

Comparative efficacy of ZnSO₄ and Zn-EDTA application for fertilization of rice (*Oryza sativa* L.)

(Vergleich der Effizienz von ZnSO₄ und Zn-EDTA Anwendung zur Düngung von Reis *Oryza sativa* L.)

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(Received 7 September 2004; accepted 30 October 2004)

Abstract

Widespread Zn deficiency for rice crop has been reported from different parts of the world, including India. To correct such deficiency, Zn is often applied to the soil as fertilizer. Its concentration in soil solution and its availability to crops is controlled by sorption–desorption reactions at the surfaces of soil colloidal materials. The objective of this study was to compare the availability and relative effectiveness of Zn from Zn-EDTA and ZnSO₄ sources by applying different Zn levels to a calcareous soil in field experiments through soil application. The uses of Zn-EDTA also increase the yield of rice dry matter yield and grain yield. Regarding maintenance of Zn in soil, it has been observed that the amount of Zn content was recorded higher with the split application of Zn-EDTA as compared to ZnSO₄ with the simultaneous 26.1% increase in the yield of rice.

Keywords: Rice, Zn fertilizers (ZnSO₄ and Zn-EDTA), extractable Zn, Zn uptake, yield

Introduction

One of the important essential micronutrients required for growth, development and yield of most crops, and especially for rice grown in low land conditions, is zinc (Zn). On average, 50% of the Indian soils are deficient in zinc (Zn), particularly in calcareous soils due to the formation of insoluble zinc hydroxide and its carbonate (Rattan & Shukla,

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1991; Singh & Abrol, 1986). However, zinc was one of the first micronutrients known to be essential for plants, animals, and man (Kabata-Pendias, 2000), and yet, in spite of that knowledge, Zn deficiencies still plague us today. Zinc plays an important role in different plant metabolism processes like the development of cell walls, respiration, carbohydrates metabolism and gene expression and its regulation (Klug & Rhodes, 1987). Zinc deficiency is the most widespread micronutrient disorder among different crops (Westfall et al. 1971; Romheld & Marschner, 1991). The deficiency of this micronutrient frequently occurs in rice which is very sensitive to low Zn supply in submerged rice soils (Hazra et al., 1987). The problem is more acute and serious for rice fields as around half of the total rice cultivation area found to be severely affected by Zn deficiency is grown mostly in submerged soils where availability of Zn is affected adversely (Mikkelsen & Kuo, 1976). Crop response to Zn fertilization varies with the Zn fertilizer source (Boawn, 1973). Zn deficiency is usually corrected through the application of an inorganic salt, mainly $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Another source are the chelated forms of Zn such as Zn-EDTA, which supplies substantial amount of Zn to the plant without interacting with soil components because the central metal ion Zn^{2+} is surrounded by chelate ligands (Mortvedt, 1979). Several studies (Prasad et al. 1976; Dhillon & Dhillon, 1983; Hergert et al. 1984) reported that, under greenhouse conditions, the application of non-chelated Zn fertilizers to calcareous soils is less effective than chelated forms of Zn.

The chelating agents DTPA (diethylenetriaminepentaacetic acid), HEDTA (hydroxyethylenediaminetriacetic acid), and EDTA (ethylenediaminetetraacetic acid) are some of the strongest synthetic chelating agents and form much stronger chelates with Zn than naturally occurring organic ligands (Norvell, 1983).

Very limited investigations about the behavior of chelated-Zn (Zn-EDTA) and its relationship with other soil properties related to rice growing on calcareous soils has been carried out under field condition. The foliar application can be more efficient, but the possibilities to apply are strongly limited after over-flooding of rice and by existing machines. Therefore, it was worthwhile to investigate the behavior of chelated-Zn in submerged soil of alkaline reaction in relation to rice through soil application. Rice was taken as a test crop as it is a major crop in West Bengal, India. The objectives of this study were to determine the relative efficacy of Zn in chelated form (Zn-EDTA) in soils of alkaline reaction over that of inorganic salt $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in relation to yield and nutrition of rice. The application of Zn-EDTA and ZnSO_4 to calcareous soil may exhibit their differential efficiency by interacting with soil components resulting in varying stability i.e., the rate of dissociation in such soil and such efficiency ultimately affect the available pool of Zn in the soil solution. Keeping these in view, the present investigation was undertaken to study the effect of two sources of Zn in relation to yield and nutrition of rice on its soil applications growing in calcareous soils under submerged conditions. The results may be helpful in planning an efficient management strategy for Zn especially for rice crop grown in calcareous submerged soils.

