RESEARCH ARTICLE

Relative yield and zinc uptake by rice from zinc sulphate and zinc oxide coatings onto urea

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Abstract Zinc (Zn) deficiency is prevalent worldwide and is a barrier to achieving yield goals in crops. It is also now recognized as a leading risk factor for disease in humans in developing countries. In general, soil application of $5-17$ kg of Zn ha⁻¹ year⁻¹ as zinc sulphate $(ZnSO₄)$ or more is recommended. However, in developing rice growing countries of Asia, $ZnSO₄$ of desired quality is not readily available and is also quite expensive, so the farmers generally fail to apply Zn, resulting in rice crop yield loss. Availability of Zn-coated urea guarantees not only the availability of quality Zn but also ensures its application. Field experiments were therefore conducted during the rice seasons of 2005 and 2006 at the Indian Agricultural Research Institute, New Delhi, to evaluate the relative efficiency of 0.5, 1.0, 1.5 and 2.0% Zn as $ZnSO₄$ - or zinc oxide (ZnO)coated ureas for rice. Soil application of $ZnSO₄$ was also compared in 2006. Rice grain and straw yields, Zn concentrations in grain and straw, and Zn uptake by rice increased with the level of Zn coating onto urea. Crop response was the highest with 2.0% ZnSO4-coated urea, and higher than with the same rate of ZnO-coated urea, possibly related to the higher water solubility of Zn in ZnSO₄. Crop

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response with ZnSO4-coated urea was also higher than with the same rate of $ZnSO₄$ and urea applied separately to the soil. However, apparent recovery data suggest that 1.0% coating with $ZnSO₄$ may be a better choice from the point of view of the utilization of applied Zn. Increased Zn concentrations in rice grain due to application of Zn-coated urea is important from the point of view of Zn nutrition of humans, since rice is the staple food in developing countries of Asia. Also, increased Zn concentrations in rice straw is of importance as regards cattle nutrition since in developing countries of Asia rice straw is the major feed for farm cattle.

Keywords Rice · Urea · Zinc-coated urea · Zinc nutrition \cdot Zinc oxide \cdot Zinc sulphate

Introduction

Zinc deficiency in soils is prevalent worldwide both in temperate and tropical climates (Katyal and Vlek [1985;](#page-6-0) Marschner [1995](#page-6-0); Adriano [2001;](#page-6-0) Normon et al. [2003;](#page-6-0) Fageria et al. [2003](#page-6-0); Prasad [2006](#page-6-0)). It is especially widespread in high pH calcareous soils (Liu et al. [1983;](#page-6-0) Katyal and Vlek [1985](#page-6-0)) and is a major barrier to achieving yield goals in developing countries. An analysis of 233,000 samples taken from different states showed that 47% of Indian soils are deficient in Zn (Takkar [1996](#page-7-0)). In India, Zn deficiency is widespread in the rice–wheat cropping system belt

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of north India, which has high pH calcareous soils (Prasad [2005\)](#page-6-0). Increase in soil pH is associated with increased sorption of Zn on soil hydroxides, carbonates and organic matter and decreased absorption by plant roots (Rupa and Tomar [1999\)](#page-6-0).

Zinc deficiency in rice is characterized by burnt dark brown patches of plants and was first reported by Nene [\(1966](#page-6-0)). Response of rice to Zn has been reported by several workers in India (Sarkar et al. [1983;](#page-6-0) Singh et al. [1983;](#page-6-0) Singh and Abrol [1986](#page-7-0); Agarwal and Gupta [1994](#page-6-0)), Philippines (Yoshida et al. [1973](#page-7-0)) and China (Liu et al. [1983;](#page-6-0) Shihua and Wenqiang [2000](#page-6-0)). Zinc is now recognized as the fifth leading risk factor in developing Asian countries (Anonymous [2007](#page-6-0)) and efforts are underway to reduce Zn deficiency in soils as it is not only a barrier to achieving crop yield goals but also results in low Zn content in grains and straw leading to poor Zn nutrition of humans and animals, a subject which has recently received considerable attention (Schardt [2006\)](#page-6-0).

