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Effects of Cu and Zn Coated Urea on Eh, pH and Solubility of Cu and Zn in Rice Soils

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ABSTRACT

The concentration of Cu (Copper) and Zn (Zinc) decreases upon flooded conditions of rice soil. To assess the effects of flooding and application of Cu and Zn coated urea on changes in Eh, pH and solubility of Cu and Zn, a glasshouse experiment was conducted at Universiti Putra Malaysia. Rice plants (30 days old seedlings of type MR-219) on two soils (riverine and alluvium and marine alluvium) were transplanted. Nine treatments with variable rates and combinations of Cu and Zn coated urea were applied. The sources of fertilizers were copper sulfate and zinc sulfate. Eh values decreased with flooding time in both soils. The changes of Eh values were more negative in control treatments and stabilized after 3 weeks of submergence. The Eh variation was not observed affectively in the treated soils however, soil pH increased with flooding time. During the 3rd week of submergence, pH was neutral (pH 7.0). In both soils, Cu and Zn treated soil showed lower Eh and higher pH values as compared to untreated soil. Concentration of Cu and Zn in soil solution decreased with flooding. The higher Cu and Zn contents in soil were recorded in treated soils. Reduced solubility of Cu and Zn in control soils was related to larger changes in Eh and pH values. Mean comparison with Tukey's HSD (Honest Significant Difference) test showed that Cu and Zn solubility decreased with decreased Eh and increased pH in the soil solution ($p < 0.05\%$).

Key Words: Redox Potential, Paddy, Coated Urea, Submergence, Acidic Soils.

1. INTRODUCTION

There are a number of physical and chemical properties of soils affecting availability of metallic ions like Cu and Zn. Among the chemical properties, soil Eh and pH are important factors with regards to soil fertility [1]. Upon submergence consecutive decrease of electron acceptors occurs as a function of Eh. Oxygen depletion occurs at Eh > 300mV, followed by the reduction of NO_3^- and Mn^{4+} at Eh of 200 mV. As all NO_3^- is reduced, iron reduction is initiated and is completed at Eh -100mV [2].

The differences between aerobic and anaerobic soils are the alteration of oxygen supply, which is mainly due to the changing redox potential and pH [3]. When oxidation and submergence combined together results in anaerobic and reduced soils which tends to converge soil pH to neutrality

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irrespective of initial pH. This phenomenon is equally observed in acidic and alkaline soils [4]. Stagnant water condition in paddy fields is reported to decrease the availability of heavy metals that attributed to the increase of adsorption of metals on hydrous Mn and Fe oxides [5] and formation of insoluble compounds with sulfides [6].

Complexes form with metals as the reduction of SO_4^{2-} to S^{2-} takes place at a low redox potential and eventually end-up immobilizing them. The metal sulfides came into existence are sturdily insoluble even in strong acidic conditions [7]. Generally, micronutrients availability increased with the increase of soil acidity. Soils in Malaysia are acidic in nature and found deficient in micronutrient contents. This is due to the continuous subsequent planting pattern; paddy to paddy [8-9]. The cropping trend and fertilization practices are influenced on micronutrients availability [10]. The chemistry of rice soils is different as compared to normal acidic soils because of their submerged conditions.

Due to pH changes the Fe^{3+} reduced to Fe^{2+} and Mn^{4+} to Mn^{2+} therefore, the uptake of Fe and Mn increased in flooded soils and Fe concentration can reach toxic level [11]. Zn and Cu availability generally decreased in lowland rice soils because of pH increased and redox potential decreased. Boron remains unchanged even after flooding and Mo concentration was found to increase in rice soils [12].

In this regard, the relationship between soils Eh, pH and Cu and Zn availability has been investigated upon the application of Cu and Zn coated urea in two main rice zones of Malaysia (Kedah and Kelantan). The main objective of this research was to evaluate the effect of Cu and Zn coated urea on the availability of Cu and Zn in paddy soils.

2. MATERIALS AND METHOD

The experiment was conducted in a glasshouse at Universiti Putra Malaysia. Two soil types used for this study were derived from riverine alluvium situated in the north-east and marine alluvium situated in the north-west of Peninsular Malaysia. Simple random soil sampling was done at two depths 0-15 and 15-30 cm; soils were homogenized to make representative soil samples. The selected soils were deficient in Cu and Zn contents. The sampling sites were located at N-05°-97370’, E-102°-29944’ (Chempaka Soil Series Kelantan) and N-06°-13422’, E-100°-29527’ (Kuala Kedah Soil Series Kedah).

