

## EVALUATION OF DIFFERENT FORMS OF ZINC ON GROWTH AND CHEMICAL COMPOSITION OF RICE PLANTS

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### ABSTRACT

The solubility of Zn and the mechanisms that control Zn solubility may vary with soil properties, such as pH, organic matter content and Clay Content. A series of laboratory and greenhouse experiments were conducted to evaluate different forms of added zinc on growth and chemical composition of rice plant. Results revealed that soluble and exchangeable fraction of zinc are very small in all treatments due to the alkalinity of the investigated soil. It was noticed that application of Zn (urea)<sub>4</sub> SO<sub>4</sub> and Zn-EDTA + urea increased the extractable fraction of Zn during the incubation periods up to 28 days. The extractable fraction of Zn bound with the organic matter gradually increase during the incubation, considerable amount of the extractable Zn were observed. It was noticed that application of organic matter may increase the organic forms of element due to the organic complexes and lesser extent as inorganic precipitates.

Results showed that addition of Zn. CA and/or Zn-EDTA with urea-N fertilizer increased the grain and straw yield of rice as compared with ZnSO<sub>4</sub> alone. The application of Zn(Urea)<sub>4</sub> SO<sub>4</sub> with organic matter gave the highest increase for both grain and straw yield of rice plant as compared with other treatments. Results revealed that application of organic matter with different forms of Zn stimulate the grain/straw ratio as compared with other treatments. Results also revealed that the addition of Zn(Urea)<sub>4</sub> SO<sub>4</sub> or Zn-EDTA with organic matter increased N,P and K amounts in the grain and straw of rice plant. The addition of organic matter with different sources of Zn improved the accumulation of nutrient elements in grain and straw of rice plant. The availability of Fe, Mn and Zn with organic matter added were markedly higher than without organic matter.

### INTRODUCTION

Zinc has been the subject of much research in agriculture because it is essential micronutrient for plants. Zinc deficiencies commonly occur in Egypt because of high soil pH. In contrast, Zn in high concentrations can be toxic to plants and animals, a subject of current environmental research (Lerch et al., 1990). The solubility of Zn in soil solution must be quantified to evaluate bioavailability and transport of zinc in soils. Zinc solubility can be represented by the total concentrations of Zn in solution or by Zn<sup>2+</sup> activity. The activity of Zn<sup>2+</sup> represents Zn availability to plants and can be used to predict possible solid phases that control Zn solubility in the soil (Lindsay, 1979). Depending on the soil and soil properties, different precipitates may be formed in soils and control Zn solubility at different levels. precipitation can occur at high pH. Gupta et al., (1987) suggested that at high pH, precipitation

reactions control Zn solubility, whereas at neutral to acidic pH specifically adsorbed Zn may control Zn solubility. They also found that precipitation or adsorption may occur between pH 6 and 7.9 and that adsorption may occur below pH 6.

*Jeffrey and Uren (1983)* concluded that at neutral to alkaline pH, specific adsorption of the hydrolyzed form of Zn [ $Zn(OH^+)$ ] may account for low soluble Zn concentrations. Various studies have shown that there may be changes in Zn solubility with other soil properties. Zn may be bound with Fe, Mn, and Al oxides, clay or organic matter in soil. Iron, Mn and Al oxides contain surface-hydroxyl functional groups that may bind metals, with increased adsorption at high pH (*Sposito, 1984*). *McBride and Blasiak (1979)* suggested that the adsorption to oxide surface having a high affinity for Zn, may be important in controlling Zn solubility.

Although it is recognised that major interactions between Zn and N occur at the plant metabolic level (*Singh and Singh, 1985*), the importance of this interaction in the low land rice has recently also been reported. Application of nitrogen fertilizer in cultivation of high yielding varieties of rice is a common practice and since rice grown soils are mostly deficient in or marginally supplied with plant available Zn, it is considered important to investigate how nitrogen application can influence the transformation of Zn in submerged soil and thus its availability to rice plants.

The objective of this research is to fractionate and evaluate different forms of added zinc on growth and chemical composition of rice plant.