In general, recommendations for soil application of Zn for crops vary from 5 to 17 kg Zn ha^{-1} in the form of ZnSO₄ (Mikkelson and Brandon [1975](#page-6-0); Fenster et al. [1984\)](#page-6-0). This product is quite costly, so small farmholders in Asia skip it resulting in reduced crop yields. Another factor that discourages the farmers from applying Zn in India is spurious ZnSO₄.7H₂O sold by unscrupulous traders. An attempt is therefore currently being made by the fertilizer industry in India to produce Zn-coated urea (also referred to as zincated urea), that would force the farmers to apply Zn to rice along with nitrogen that they mostly apply. $ZnSO_4 \cdot H_2O$ is generally used for coating urea because it contains 33% Zn and therefore lesser quantities are needed for coating. In addition to $ZnSO_4 \tcdot H_2O$, ZnO which contains 80% Zn is also being investigated for coating urea. The present investigation was therefore conducted to study the relative efficiency of $ZnSO₄$ - and ZnO-coated ureas for rice.

Materials and methods

The field experiments were conducted during the rainy seasons (July–November) of 2005 and 2006 at the research farm of the Indian Agricultural Research Institute, New Delhi, India. To avoid residual effects, the experiment in 2006 was conducted in a separate site in the same field. The Institute farm is located at $28^{\circ}58'$ N, $77^{\circ}10'E$ with an elevation of 228 m a.s.l. There are reports that response of rice to Zn fertilizers is related to the water soluble Zn content in them (Slaton et al. [2005\)](#page-7-0), and Westfall and Gangloff [\(2001](#page-7-0)) observed that Zn fertilizers must contain at least 50% water soluble Zn. Chemical analysis of available nutrients for the experimental soil was conducted by using the Subbiah and Asija ([1956\)](#page-7-0) procedure for determination of available N, Olsen's method for available P (Olsen et al. [1954\)](#page-6-0), the 1 M ammonium acetate method for available K determination (Hanway and Heidel [1952](#page-6-0)), and the chromic acid oxidation method for organic C (Walkey and Black [1934\)](#page-7-0). The experimental soil was low in available N (230 kg N ha^{-1}), medium in available P $(18.6 \text{ kg } P \text{ ha}^{-1})$ and K $(228 \text{ kg } K \text{ ha}^{-1})$, and also medium in organic C content (0.54%). The pH of the soil was 8.2 (1:2.5 soil:water ratio) and DTPAextractable Zn (Lindsay and Norvell [1978](#page-6-0)) in the soil was 0.68 mg kg⁻¹ soil. The critical level of "DTPAextractable'' Zn for rice grown on alluvial soils in the rice–wheat belt of North India varies from 0.38–0.90 mg kg^{-1} soil (Takkar et al. [1997](#page-7-0)).

There were nine treatments consisting of eight combinations of two coating materials $(ZnSO₄$ and ZnO) and four levels of Zn coating (0.5, 1.0, 1.5 and 2.0% w/w of prilled urea) and a no Zn control. In 2006, one additional treatment of separate soil applications of 5 kg Zn ha^{-1} as ZnSO₄ was also added to the soil surface (broadcast and incorporated), which is the general recommendation for rice in India (Rattan et al. [1997\)](#page-6-0). It was incorporated in soil after final puddling and before transplanting of rice. The field experiment was conducted in a randomized block design with three replications All plots received 120 kg N ha^{-1} as urea. ZnSO₄ and ZnO-coated urea was obtained from the Indo-Gulf Fertilizers, Jagdishpur (UP), India.