A total of 54 pots with 10 kgs of soil in each pot were filled with two soil types. Rice Plants (MR-219) were transplanted into the pots (four plants pot^{-1}) after 30 days of planting nursery. Copper and Zn coated urea applied at once; P and K were applied after 15 days of planting, at the rate of 70 kg ha^{-1} in the form of triple super phosphate (1.03 g TSP pot^{-1}) and muriate of potash (MOP 0.792 g pot^{-1}). The fertilizer doses were calculated according to the surface area of pots (πr^2). The water level was maintained in each pot at 5 cm above soil surface and was maintained throughout the crop period. Basic information regarding the soil physical and chemical characteristics is given in Table 1.

The experiment was arranged in a RCBD (Randomized Complete Block Design), where sources of Cu and Zn fertilizers were copper sulphate ($CuSO_4$) and zinc sulphate ($ZnSO_4$). The Cu and Zn were applied either alone/ combine coated urea, replicated in 3 pots. Nine treatments were used in this study namely; T1 was control which contained no Cu and Zn, from T2-T9 contained Cu and Zn in coated form. The detail of the treatments is presented in Table 2.

Soil redox potential (Eh) and pH were determined directly from the situ in each pot with portable Eh and pH meter (Hanna instrument Hl 8424 portable pH/ORP meter). The extractable Cu and Zn in soils were determined by using Mehlich-I (soil to solution ratio 1:5, shaking time 15 minutes) and their concentrations were analyzed by using Atomic Absorption Spectrophotometer (Perkin Elmer AAnalyst 400) [13-14]. Soil texture was determined by the pipette method [15]. Total N in the soil was determined by the Kjeldhal method on Auto Analyzer (Lachat Instrument Quik Chem FIA+ 8000) [16]. Soil extractable P was obtained by the method of Bray 2 [17]. Exchangeable K was analyzed by 1N NH_4OAc maintained at pH 7 [18].

The data were analyzed using Statistix 8.1 software. All data were subjected to the ANOVA (Analysis of Variance) for the RCBD, followed by the mean comparison by using Tukey's standardized range test (HSD) at 5% level of significance.

3. RESULTS AND DISCUSSION

The analysis of the soil extractable Cu and Zn in both soils showed the deficiency at their critical range (0.11

TABLE 1. SOIL DESCRIPTION IN TERMS OF PHYSICAL AND CHEMICAL CHARACTERISTICS

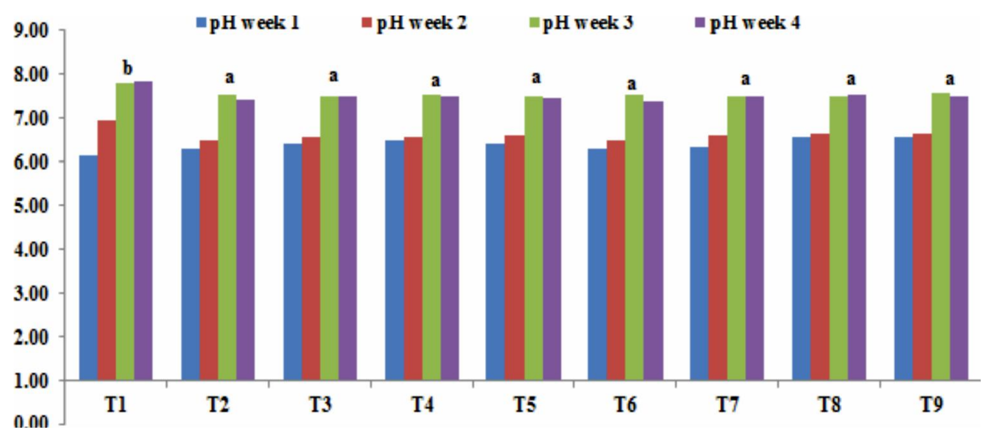
Soil Physical Characteristics		
	Chempaka	Kuala Kedah
Sand (%)	26.05	0.43
Silt (%)	38.51	45.75
Clay (%)	35.41	53.81
Texture	Clay loam	Silty clay
Soil Chemical Characteristics		
pH	5.12	5.29
Total N (%)	0.18	0.15
Extractable P mg kg-1	20.5	21.9
Exchangeable K cmol (+) kg-1	0.18	0.17
Zn mg kg-1	0.90	1.10
Cu mg kg-1	0.11	0.15