## MATERIALS AND METHODS

### Pot experiment :

Green house experiment was conducted in National Research Centre (NRC) and designed as randomized complete block with three replicates. Plastic pots each contained 10kg of air dried soils, were used. The investigated soil which collected from Moshtohor village characterized by pH 8.36; EC 0.16 dS.m<sup>-1</sup>; clay content 46.5%; silt 34.8%; sand 18.7%; CaCO<sub>3</sub> 1%; organic matter 0.57%, total nitrogen 0.034%; available-P 12.5 ppm; available-Fe 1.88ppm and available-Zn 0.50 ppm. Pots were treated with the examined fertilizers as follows :

- Zn(urea)<sub>4</sub> SO<sub>4</sub>.
- Zn.CA + urea
- Zn SO<sub>4</sub> + urea
- Zn-EDTA + urea
- Zn (urea) SO<sub>4</sub> + FM.
- Zn.CA + FM
- ZnSO<sub>4</sub> + FM
- ZnEDTA + FM
- Control soil

Nitrogen was applied at a rate of 60 mgN/Kg soil either by urea or Farmyard manure (FM) under subsurface condition. The characteristics of the farmyard manure was presented in Table (1). The different sources of zinc were applied at a rate of 12mg. Zn/Kg in the forms that previously mentioned. Phosphorus and potassium were applied at rates of 50 and 40mg/kg as superphosphate and potassium sulphate respectively, Fe-EDDHA, MnSO<sub>4</sub>

and CuSO<sub>4</sub> were added at the rate of 5, 5 and 5mg of Fe, Mn and Cu /kg soil. The pots were transplanted with three 21-day old seedling of (*Oriza sativa* L.) C.V. Giza 171, and kept under continuous flooding through the growth period.

At harvest, the plant parts were separated into grain and straw. The oven dry weight of each part was recorded, ground and prepared for analysis. Total N, P, and K in plant were determined as described by Bremner and Mulvaney (1982), and total Fe, Zn and Mn were determined as described by Black (1982).

**Table (1): Chemical properties of farmyard manure (FM) :**

Properties	PH	Organic carbon %	Total nitrogen %	C/N ratio	Total (%)			Available micro-nutrient (ppm)		
					P	K	So <sub>4</sub> <sup>2-</sup>	Fe	Mn	Zn
Farmyard manure (FM)	7.30	20.31	1.52	13.4	0.92	1.43	1.24	212	127	98

Agronomic efficiency "yield increase per unit of N-applied", physiological efficiency" yield increase per additional unit of N uptake above control" were calculated according to *Buresh et al., (1988)*.

$$\text{Agronomic efficiency} = \frac{\text{Grain yield (fertilized)} - \text{grain yield (control)}}{\text{N- applied}}$$

$$\text{Physiological efficiency} = \frac{\text{Grain yield (fertilized)} - \text{grain yield (control)}}{\text{N-uptake (fertilized) - N-uptake (control)}}$$

**Incubation experiment :**

Three hundred grams of 2mm sieved of air dry soil were treated with 300mg N and 12mg-Zn in wide mouth 400ml plastic containers as follows :

- Zn (urea)<sub>4</sub> SO<sub>4</sub>.
- Zn. CA + urea
- Zn SO<sub>4</sub> + urea
- Zn-EDTA + urea
- Zn (urea) SO<sub>4</sub> + FM.
- Zn. CA + FM
- Zn SO<sub>4</sub> + FM
- Zn EDTA + FM

Preparation of zinc urea sulphate was described as metal salt urea complexes after *El-Aila et al., (2002)*. Treatments were triplicated and kept under flooded condition during the incubation periods. Soil samples were taken at intervals of 1, 7, 14, 28, and 56 days. Sequential extractions were carried out according to *Abou Seeda, (1987)* and determined according the method described by *Cottenie et al., (1982)*, the extraction procedure was presented in Table (2).