The experimental field was disk-ploughed twice, puddled thrice with a puddler in standing water and levelled. At final puddling, 26 kg P ha^{-1} as single superphosphate and 33 kg K ha⁻¹ as KCl was broadcast. Nitrogen at 120 kg N ha^{-1} as prilled urea or Zn-coated urea was band applied in two equal splits, half 10 days after transplanting (DAT) and the other half at panicle initiation (40 DAT). Thus, Zn in zincated urea was band applied. When applied at the site, Zn-coated urea supplied 1.3, 2.6, 3.9 and 5.2 kg

Zn ha^{-1} for the 0.5, 1.0, 1.5 and 2.0% coatings, respectively. To make up for the short fall of N in Zncoated ureas, calculated amounts of additional N as prilled urea were added in plots receiving Zn-coated ureas.

Two to three 25-day-old seedlings of basmati (aromatic) rice variety 'Pusa Sugandh 5' were transplanted on hills spaced at $20 \times 10 \text{ cm}^2$ in the second week of July in both years of study. 'Pusa Sugandh 5', a derivative of Pusa $3A \times$ Karnal Basmati, is a semi-dwarf (90–100 cm height), high yielding basmati rice variety released in the year 2004 by the Indian Agricultural Research Institute, New Delhi, for commercial cultivation.

Rice was harvested in the first week of November in both the years of study. Ten hills were randomly selected in each plot for measuring plant height and fertile tillers hill⁻¹ 10 days before harvest and the average values were computed. Similarly, 10 panicles were randomly selected from each plot for recording the data on yield attributes (panicle length, panicle weight, grains panicle⁻¹ and 1,000-grain weight). At harvest, grain and straw yield was recorded for each plot of the experiment, and samples of grain and straw were drawn from each plot for the chemical analysis for Zn concentrations. Zinc in grain and straw samples was analysed on a di-acid (HClO₄ + $HNO₃$ in 3:10 ratio) digest on an Atomic Absorption Spectrophotometer (Prasad et al. [2006](#page-6-0)). Thereafter, the uptake of the Zn was calculated by multiplying Zn concentrations with their respective plot yield of grain and straw of rice.

Apparent recovery (AR) of applied Zn was calculated by using the following expressions as suggested by Fageria and Baliger [\(2003](#page-6-0)):

 $AR_{zn} = (U_{Zn} - U_{Pu})/Zn_a$

where,

ARzn refers to apparent recovery of zinc

 U_{Zn} refers to the Zn uptake in zincated urea plot $(kg ha^{-1})$

 U_{Pu} refers to the Zn uptake in uncoated urea plot $(kg ha^{-1})$

 Zn_a refers to the amount of Zn applied (kg ha⁻¹).

All the data obtained from rice crop for the consecutive 2 years were statistically analysed using the F-test as per the procedure given by Gomez and Gomez [\(1984\)](#page-6-0). LSD values at $P = 0.05$ were used to determine the significance differences between treatment means.

Results

Grain yield

Data on yields are in Table [1.](#page-3-0) In 2005, a significant increase in grain yield of rice over prilled urea was obtained with 1.0, 1.5 and 2.0% ZnSO₄ and with 2.0% ZnO-coated urea. In 2006, a significant increase in rice grain yield was obtained with 1.0, 1.5 and 2.0% coating with $ZnSO₄$ or ZnO -coated urea and with soil application of ZnSO₄. Also, the 2.0% coating with either Zn source gave higher grain yield of rice than 1.0% coating of Zn. In both years, the percentage increase in grain yield of rice was always greater with $ZnSO₄$ -coating than with ZnO -coating. The better response of rice to $ZnSO₄$ was due to it being 100% water soluble as compared to ZnO, which is insoluble in water [a 4% commercial product AdNano[®] ZnO20 dispersion in water has only 5.4 ppm of Zn ions in solution (via internet)]. Slaton et al. [\(2005](#page-7-0)) also reported that Zn fertilizer ZnSO31 having 100% water soluble Zn (WSZn) produced significantly more rice grain than ZnOxS36 containing only 14% WSZn. Water soluble Zn is more mobile and can easily absorbed by rice plant roots. Giordano and Mortvedt [\(1972](#page-6-0)) reported that the movement of Zn fertilizer 4 weeks after application was 20 mm for ZnSO₄ and 5 mm for ZnO.

Straw yield

A significant increase in straw yield of rice was obtained only in 2006 when all the Zn-coated ureas and soil application of $ZnSO₄$ produced significantly more straw than uncoated urea, and 2.0% ZnSO₄coated urea produced significantly more than 0.5 and 1.0% ZnSO4- and ZnO-coated ureas. The highest straw yield of rice was recorded with 2.0% ZnSO₄coated urea during both years.

Zinc concentrations in grain

Data on zinc concentrations are in Table [2](#page-3-0). In 2005, Zn concentrations in rice grain were significantly

Treatments	2005		2006	
	Grain yield $(t \, ha^{-1})$	Straw yield $(t \, ha^{-1})$	Grain yield $(t \, ha^{-1})$	Straw yield $(t \, ha^{-1})$
Prilled urea	4.02	10.0	3.95	8.78
0.5% ZnO-coated urea	4.28	10.5	4.22	9.50
0.5% ZnSO ₄ -coated urea	4.52	10.5	4.37	9.74
1.0% ZnO-coated urea	4.45	10.5	4.47	10.00
1.0% ZnSO ₄ -coated urea	4.65	10.8	4.68	10.40
1.5% ZnO-coated urea	4.61	10.7	4.75	10.50
1.5% ZnSO ₄ -coated urea	4.89	11.2	5.04	10.80
2.0% ZnO-coated urea	4.78	10.9	5.12	10.80
2.0% ZnSO ₄ -coated urea	5.03	11.3	5.26	11.20
Separate soil application of 25 kg $ZnSO4$ ha ⁻¹	-		5.18	11.05
LSD $(P = 0.05)$	0.7	NS	0.52	0.64

Table 1 Grain and straw yield of rice as influenced by Zn-coated urea applications

Table 2 Zinc concentration in rice as influenced by Zn-coated urea applications

Treatment	Zinc applied $(kg ha^{-1})$	Zinc concentration (mg kg^{-1} DM)			
		2005		2006	
		Grain	Straw	Grain	Straw
Prilled urea	$\boldsymbol{0}$	29.7	60.3	30.7	65.4
0.5% ZnO-coated urea	1.3	31.0	72.7	33.1	76.0
0.5% ZnSO ₄ -coated urea	1.3	33.5	77.6	36.5	78.7
1.0% ZnO-coated urea	2.6	34.6	75.6	38.1	78.8
1.0% ZnSO ₄ -coated urea	2.6	37.9	80.5	40.1	84.1
1.5% ZnO-coated urea	3.9	38.9	78.7	41.1	84.1
1.5% ZnSO ₄ -coated urea	3.9	40.4	81.9	43.0	87.9
2.0% ZnO-coated urea	5.2	41.6	81.5	44.4	88.6
2.0% ZnSO ₄ -coated urea	5.2	44.0	88.5	50.8	96.1
Separate soil application of 25 kg $ZnSO4$ ha ⁻¹	5.3			45.3	93.2
LSD $(P = 0.05)$		5.31	14.21	2.25	4.75

increased over prilled urea with 1.0, 1.5 and 2.0% ZnSO4-coated urea and 1.5 and 2.0% of ZnO-coated urea. Further, Zn concentrations in grain were higher with a $ZnSO_4$ -coating of 2.0% than 1% $ZnSO_4$. In 2006, all Zn-coated ureas significantly increased Zn concentrations in rice grain and, at all levels of coatings, ZnSO4-coated urea recorded significantly higher Zn concentrations in rice grain. Also, there was a stepwise significant increase in $ZnSO₄$ -coatings from 0.5 to 2.0%. Application of 2.0% ZnSO₄-coated urea also gave significantly higher concentrations of Zn in grain than separate soil application of ZnSO₄. The highest Zn concentrations in rice grain was recorded with 2.0% ZnSO₄-coated urea in both years and was 44 mg kg^{-1} in 2005 and 50.8 mg kg^{-1} in 2006.

