

Original Research Article

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Effect of Zinc Fertilizer Levels and Application Methods on Zinc Fractions and Grain Yield of Maize

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ABSTRACT

Zinc deficiency in soil is induced due to soil micronutrient depletion from intensification of cultivation, application of high analysis NPK fertilizers and lesser use of organic manure. