zn can enhance the NUE. The effectiveness of Cu has already been verified as urease inhibitor (Junejo et al., 2013). For cereal production the Cu and Zn are essentially required to complete their physiological and biochemical process. Therefore, a dire need is to conduct a study on both Cu and Zn as coating of urea to see their effect on N losses and to provide essential Cu and Zn in soil and plants.

### **1.1 Problem testimonial**

Oxygen depletion in submerged paddy soils change the absorption and forms of applied as well as native essential nutrients. Therefore the concentration and availability of required macro and micronutrients is expressively influenced under flooded rice soil (Fageria et al., 2011). Consequently the application of essential nutrients at controlled condition is an indispensable approach to reach at the desired rice yield. In this regard the current study was designed which particularly focusing on coating urea with Cu and Zn. As Cu and Zn serves as urease inhibitors and improves the N-uptake and its efficiency.

Copper and Zn were applied individually and in the combination at different rates and applications (surface/ direct broadcasting and coated with urea) under the current study. So the investigation can reasonably assess the rates of Cu and Zn fertilizers coated with urea and their effect on sustenance of rice crop and N-efficiency. The efficiency of the Cu and Zn coated urea was equally examined on acidic and alkaline soils.

### **1.2 Objectives**

The research was conducted on the following objectives:

1. To evaluate Cu and Zn status of various rice soils of Peninsular Malaysia.
2. To determine the effect of Cu and Zn coated urea on ammonia volatilization loss.
3. To assess the influence of Cu and Zn coated urea in rice soils on availability of Cu and Zn.
4. To determine the response of Cu and Zn coated urea on rice yield and its components in acidic soils.
5. To evaluate the consequences of Cu and Zn coated urea on the rice yield under field conditions of alkaline soils.

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