Materials and methods

One surface soil (0–15 cm depth) was collected from Mollisol (Kakdwip series), of alkaline soil reaction in the district of 24-Pargonas (South), West Bengal, India. It was analyzed for its different physico-chemical properties namely, pH, organic C, clay, Ca^{+2} , Mg^{+2} , Na^+ , K^+ etc (see Table I) following standard methods Jackson (1973) and Black et al. (1965). DTPA extractable Zn in soil was also measured by using the methodology outlined by Lindsay and Norvell (1978).

Table I. Physico – chemical properties of the soil.

Soil properties	Values
PH (H ₂ O) 1:2.5	8.8
EC (H ₂ O) 1:5 [dS m ⁻¹]	3.2
Org. C (g kg ⁻¹)	2.9
Sand (%)	80.5
Silt (%)	12.2
Clay (%)	7.3
Texture	Loamy sand
Order	Mollisol
DTPA–extractable Zn (mg kg ⁻¹)	0.38
Ca ⁺² (mg kg ⁻¹)	1.70
Mg ⁺² (mg kg ⁻¹)	2.05
Na ⁺ (mg kg ⁻¹)	36.96
K ⁺ (mg kg ⁻¹)	46.20
Cl ⁻ (mg kg ⁻¹)	38.0
HCO ₃ ⁻ (mg kg ⁻¹)	12.00

Field experiment

During the years 1999–2000 and 2000–01 field experiments on rice (cv. IET–4094; local name: Kshitish) were conducted in Kakdwip farm; Bidhan Chandra Krishi Viswavidyalaya; West Bengal, India (22°57' N latitude and 88°20' E longitude, average altitude of 7.8 m above mean sea level) to examine the utilization of added Zn towards the nutrition and yield of rice. The experimental field was laid out with a number of sub plots measuring 5 m long and 4 m wide having an area of 20 m² surrounded by bunds of 0.30 m width with sufficient height to check the mixing of different treatment materials.

Treatment descriptions

Treatments Description

- S0 – Control (no application of ZnSO₄. 7H₂O or Zn-EDTA)
- S1 – 0.5 kg Zn ha⁻¹ as Zn-EDTA after 14 days of transplanting (DAT)
- S2 – 1 kg Zn ha⁻¹ as Zn-EDTA after 14 days of transplanting
- S3 – 1 kg Zn ha⁻¹ as Zn-EDTA (application of Zn as Zn-EDTA in two equal splits; 0.5 kg Zn ha⁻¹ as Zn-EDTA at grand tillering stage i.e., 14 DAT and 0.5 kg Zn ha⁻¹ as Zn-EDTA at panicle initiation stage i.e., 49 DAT)
- S4 – 0.5 kg Zn ha⁻¹ as ZnSO₄. 7H₂O after 14 DAT
- S5 – 1 kg Zn ha⁻¹ as ZnSO₄. 7H₂O after 14 DAT
- S6 – 1 kg Zn ha⁻¹ as ZnSO₄. 7H₂O (application of Zn as ZnSO₄. 7H₂O in two equal splits; 0.5 kg Zn ha⁻¹ as ZnSO₄. 7H₂O at grand tillering stage i.e., 14 DAT and 0.5 kg Zn ha⁻¹ as Zn-EDTA at panicle initiation stage i.e., 49 DAT)

Irrigation channels measuring 0.5 m wide were in between the replications in order to ensure easy and uninterrupted flow of irrigation water where an individual plot was made independently irrigated from the irrigation channels. The experiment was laid out in a randomized block design (RBD) and the respective treatments were applied to each plot. Each treatment was replicated three times. All the plots of experiments received recommended applications of NPK fertilizers in the ratio of 100:60:60 kg as N: P₂O₅: K₂O

respectively one day before transplanting through soil application. The sources of NPK nutrients were urea, single super phosphate, and muriate of potash respectively. All Zn treatments were given through soil application. Two heels comprised of six rice seedlings (cv. IET 4094, local name Khetish) were transplanted in each plot with the spacing 20×10 cm. There was also a control series in which the rice seedlings were transplanted immediately after flooding the soil. Experimental design, treatments etc. in the year 2000–2001 were the same as followed in the year 1999–2000.

Soil (0–10 cm depth) and plant samples (only shoots) were collected at intervals of seven days up to 63 days of crop growth from five to six randomly selected locations in each plot in submerged condition. 10 g of soil was taken for estimation of DTPA-extractable zinc content of the soil. 0.005 M DTPA solution was used to extract the available pool of zinc (Lindsay & Norvell, 1978).

Plant samples were washed initially by tap water followed by dilute hydrochloric acid (0.05 N), deionised water and finally with Zn free double distilled water. Each plant sample was chopped separately and dried under sunlight. 50 mg dried plant sample was digested with triacid mixture: HNO_3 : HClO_4 : $\text{H}_2\text{SO}_4 = 10:4:1$ for analysis of Zn in the tissues (Jackson, 1973).