TABLE 2. TREATMENTS DETAIL OF THE APPLIED FERTILIZERS

Treatments	Urea (kg ha^{-1})	Zn (kg ha^{-1})	Cu (kg ha^{-1})
T-1/Control	Un-coated 140	0	0
T-2	Coated 140	10	0
T-3	Coated 140	7	0
T-4	Coated 140	0	5
T-5	Coated 140	0	3
T-6	Coated 140	10	5
T-7	Coated 140	10	3
T-8	Coated 140	7	5
T-9	Coated 140	7	3

and 0.85, 0.15 and 0.91 mg kg^{-1}) for Chempaka and Kuala Kedah soil series respectively (Table 1). Both soil series were acidic in nature. The Chempaka series has pH values ranging from 4.97-5.31, and the Kuala Kedah has pH values ranging from 5.0-5.56. The N percentage was low in both soils. This decline in N is the evidence of N-losses from agricultural fields which is commonly observed in areas where common urea is being applied [19].

Soil pH and Eh were measured according to the scheduled time frame (weekly basis till fourth week of sowing). Results revealed that the soil pH increased and the Eh decreased until it reached at negative values. ANOVA computed for means revealed that treatment effect was highly significant on soil pH and Eh ($p < 0.01$). However, the difference between two soils and interaction of soil and treatment was non-significant ($p > 0.05$). The rate and combination of the treatments significantly affected the pH and Eh values. Soil pH and Eh alteration is due to oxygen depletion. It was observed pH started to elevate in both soils in control treatment (no application of coated urea) which continued for a month and stayed in it until the crop cultivation (Fig.1). The Cu and Zn coated urea played a key role in maintaining the soil pH around the optimal plant value (6.5). The range of soil pH under control (un-coated urea with no application of Cu and Zn) was 6.0-7.9 from 1-4week of crop sowing; conversely under the Cu and Zn coated urea pH was reported between 6.0 and 6.5 in both soils as the statistical analysis showed no significant difference in soils interaction. The pH under the Cu and Zn coated urea treated soils was at its marginal range because of steady mechanism of hydrolysis rate of urea. These results are in agreement of Jiang et. al. [20], who have reported that pH at its peak, occurred at day 5 after application of un-coated urea, which associated with the accelerated urea hydrolysis. After three months of sowing, pH becomes acidic as it was before. The chemical changes regarding redox potential and pH in this study were almost similar to the values reported by Rostaminia [21].



	Factor	F-value	P-Value	HSD Value
Treatments	Week1	3.60**	0.0000	0.033
	Week2	7.78**	0.0000	0.240
	Week 3	0.67**	0.0000	0.330
	Week4	0.88**	0.0000	0.334

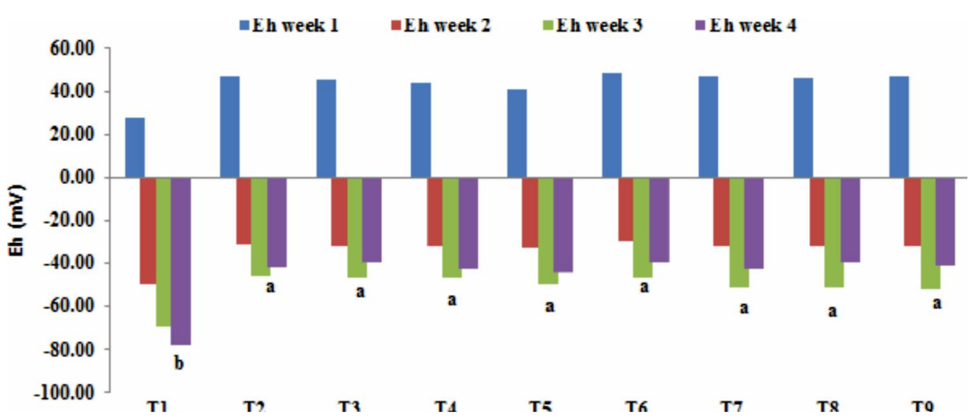
Treatments Effect on Soil pH was Highly Significant p<0.001)
** Highly Significant
HSD (Honest Significant Difference)