**Table (2) : Sequential extraction procedures for determination the extraction fraction of zinc after *Miller et al., (1986)*.**

Extractable fraction of zinc	Extractant solution	Conditions
Soluble and exchangeable zinc	0.05 M CaCl <sub>2</sub>	Shaken 24h
Specifically sorbed by organic sites	Acetic acid (25%)	Shaken 24h
Specifically sorbed by organic sites	0.1M potassium pyrophosphate	Shaken 24h
Occluded forms by free oxides	0.1M oxalic acid + 0.175M ammonium oxalate at pH 3.25	Shaken 24h

## RESULTS AND DISCUSSION

### Extractable fraction of Zn in soil :

Sequential extraction of Zn are presented in Fig. (1); allowed to distinguish four Zn-fraction which differ in mobility and availability to the plants. Water and exchangeable fractions of zinc are considered as the most available forms, which are loosely held by surface association (Schalscha et al., 1982). Results also reveal that soluble and exchangeable fractions of zinc are quite low due to the alkalinity of the investigated soil. It has been observed that water and exchangeable fractions are very small in all treatments which increased with time up to 28 days and does not exceed  $5.4 \text{ mg Kg}^{-1}$  soil. Abou Seeda (1987) and Sarkar and Deb (1990), stated that the amount of Zn present in water soluble and exchangeable forms was comparatively small. It was noticed that Zn (urea)<sub>4</sub> SO<sub>4</sub> + OM gave the highest amount of zinc. This result could be attributed to the formation of carboxylic acids substances e.g., humic and fulvic acids that improve the adsorption capacity and also increase the mobilizable fraction of Zn as well. Kirk et al., (1993) reported that the mechanism of humic and fulvic acids adsorption involves ligand exchange. Sachdev and Deb, (1990), reported that application of farmyard manure increased utilization of Zn fertilizer by rice plant. They carried out laboratory and green house experiments and found that application of organic matter enhanced desorption under flooded-dried and alternate wetting and drying but decreased it under pre-flooded. They also stated that variation in Zn desorption among soils and moisture treatments is the result of changes in soil pH, Fe-oxides, bonding energy constant and free energies for Zn adsorption. Biswapati et al., (2000), stated that higher level of zinc (5.0 mg/kg) and its enrichment with organic manures increased the amount of zinc present in water-soluble and exchangeable, complexed, organically bound and occluded forms and also resulted in a significant residual effect on the subsequent crops.

In the second extracting step acid soluble Zn was determined through removing adsorbed and weakly bound of Zn. It was observed that decreasing the pH of the extracting solution increase the extractable fraction of Zn through increasing the solubility product of the element. Results reveal that application of Zn(urea)<sub>4</sub>SO<sub>4</sub> and Zn EDTA + urea increase the extractable fraction of Zn during the incubation period up to 28 days. It is noticed that ZnSO<sub>4</sub> + urea treated soil decreased the extractable fraction of Zn as compared with ZnSO<sub>4</sub>+OM particularly after 28 days of incubation. This phenomenon was clearly illustrated by Borges- Perez et al., (1994) and Abou Seeda (1987). They reported that such decrease may be explained by the completion of conversion of higher amorphous oxides to their predominant divalent cations Ca<sup>++</sup> and Mg<sup>++</sup>, and also organic matter may increase the extractable fraction of Zn by acetic acid up to 28 days due to organic acid production through the composting process of the organic matter.