At harvest, the yield of rice grain was recorded from each plot and analyzed for total Zn described by Jackson (1973). Leaves and stem samples were taken at harvest for recording dry matter yield. At each sampling, a one meter long row was randomly selected. The plants were harvested at the ground level. Leaves and stems were taken together for their total dry weight determination. The samples were then thoroughly washed to remove all soil particles and other materials adhered to it. The samples were then dried in an air oven at a temperature of $65 \pm 5^\circ\text{C}$.

All the measured Zn data including both soils and plants were statistically analyzed for critical difference using the test of Newman-Keuls (at the 0.05 probability level) using the statistical computer program MSTAT, version 5 (New Delhi, India). Non linear correlations and regressions equations were also calculated using the same computer package.

Results

DTPA-extractable Zn in soil

The average amount of DTPA-extractable Zn in soil as affected by the application of different sources of Zn during the year 1999–2000 and 2000–2001 is presented in Figure 1.

The results show that the periodic changes of DTPA-extractable Zn content during both the years showed a similar pattern of changes. However, the amount of Zn content in soil varies significantly with treatments. The Zn content in soil decreases significantly in the treatment S0 where no Zn was applied throughout a 63-day period of rice growth over the initial Zn content (0.51 mg kg^{-1}). Comparing the result of different treatments, it was observed that irrespective of different modes of application of a particular Zn source and level, the amount of Zn content in soil was relatively higher in the treatment where chelated-Zn was applied during both the years. Among the particular Zn sources, the amount of Zn content was maintained significantly highest amount in the treatment S3, where chelated-Zn (Zn-EDTA) was applied in two equal splits as compared to S1 and S2 treatments, where 0.5 and 1 kg Zn ha^{-1} were applied as basal in the form of Zn-EDTA. Further, the maintenance of DTPA-extractable Zn was recorded next superior in the treatment S3 (1 kg Zn ha^{-1} Zn-EDTA, two equal splits) than that of the treatment S6,

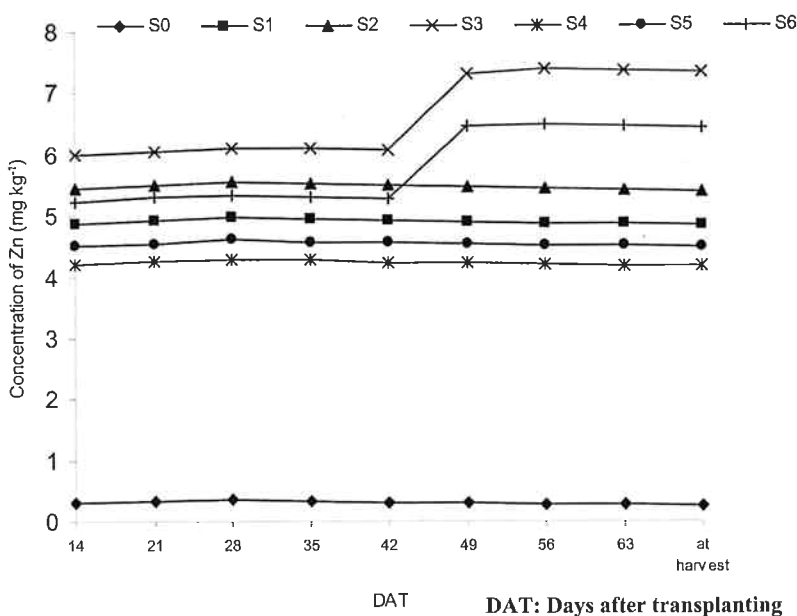


Figure 1. Effect of soil application of different sources of Zn on the periodic changes in Zn concentration in soil (mean of 1999–2000 and 2000–2001).

where 1 kg Zn ha⁻¹ was applied as two equal splits in the form of inorganic salt of Zn (ZnSO₄·7H₂O).

Zn content in rice

The results (Figure 2) show that the amount of Zn content in dry matter of rice gradually increases during the initial period of growth and thereafter, the content decreases at 63 days of growth irrespective of treatments during both the years. Such changes in Zn content in rice dry matter, however, varied with different sources of Zn, being greater with the application of chelated-Zn as compared to corresponding levels of ZnSO₄ application. The greater amount of Zn content in rice dry matter was maintained in S3 treatment where split application of chelated-Zn was applied at 63 days of crop growth during both the years, which was next followed by the treatment S5, where Zn @ 1 kg ha⁻¹ Zn as ZnSO₄ was applied at the time of transplanting.