FIG. 1. SOILPH AT FIRST FOUR WEEKS UNDER TREATED SOILS

The Eh and pH are the key factors in terms of soil fertility [21]. Eh and pH remained fluctuated in paddy fields and turns as compels towards the availability of applied and native elements [22]. These changes in Eh and pH are because of the oxygen depletion. Majority of oxidation and reduction reactions in sub-merged soils are the result of either intake or production of H^+/OH^- ions [23]. From the first four weeks, the Eh values declined sharply. The current study proved that soils were under oxidized condition in the first week and started to reduced in the second week of the experiment. The lowest soil Eh (- 82 mV) was observed at the fourth week of study for the control treatment and this soil condition persisted for the next two months of the experiment. Under the application of Cu and Zn coated urea, the soil Eh was recorded at +40 at 1st week and -40 mV till the 4th week of crop sowing (Fig. 2 in T-6 where Cu was applied at the rate of 5 kg ha^{-1} and Zn at the rate of 10 kg ha^{-1}). The redox potential was between +10 mV to -80 mV from the first day of sowing till the third week, for surface applied soils. Whereas, Cu and Zn coated urea applied soils, Eh ranged between +15 mV to -40 mV (Fig. 2).

Cu and Zn availabilities were highly affected under the waterlogged rice soils. This study reported that Cu and Zn inhibited during the first three weeks. The observation indicated that, submergence compact Cu and Zn contents in the soils. The average Cu contents during the first three weeks under surface applied Cu and Zn were 0.79 mg kg^{-1}. This concentration was much improved (1.08 mg kg^{-1}) with the application of Cu and Zn coated urea (T=6; Zn10 + Cu5 kg ha^{-1}) in both soils. This is because of slow release mechanism of the fertilizer. Statistical analysis showed non- significant difference between two soils ($p > 0.05$) for Cu and Zn. The interaction between soil and treatment was also non-significant ($p > 0.05$). However, the difference among the treatments was highly significant ($p < 0.001$) (Figs. 3-4).

The least Cu and Zn contents were observed from control treated soils. The application of Cu and Zn coated urea enhanced the Zn solubility. The average Zn contents under the surface applied Cu and Zn coated urea were 1.33 mg kg^{-1} during the first week. This concentration

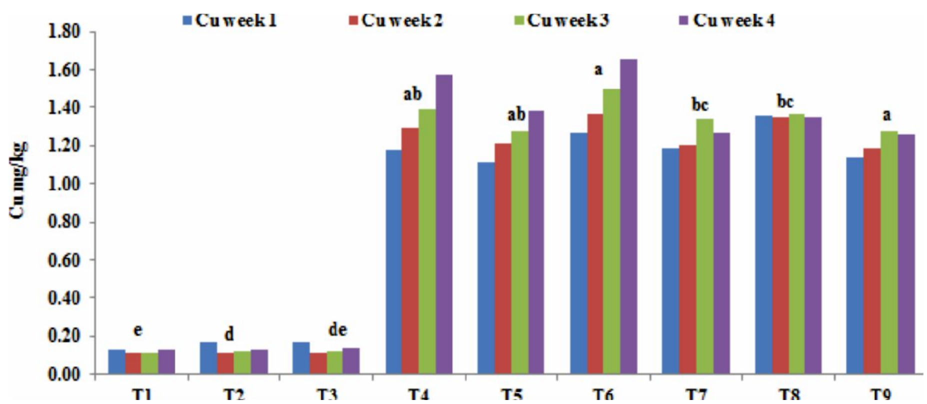


	Factor	F-value	P-Value	HSD Value
Treatments	Week1	41.40**	0.0000	4.52
	Week2	31.06**	0.0000	4.87
	Week 3	52.42**	0.0000	4.31
	Week4	92.95**	0.0000	4.30

Treatments Effect on Soil Eh was Highly Significant p<0.001)
**Highly Significant
HSD (Honest Significant Difference)