Zinc concentrations in straw

In 2005, all Zn-coated ureas except 0.5% ZnOcoating of prilled urea were similar and gave significantly higher Zn concentrations than prilled urea. Also, the difference between successive levels of Zn coatings, i.e. 1.0 to 1.5% and 1.5 to 2.0%, was significant for both $ZnSO₄$ and ZnO . However, the difference between 0.5 and 1.0% coating was significant for ZnSO4- but not for ZnO-coated urea. Zn concentrations in straw with 2.0% ZnSO₄-coated urea did not differ significantly from those obtained with separate soil applications of ZnSO4. Nevertheless, the highest Zn concentrations in rice straw was recorded with 2.0% ZnSO₄-coated urea in both years and was 88.8 mg kg⁻¹ in 2005 and 96.1 mg kg⁻¹ in 2006.

Zinc uptake in grain

Data on Zn uptake and Zn apparent recovery by rice are in Table 3. In 2005, coating urea with 1.5 or 2.0% ZnSO4 or ZnO-coated urea were similar and gave significantly higher Zn uptake by rice grain than prilled urea. In 2006, all coating levels except the 0.5% ZnO-coating increased Zn uptake in rice grain. Also, coating urea with 2.0% ZnO or ZnSO₄ was similar with separate soil application of $ZnSO₄$ and gave significantly higher Zn uptake by rice grain than 1.0% coating with $ZnSO₄$ or ZnO. Nevertheless, the highest Zn uptake in rice grain was recorded with 2.0% ZnSO₄-coated urea and was 220 g Zn ha⁻¹ in 2005 and 268 g Zn ha^{-1} in 2006.

Zinc uptake in straw

In 2005, Zn uptake by rice straw was similar with all Zn coatings (except the 0.5% ZnO coating) and was significantly higher than with prilled urea alone (Table 3). In 2006, all Zn coatings gave significantly higher Zn uptake and were higher with coatings of ZnSO4 than ZnO. Further, Zn uptake by rice straw increased with each successive level from 0.5 to 2.0% with either Zn source coated onto urea prills. Coating urea with $ZnSO_4$ at 2.0% resulted in the highest Zn uptake for both years, and it was also superior to separate soil application of ZnSO4.

Total (grain + straw) Zn uptake by rice

Since rice straw accounted for about 80% of Zn taken up by rice crop, total Zn uptake by rice followed nearly the same pattern as Zn uptake by rice straw. Total Zn uptake by rice was the highest with 2.0% ZnSO4-coated urea.

Apparent recovery of Zn (AR_{Zn})

As expected, apparent recovery of applied Zn decreased with an increase in the level of Zn coating onto urea (therefore decreasing the rate of applied

Zn). In both years, the highest AR_{Zn} was recorded with the 0.5% Zn coating, and it was always higher at each level of urea coatings with $ZnSO₄$ than ZnO . Also, the differences in AR_{Zn} between the $ZnSO_4$ and ZnO coatings onto urea declined as the level of Zn coatings increased.

Discussion

Results of this present study showed that a significant increase in rice grain yields was obtained when urea was only coated with a minimum of 1% Zn (supplying 2.6 kg Zn ha⁻¹ equivalent to 13 kg ZnSO₄ ha⁻¹) or more. The highest grain and straw yield of rice was obtained with 2.0% Zn-coated urea, and at that level of coating was similar to that from the separate broadcast and incorporation of ZnSO4. However, Zn concentrations in grain and straw of rice increased with successive increases in the level of coating and the highest values were obtained with 2.0% Zn coating. This was also true for Zn uptake. As regards Zn concentrations and uptake by rice, concomitant application of Zn and urea as Zn-coated urea was more effective than their separate soil application as is the general practice. Application of Zn-coated urea also had the advantage of split application and banding of Zn close to the growing rice plants, which increased its uptake before applied Zn reacted with water and $CO₂$ in soil solution and converted it to $ZnCO₃$, which makes it less available to plants as pointed out by Yoshida et al. [\(1971](#page-7-0)).