The percentage increase of Zn content in rice dry matter was recorded relatively higher in the treatment where chelated-Zn was applied, being highest (52.5%) in the S3 treatment receiving split application of chelated-Zn. The results also show that the percentage increase of Zn content in rice dry matter was always recorded at a lower value with the treatment receiving different modes of ZnSO₄ application (S4, S5 and S6 treatments) corresponding to the result of chelated-Zn (S1, S2 and S3). The results of coefficient correlation (see Table II) showing the relationship between the Zn content in dry matter and Zn content in soil show that the amount of Zn content in soil has been found to be significant positively correlated with the Zn content of dry matter at different periods of crop growth during both the years. However, the Zn content in dry matter was more significantly correlated with the Zn content in soil at 56 ($r=0.931^{**}$) and 63 ($r=0.930^{**}$) days of crop growth during the year 1999–2000, which was also similarly correlated for the year 2000–2001.

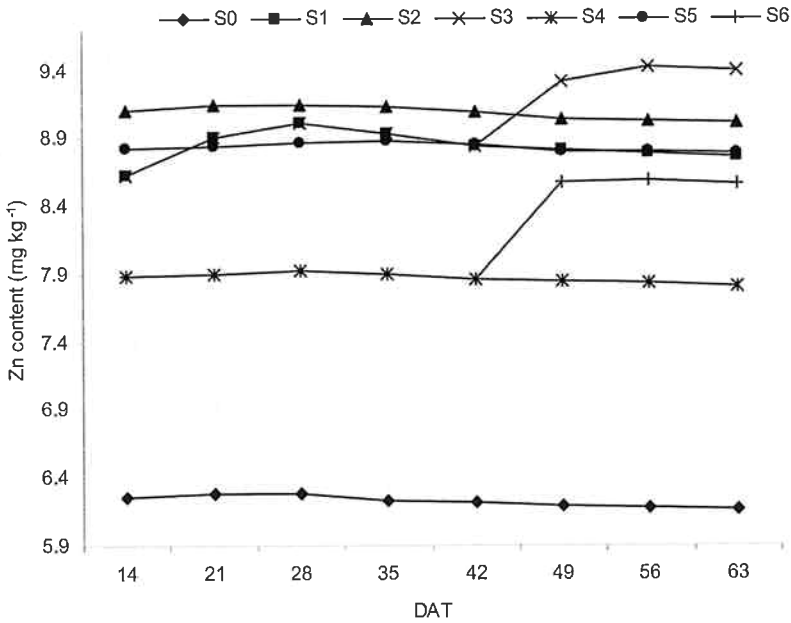


Figure 2. Effect of soil application of different sources of Zn on the changes of Zn content (mg kg⁻¹) in dry matter of rice during the year (mean of two years).

Table II. Regression equations and correlation co-efficient (*r*) showing the relationship between Zn content in dry matter (Y) vs Zn content in soil (X) during the winter seasons 1999–2000 and 2000–2001.

Parameters	DAT [#]	Regression equation	Correlation co-efficient (<i>r</i>)
1999–2000			
Zn content in dry matter (Y) vs Zn content in soil (X)	14	Y = 0.451X + 6.21	0.886*
	21	Y = 0.449X + 6.20	0.887*
	28	Y = 0.417X + 6.17	0.893*
	35	Y = 0.481X + 6.18	0.891*
	42	Y = 0.483X + 6.15	0.889*
	49	Y = 0.438X + 6.30	0.925**
	56	Y = 0.447X + 6.26	0.931**
63	Y = 0.447X + 6.25	0.930**	
2000–2001			
Zn content in dry matter (Y) vs Zn content in soil (X)	14	Y = 0.451X + 6.20	0.884*
	21	Y = 0.472X + 6.18	0.887*
	28	Y = 0.483X + 6.16	0.891*
	35	Y = 0.483X + 6.12	0.892*
	42	Y = 0.473X + 6.13	0.887*
	49	Y = 0.435X + 6.30	0.918*
	56	Y = 0.440X + 6.28	0.923**
	63	Y = 0.438X + 6.28	0.921**

DAT = Days after transplanting.

Zinc content and uptake of rice grain and straw

The results for the mean Zn content in and uptake by grain and straw in rice during the winter seasons 1999–2000 and 2000–2001 are presented in Figures 3, 4, 5, and 6 respectively.