FIG. 2. SOIL EH AT FIRST FOUR WEEKS UNDER TREATED SOILS

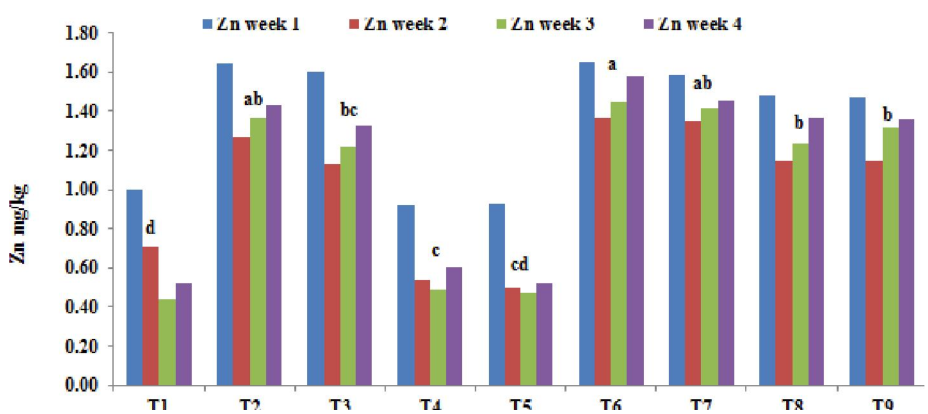
was gradually decreased in the following week, at 2nd week the Zn content reductions occurred and recorded as 0.99 mg kg^{-1} due to submergence conditions and oxygen depletion. The other reasons are the hydrolysis rate of urea which was reduced by coated and slowly dissolved in the later weeks. After 2nd week of experiment the Zn contents were gradually increased and reached at 1.052, 1.134 mg kg^{-1} respectively. The Zn absorption in Cu and Zn treated soils were remained available throughout the crop period (T6 in Figs. 3-4.). The rate and combination



	Factor	F-value	P-Value	HSD Value
Treatments	Week1	925.64**	0.0000	0.080
	Week2	1035.83**	0.0000	0.083
	Week 3	4132.01**	0.0000	0.044
	Week4	1797.51**	0.0000	0.070

Treatments Effect on Extractable Cu was Highly Significant $p<0.001$)
** Highly Significant
HSD (Honest Significant Difference)

FIG. 3. SOIL EXTRACTABLE CU AT FIRST FOUR WEEKS UNDER TREATED SOILS



	Factor	F-value	P-Value	HSD Value
Treatments	Week1	229.13**	0.0000	0.112
	Week2	182.99**	0.0000	0.130
	Week 3	644.71**	0.0000	0.080
	Week4	1773.53**	0.0000	0.048

Treatments Effect on Extractable Zn was Highly Significant $p<0.001$)
** Highly Significant
HSD (Honest Significant Difference)

FIG. 4. SOIL EXTRACTABLE ZN AT FIRST FOUR WEEKS UNDER TREATED SOILS

affected on Cu and Zn contents. The T6 which was comprises of $ZnSO_4$ 10kg ha^{-1} and $CuSO_4$ 5 kg ha^{-1}, was significantly different as compared with control. The coated fertilizers facilitated the soil to synchronize the nutrients solubility according to the plants requirement. The slow release mechanism of such fertilizer reduces the rate of hydrolysis and provides the nutrients accordingly [23]. Therefore, the application of essential nutrients in coating fertilizer is indispensable technique.

4. CONCLUSION

Present study revealed the positive response of Cu and Zn coated urea on Cu and Zn contents in submerged paddy soils. Under the control (NPK without Cu and Zn application) treated soil the pH increased gradually (5.5-7.8) and Eh decreased to the reduced soil conditions (+30 to -80 mV). The increase in pH and decrease in Eh affected the Cu and Zn availability under control (NPK application). The combined Cu and Zn coated urea had positive effect on controlling such fluctuating properties, pH ranging from 6.0-6.5 and Eh ranging from +40 to -40 mV under Cu and Zn coated urea treated soils. Cu and Zn coated urea reduced the rate of urea hydrolysis and Cu and Zn served as urease inhibitors to nourish the crop accordingly.

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