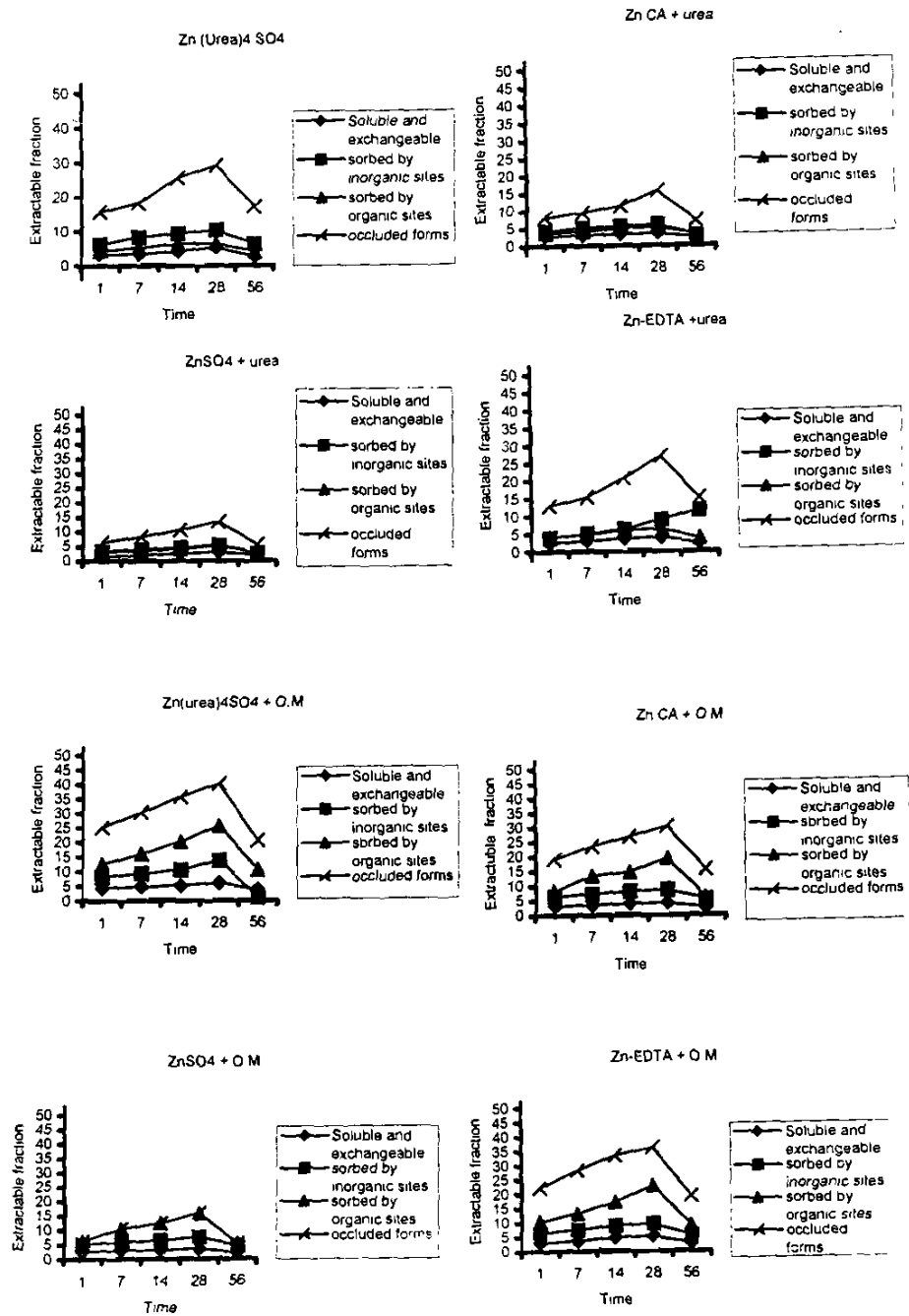


Fig. (1): Effect of different forms of zinc on the extractable fraction of Zn in soil (ppm).

The extractable fraction of Zn by pyrophosphate and oxalic acid are illustrated in Fig. (1). Results reveal that extractable fraction of Zn bound with the organic matter gradually increase during the incubation. It can be noticed that application of organic matter may increase the organic form of element due to the organic complexes and lesser extent as inorganic precipitated. Tsutsuki and Kuswatsuka (1992) stated that organic matter may act as a template for metals complexation and binding, both processes may increase Zn adsorption. Application of organic matter increased the occluded Zn during the incubation periods Fig.(1). Similar trend was noticed by Inoue (1990) who reported that humin-metal complexes in the presence of organic matter added are formed with polymerized and monomeric Zn species (occluded forms) and also Sarkar and Deb (1990) stated that fertilizer zinc added to alluvial soils was transformed into occluded and residual forms. Slaton *et al.*, (2001) determined the relative distribution of different forms of Zn in some rice growing soils. Hardly 16% of the total Zn was found to occur in the four active forms of which iron oxide bound forms constituted the major portion. Besides, when Zn was applied to the soil as fertilizer much of it was found to be transformed to iron oxide bound forms. They suggested that the important role of iron oxide in controlling Zn availability in submerged soils. They also did a critical study relating the transformation of Zn with that of iron in submerged soils and showed that the reduction of  $Fe_2O_3$  and subsequent formation of amorphous hydrated oxides of iron played the most significant role in controlling Zn availability in submerged soils.

**Pot experiment :**

**Grain and straw yield production :**

Grain and straw yield production of rice as a function of different forms of zinc and nitrogen are presented in Table (3). Results reveal that the differences in grain and straw yield of rice among zinc forms were highly significant. It can be observed that the addition of Zn.CA and/or ZnEDTA with urea-N fertilizer increase the grain and straw yield of rice as compared with  $ZnSO_4$  alone. The average increases are 30.77, 17.8% and 19.4, 12.1% for grain and straw respectively. Bansal and Nayyar (1989) reported that grain yield increased with increasing Zn rate up to 7.1 and 7.6 t/ha with 6.0 ton with  $ZnSO_4$  and Zn-EDTA respectively. Straw yield and Zn uptake followed the same trends. Results reveal that application of  $Zn(urea)_4SO_4$  gave the highest increase for both grain and straw. The average increases are 43.7% and 33.6% for grain and straw as compared with  $ZnSO_4$  respectively. Mali and Shaikh, (1994) stated that plant Zn content and available soil Zn were increased by applied Zn specially with zincated urea. Sarkar and Deb (1990) stated that uptake and utilization of fertilizer zinc by rice plant was considerably higher, when zincated urea was added at a rate of 5kg Zn/ha in alluvial soil. Application of liquid chelated and inorganic-Zn sources at rates from 1.0 to 2.0 lb Zn/acre produced high yield (Slaton *et al.*, 2001).

Results reveal a positive correlation between the addition of  $Zn(urea)_4SO_4$  and the organic matter because they render strong binding sites for Zn. Only chelating agent was able to desorb Zn, indicating that both weakly (electrostatically) and specifically bound fractions of applied Zn could

easily equilibrate with the equilibrium soil solution to replenish any decrease in Zn concentration (Ando *et al.*, 1983, Chandler and Brooks, 1991; Flessa and Fischer, 1992).

The addition of organic matter with ZnSO<sub>4</sub> or Zn-EDTA had a pronounced effect on grain and straw yield of rice plant as compared with ZnSO<sub>4</sub>+OM. However, Zn(urea)<sub>4</sub>SO<sub>4</sub> + OM was more effective on both grain and straw yield of rice than the other treatments. Sachdev and Dep, (1990) stated that application of FYM to rice increased the yield and also increased the Zn content in both grain and straw. Slaton *et al.*, (2001) reported that application of 10 t FYM/ha enhanced the rice yield production. It has been stated by Biswapati *et al.*, (2000) that application of organic matter were found to be beneficial in maintaining a higher proportion of applied Zn in the active forms and thus to benefit the Zn nutrition of rice. Singh and Singh. (1985) observed that Zn mobilized under reducing conditions in the soil becomes associated with organic matter which are effective in enhancing the mobilization of zinc.

**Grain/straw ratio, agronomic and physiological efficiency :**

Data of Table (3) illustrate that grain/straw ratio, as well as agronomic and physiological efficiency could be affected by the addition of different sources of zinc and nitrogen. Results revealed that application of organic matter with different forms of zinc stimulate the grain/straw ratio as compared with other treatments. This result could be explained on the basis of the positive effect of organic matter on zinc absorption which may be associated with the acidulation effect of these compound on the native organic matter and subsequent release of inorganic form of N-utilized by plant (Nograle *et al.*, 1991).

**Table (3): Average of grain and straw yields, agronomic and physiological efficiencies as affected by different forms of zinc applied to rice plants**

Treatments	Grain yield (kg/ha)	Straw yield (kg/ha)	Grain/straw ratio	Efficiency (kg grain per kg N)	
				Agronomic	Physiological
Zn(Urea) <sub>4</sub> SO <sub>4</sub>	52.3	67.6	0.77	36.16	3.9
ZnCA + urea *	47.6	60.4	0.78	28.33	4.5
ZnSO <sub>4</sub> + urea	36.4	50.3	0.71	9.6	3.8
Zn-EDTA + urea *	42.9	56.7	0.75	20.5	4.4
Zn(urea) <sub>4</sub> SO <sub>4</sub> + O.M.	56.4	72.1	0.78	43.0	3.2
Zn.CA + O.M.	51.2	66.8	0.76	34.3	3.2
ZnSO <sub>4</sub> + O.M.	40.3	55.3	0.72	16.16	3.2
Zn-EDTA + O.M.	48.7	60.9	0.79	30.16	3.2
Control	30.6	43.2	0.70	-	-
L.S.D. 5%	3.36	5.21	-	-	-

Agronomic efficiency (grain yield increase per unit of N-applied) was increased due to application of organic matter with different forms of zinc, as compared with only addition of organic matter. This phenomenon could be explained by the degradability of the organic matter since it breaks down at a slower rate particularly under flooded condition. The slower rate of decomposition takes place in flooded condition which might be expected to retard the release of nitrogen. The low requirement of the anaerobic

organisms for nitrogen causes organically bound. This process may regulate as well as prevent N-Loss (Abou Seeda 1997 and Abou Seeda et al., 1997).

Physiological efficiency (grain yield increase per unit of N-taken up above the control treatment) was used to assess whether high rate of N-application can affect the rice utilized nitrogen for the formation of grain. Results reveal that application of Zn.CA or Zn-EDTA with added urea gave the highest physiological efficiency as compared with other treatments.

**Nutritional status of plants :**

Data in Tables (4 & 5) show that the content of N, P, K, Fe, Zn and Mn in grain and straw of rice plants were influenced by the addition of different sources of zinc in combination with organic and inorganic nitrogen fertilizers. The magnitude variations of N, P, K, Fe, Zn and Mn uptake with respect to source of zinc were very clear. The application of Zn.CA + urea slightly increased the nitrogen content in grain and straw of rice plants. While the addition of Zn(urea)<sub>4</sub>SO<sub>4</sub> has more pronounced effect on nitrogen content in grain and straw of rice plant. This phenomenon may be related to the structure of the organic molecule and the ability of urea and Zn to form stable complexes through a ligand exchange reaction (Fox and Comerford, 1990 and Cajuste et al., 1996).

Biswapati et al., (2000) reported that application of organic matter was found to be beneficial in maintaining a higher proportion of applied Zn in the active forms and thus to benefit the Zn nutrition of rice. They also reported that application of organic matter might be useful in overcoming the adverse effect of P application on availability of Zn in soils to rice plant. It was observed that the addition of organic matter with sources of Zn increased total-N in grain and straw of rice plant due to improving the nutritional status particularly nitrogen form in the soil.

Results also reveal that the addition of Zn(urea)<sub>4</sub>SO<sub>4</sub> or Zn-EDTA with organic matter increased phosphorous and potassium amounts in the grain and straw of rice plant. It was noticed that the addition of organic matter with different sources of Zn improved the accumulation of nutrient elements in grain and straw of rice plants as compared with organic matter added only. This result could be explained by increasing the solubility of nutrients through the complexation phenomenon with soluble organic matter produced during the decomposing processes of organic matter (El-Aila et al., 2002).

The treatments of zinc with organic matter increased Fe, Zn and Mn of grain and straw of rice. It was observed that the addition of Zn(urea)<sub>4</sub>SO<sub>4</sub> or Zn-EDTA with organic matter gave the highest value of Fe, Mn and Zn as compared with other treatments. The availability of Fe, Mn and Zn with organic matter added was remarkably higher than without organic matter added. Such addition may regulate the mobilization of some nutrients through the degradability of the organic matter added and could be attributed to the formation of carboxylic substances that improve the absorption capacity and also increase the mobilizable fraction of Fe, Mn and Zn as well. Partitt et al., (1977) reported that the mechanism of humic and fulvic acid adsorption involves ligand exchange.



**Table (4) : Total N, P, N, Fe, Zn and Mn contents in rice grain as affected by different forms of zinc.**

Treatments	mg/pot					
	N	P	K	Fe	Zn	Mn
Zn(urea) <sub>4</sub> SO <sub>4</sub>	847.2	219.6	904.7	26.1	24.0	15.6
Zn.CA + urea	671.1	147.5	733.04	23.8	18.5	12.3
ZnSO <sub>4</sub> + urea	444.0	80.1	516.8	7.28	6.91	3.6
Zn-EDTA + urea	570.5	141.5	643.5	17.1	12.4	10.2
Zn (urea) <sub>4</sub> SO <sub>4</sub> + O.M.	1082.8	293.2	1105.4	33.8	27.1	19.2
Zn.CA + O.M.	921.6	209.9	947.2	27.1	20.9	15.3
ZnSO <sub>4</sub> + O.M.	588.3	104.7	604.5	10.07	8.46	5.23
Zn EDTA + O.M.	842.5	170.4	15.5	20.9	15.5	14.1
Control	293.7	58.1	309.0	4.8	3.6	4.5