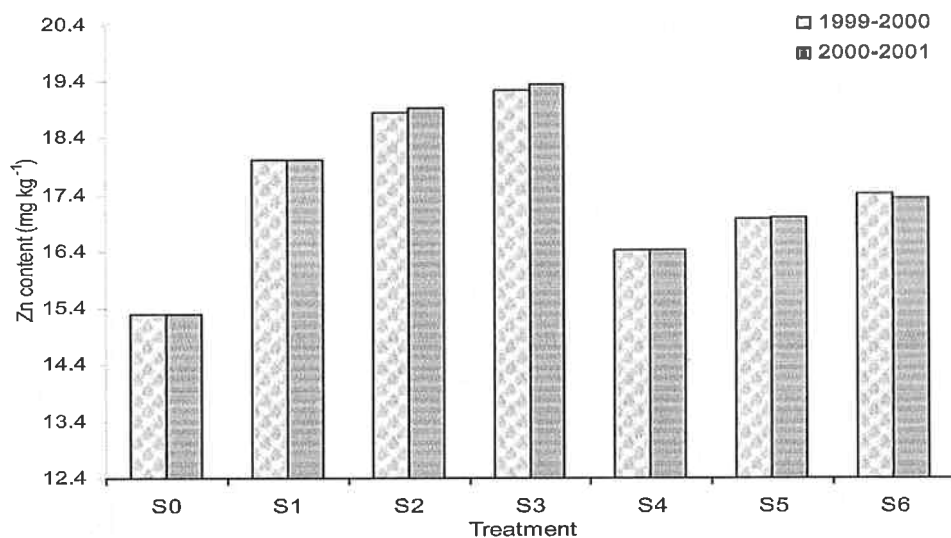


Figure 3. Effect of soil application of different sources of Zn on the mean changes of Zn content (mg kg⁻¹) in grain during the year 1999–2000 and 2000–2001.

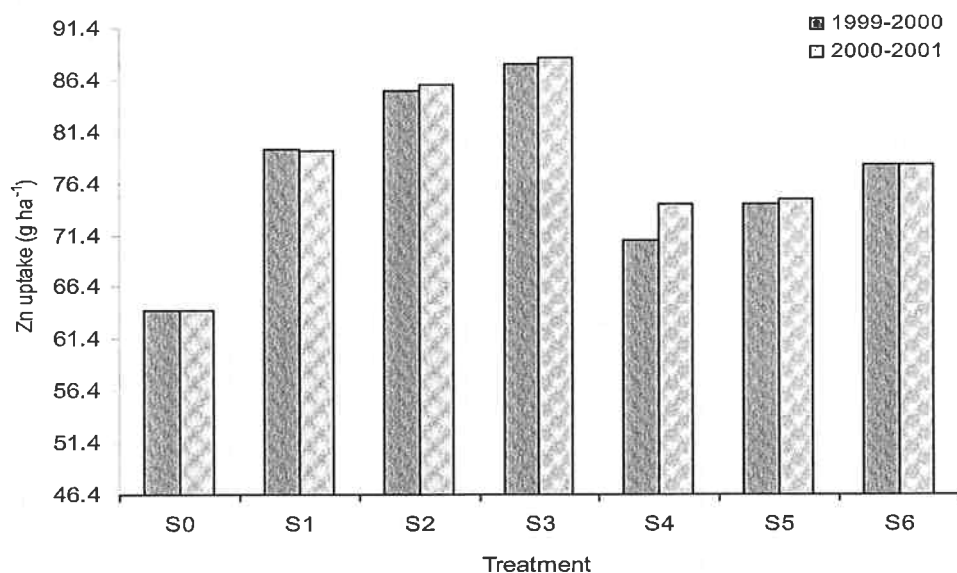


Figure 4. Effect of soil application of different sources of Zn on the mean changes of Zn uptake (g ha⁻¹) by grain during the year 1999–2000 and 2000–2001.

The amount of Zn content in rice grain and straw significantly varied with different sources of Zn application. The amount of Zn content in both grain and straw was always significantly higher with the application of different levels and modes of chelated-Zn (Zn-EDTA) as compared to ZnSO₄ application, being significantly highest content in grain (19.3 mg kg⁻¹) and straw (17.8 mg kg⁻¹) in the treatment S3 where chelated-Zn was applied as two splits during the year 1999–2000. The same trend of changes was also observed in the Zn content