An advantage of band application over broadcast soil application of Zn has been reported by Vitosh et al. ([1981\)](#page-7-0) and Grewing et al. ([1988\)](#page-6-0), who also observed that much smaller doses are required when Zn is banded. For example, Grewing et al. ([1988\)](#page-6-0) suggested band application of 1.0–5.5 kg ZnSO₄ ha⁻¹ as against $5.6-11.0$ kg $ZnSO₄$ ha⁻¹ for broadcast and incorporation. No reports on split application of Zn were found. In the present study, split application was necessitated because the material tested was Zncoated urea and urea is split applied. However, the results obtained showed that split application of Zn had no disadvantage especially when small doses are applied.

The mobility of Zn in plants is low (Mengel and Kirkby [1987](#page-6-0)) and Zn in older leaves becomes highly immobile (Rinne and Langston [1960\)](#page-6-0). This would explain why the concentration of Zn in rice straw was nearly twice that in rice grain. Zinc uptake by rice straw was still higher than Zn uptake in rice grain because straw yield was more than twice the grain yield in both the years of study. Lakshmanan et al. ([2005\)](#page-6-0) also reported that Zn uptake in rice grain (variety Pusa Basmati 1) varied from 130 to 162 g ha⁻¹ while in straw it varied from 797 to 931 g ha^{-1} .

As regards the relative value of the coating materials, $ZnSO₄$ is water-soluble and therefore readily available, making its effects visible in the plants, while ZnO is sparingly soluble and is not readily available. Water solubility of zinc sources is considered an important criterion for Zn availability (Slaton et al. [2005\)](#page-7-0). Westfall and Gangloff ([2001\)](#page-7-0) observed that the effectiveness of six granulated Zn fertilizers decreased as the per cent water soluble Zn decreased in them, and concluded that at least 50% water-soluble Zn was considered desirable. To obtain this, Zn fertilizer manufacturers are producing mixtures of ZnSO4 and ZnO, which are referred to as Zn oxysulphates. Mikkleson and Brandon [\(1975](#page-6-0)) and Nayyar et al. ([1990\)](#page-6-0) also showed that ZnO was inferior to ZnSO4, both in grain yield and Zn uptake. However, the solid phase equilibria studies by Lindsay [\(1991](#page-6-0)) showed that, even in calcareous soils of pH 8.0, ZnO would maintain a Zn concentration of approximately 10^{-4} M Zn²⁺ or higher; higher than that maintained by soil Zn $(10^{-11}$ M). This concentration is much higher than the critical limit of 10^{-7} to 10^{-8} M Zn suggested by Carrol and Loneragan [\(1969](#page-6-0)) for plant growth. Thus, Zn from ZnO-coated urea will also make Zn available to rice. The results of the present study show that Zn availability from ZnO-coated ureas to rice is much slower and becomes available only at later growth stages, and thus remained more in straw than in grain.

Zinc deficiency is now recognized as the fifth leading risk factor for disease in humans in developing countries (Anonymous [2007\)](#page-6-0) and some efforts are therefore being made to produce cereal varieties that can absorb more Zn (Welch and Graham [1999\)](#page-7-0) so that nutritional demands of Zn of humans are more easily met, especially in developing countries of Asia where rice forms the staple diet. The results of our research show that use of Zn-coated urea could help in this direction.

Conclusions

It is concluded that $ZnSO₄$, because of it being soluble in water, is a better material than ZnO for coating urea and a 1.0% coating may be sufficient for higher productivity of rice, increased Zn concentrations and uptake by rice grain, and also a higher recovery of applied Zn.

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