**Table (5) : Effect of different forms of zinc on N, P, K, Fe, Zn and Mn contents of straw (mg/pot).**

Treatments	mg/pot					
	N	P	K	Fe	Zn	Mn
Zn(urea) <sub>4</sub> SO <sub>4</sub>	419.1	102.7	473.2	20.9	19.6	16.9
Zn.CA + urea	314.0	84.5	344.2	17.5	15.7	12.0
ZnSO <sub>4</sub> + urea	166.9	65.2	197.3	8.1	7.1	5.0
Zn-EDTA + urea	260.8	79.3	289.1	13.6	11.3	10.2
Zn (urea) <sub>4</sub> SO <sub>4</sub> + O.M.	591.2	116.8	641.6	23.7	21.6	19.4
Zn.CA + O.M.	414.1	100.2	427.5	20.0	18.7	16.0
ZnSO <sub>4</sub> + O.M.	265.4	49.7	282.0	9.9	8.8	6.6
Zn EDTA + O.M.	272.7	63.3	289.3	12.6	11.6	9.74
Control	90.7	34.5	99.3	5.6	5.1	3.8

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تقييم الصور المختلفة للزنك على النمو والتركيب الكيماوى لنباتات الأرز  
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أقيمت تجارب زراعية ومعملية بهدف تقييم إضافة الصور المختلفة للزنك على النمو والتركيب الكيماوى لنبات الأرز حيث تشير النتائج المتحصل عليها إلى أن الاستخلاص المتتابع (Sequential extraction) لعنصر الزنك فى الأراضى الغدقة توضح أن كمية الزنك الذائبة والمتبادلة قليلة جداً نظراً لارتفاع رقم pH الأرض عن ٧ .

أدت إضافة مركب  $Zn(urea)_4SO_4$  والزنك المخلبي Zn-EDTA إلى زيادة الزنك المستخلص من التربة حتى ٢٨ يوماً من فترة التحسين، فى حين زادت كمية الزنك المرتبطة عضوياً خلال فترة التحسين نتيجة لإضافة المادة العضوية مما يؤكد تحول الصور غير العضوية (Inorganic form) والمترسبة (Precipitated form) إلى الصور العضوية (Organic form) والتي تكون أكثر حركية أو أكثر تيسراً وعليه فإن أعلى قيمة للزنك المستخلص كانت على الترتيب التالى :

الممسوكة (occluded form) > العضوية (organic form) > الممصة (adsorbed form) > الذائبة والمتبادلة (water soluble + exchangeable form)

أظهرت النتائج أيضاً أن إضافة حامض الستريك (Citric acid) للزنك أو الزنك المخلبي ZnEDTA أدت إلى زيادة وزن الحبوب والقش لنباتات الأرز بالمقارنة مع كبريتات الزنك  $ZnSO_4$  .

تشير النتائج أن إضافة مركب  $Zn(urea)_4SO_4$  مع المادة العضوية أدت إلى إعطاء أعلى زيادة فى محصول الحبوب والقش لنباتات الأرز مقارنة بباقي المعاملات .  
أدت إضافة المادة العضوية مع الصور المختلفة للزنك إلى زيادة نسبة الحبوب/ للقش (Grain/Straw ratio) .

كما أدت إضافة مركب  $Zn(urea)_4SO_4$  ، (Zn-EDTA) مع المادة العضوية إلى زيادة كمية النيتروجين والفسفور والبوتاسيوم فى الحبوب والقش لنباتات الأرز .  
أدت إضافة المادة العضوية إلى تحسين الحالة الغذائية لنباتات الأرز وذلك عن طريق تيسر عنصر الحديد والمنجنيز والزنك للنباتات مما أدى إلى زيادة تراكمها فى الحبوب والقش، لذلك كان للمادة العضوية دوراً هاماً فى معدل إطلاق العناصر الغذائية وزيادة حركتها وتيسرها للنباتات النامية .