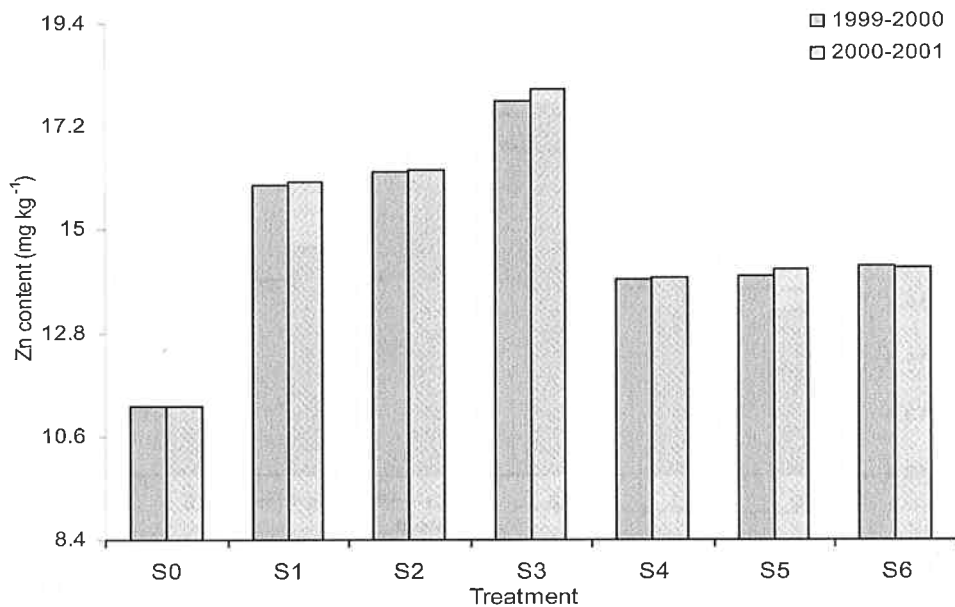


Figure 5. Effect of soil application of different sources of Zn on the mean changes of Zn content (mg kg^{-1}) in straw during the year 1999–2000 and 2000–2001.

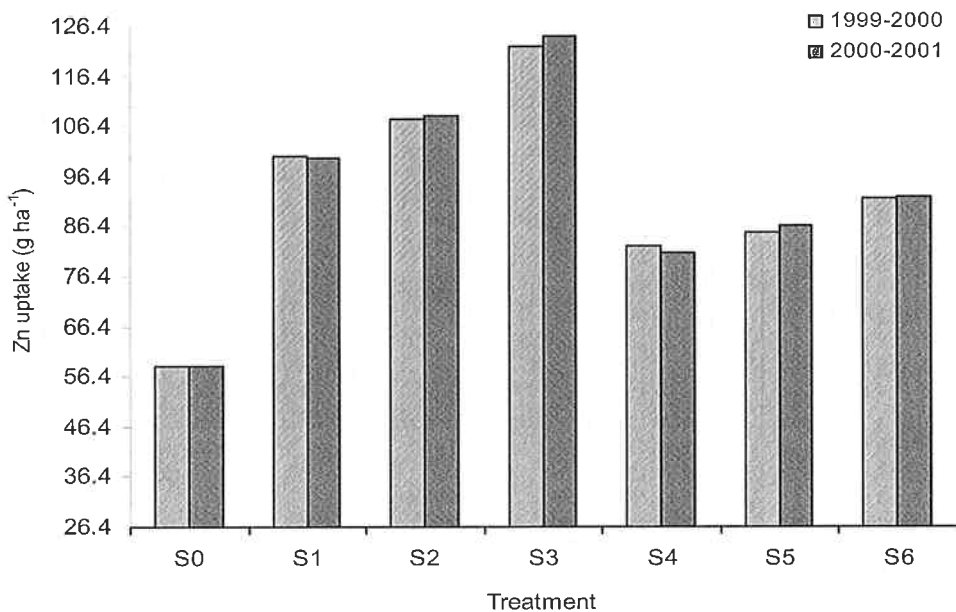


Figure 6. Effect of soil application of different sources of Zn on the mean changes of Zn uptake (g ha^{-1}) by straw during the year 1999–2000 and 2000–2001.

in grain and straw during the following year. The highest uptake of Zn by grain (88.5 g ha^{-1}) and straw (124.3 g ha^{-1}) was recorded significantly highest in the treatment S3 during the year 2000–2001. The results further show that the mean percentage increase of Zn content in

grain was recorded highest, being 26.1% higher in the S3 treatment over that of the control where no Zn was applied, while that of the same content in grain was recorded a decrease, being about 10% decrease in S6 treatment (split application of ZnSO_4) over that of the S3 (split application of Zn-EDTA). Similarly, the percentage increase of Zn content in and uptake by straw was also recorded highest by the S3 (chelated Zn) treatment as compared to other treatments. The changes in Zn content in and uptake by grain in both the years followed in the order of: S3 > S2 > S1 > S6 > S5 > S4 > S0.

Yield of grain and straw

The results show that the yield of both rice grain (Figure 7) and straw (Figure 8) was significantly increased with the application of different sources of Zn.

The highest yield of both grain (4.56 t ha^{-1}) and straw (6.88 t ha^{-1}) during both the years was recorded in the treatment S3 where 1 kg ha^{-1} Zn as Zn-EDTA was applied as two equal splits. However, the yield of both grain and straw showed the following trend of changes: S3 > S2 > S6 > S1 > S5 > S4 > S0.

The percentage increase recorded highest for grain (about 9%) and straw (32.37%) in the treatment (S3) over control, while that of the same increase was recorded highest in the ZnSO_4 treatment to only about 7 and 24.5% over control respectively.

In general, the results described the influence of applied soil Zn on the uptake and yield of rice. The time of Zn application in soils also has the greater influence on rice yield. The results are novel especially for India and other developing countries, because in the most cases ZnSO_4 is applied. However, in India Zn-EDTA is rarely used for rice crops. But from this

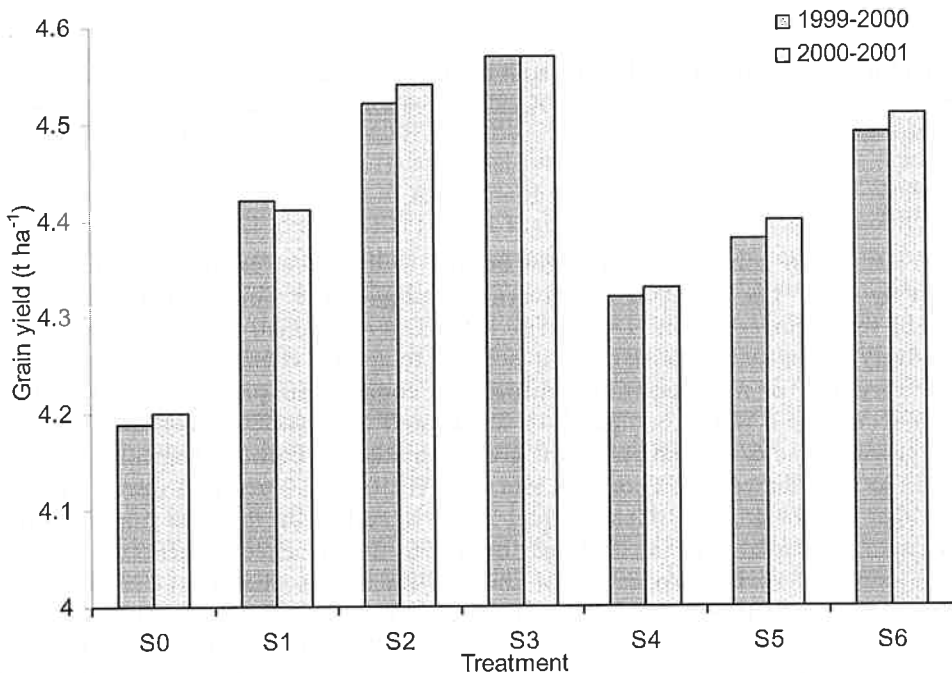


Figure 7. Effect of soil application of different sources of Zn on the grain yield (t ha^{-1}) during the year 1999–2000 and 2000–2001.

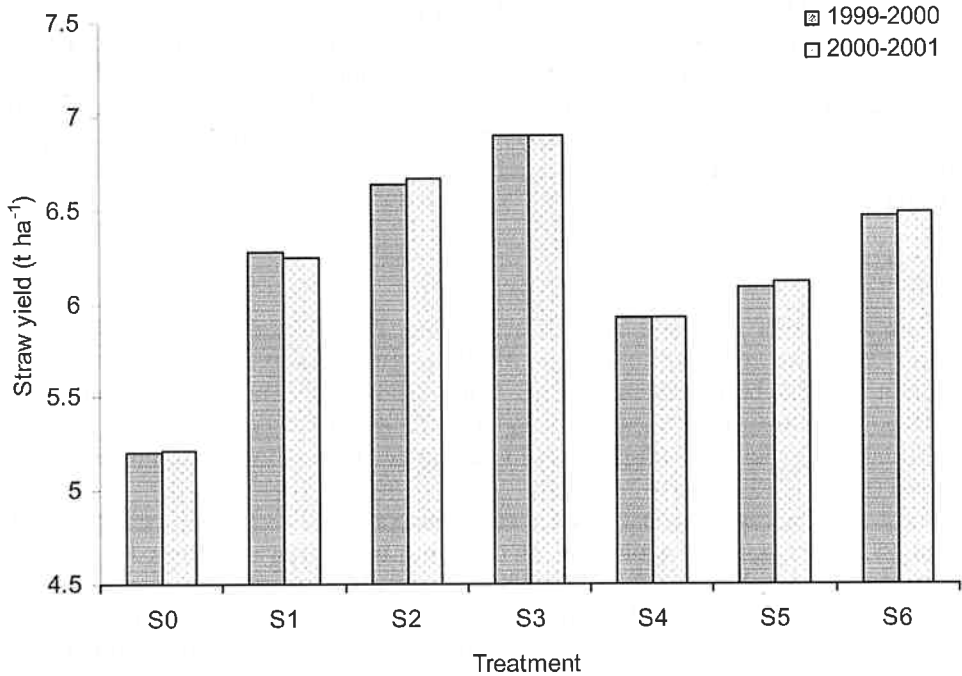


Figure 8. Effect of soil application of different sources of Zn on the straw yield (t ha^{-1}) during the year 1999–2000 and 2000–2001.

experiment it has been observed that the split application of Zn-EDTA (1 kg Zn ha^{-1} as Zn-EDTA) enhances rice yield. So Zn-EDTA can be recommended as a better source of Zn for rice crops.

Discussion

The decrease of Zn content in soil might be due to the effect of submergence as well as depletion by crop. The result of the present investigation is similar to that of the result reported by several investigators (Dutta et al. 1989; Das & Mandal, 1988; Prasad et al. 1991). The relatively higher maintenance of Zn in soil due to applied chelated-Zn may be attributed from the very little or no interaction between soil components preventing various harmful reactions occurring in soil as compared to soil treated with ZnSO_4 which enhances greater fixation, adsorption etc, resulting from the greater interaction between soil components. The results are in accordance with Giordano and Morvedt (1973). Ortiz and Garcia (1998) also reported that the chelated-Zn (Cosmo-Quel-Zn) is fixed less Zn than the sulphate source.

Increase in the Zn content in rice might be due to the presence of increased amounts of Zn in soil solution by the application of chelated-Zn that facilitates greater absorption of Zn as compared to ZnSO_4 application. The results are in agreement with the findings of Chatterjee and Mandal (1985). Mehdi et al. (1990) who reported that the relative effectiveness was in order of $\text{Zn-EDTA} > \text{Zn}(\text{NO}_3)_2 > (\text{NH}_4)_2\text{ZnO}_2 > \text{ZnSO}_4 > \text{ZnCl}_2$. Srivastava et al. (1999) also studied the comparative efficiency of different sources of Zn for low land rice production and reported that out of various sources, the chelated-Zn

(Zn-EDTA) was the most efficient sources of Zn for low land rice production. Singh et al. (1999) also reported that the application of the different sources of Zn up to 10 mg kg^{-1} increased the Zn concentration of rice leaves, being a higher uptake with Zn-EDTA than ZnSO_4 .

The highest uptake of Zn by grain and straw was recorded significantly highest in the treatment S3 during both the years of experiment. Zinc content and uptake of rice grain and straw of the present investigation confirmed the results reported by Ugurluoglu and Kacar (1996) who studied the efficiency of ZnO , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and Zn-EDTA on rice and reported that the application of Zn at the rate of 8 mg kg^{-1} as Zn-EDTA was found most effective in the enhancement of Zn content in rice plants. Rattan and Shukla (1991) studied the efficiency of Zn sources on rice *cv.* Pusa - 33 in Typic Ustipsament and reported that the Zn content and uptake by rice were in the order of Zn-EDTA > Zn-DTPA > ZnSO_4 . The results pointed out that the uptake of Zn by grain and straw was also recorded significantly higher in the treatment where different levels and modes of chelated-Zn were applied in both the years, suggesting a greater efficiency of chelated-Zn for the absorption of the Zn by straw and grain as compared to inorganic source, ZnSO_4 . This observed fact might be due to the greater production of grain and straw resulting from the higher content of Zn in plant by the application of chelated-Zn.

The increase in both grain and straw yield with Zn-EDTA application might be due to the relatively greater amount of Zn uptake compared to ZnSO_4 application. The results are in agreement with Takkar and Singh (1989), who reported that the efficiency of the chelated-Zn was proved superior towards increase in yield of rice grain than that of equivalent amount of Zn application as ZnSO_4 . Saravanan and Ramanathan (1988) also reported that the highest paddy yield was obtained at $25 \text{ kg ZnSO}_4 \text{ ha}^{-1}$ and also observed that the yield was positive correlated with soil Zn content.

Conclusions

The amount of available Zn content in soil was relatively higher with the split application of Zn-EDTA as compared to the ZnSO_4 application, which suggests that the application of chelated Zn (Zn-EDTA) either, as basal or split, was found to be superior in maintaining Zn in soil solution. From the present investigation, it is clearly found that the residual effect of chelated Zn (Zn-EDTA) in maintaining Zn in soil also recorded more than that of ZnSO_4 . The results further show that the amount of Zn content in dry matter, straw and grain was recorded highest with the application of chelated Zn particularly, when it is applied in two splits (first at grand tillering and second at panicle initiation stage) than that of inorganic ZnSO_4 application. The amount of Zn content in soil has been found to be significant positively correlated with the Zn content of dry matter straw and grain. The highest uptake of Zn by grain and straw was also recorded significantly highest in the treatment where the split application of chelated Zn was applied. The results further show that the mean percentage increase of Zn content in grain was recorded highest in the S3 treatment (split application of Zn-EDTA) over that of control, while the S6 treatment, with the split application of ZnSO_4 over that of split application of Zn-EDTA, recorded a decrease in the same content in grain. This experiment is focused on only Zn application through soil towards the yield of rice, however the efficiency of Zn fertilizers between foliar application and soil application is demanding. Therefore, for better understanding of efficiency of Zn fertilizer in relation to soil application vis-à-vis foliar application for rice yield needs to be further investigated.

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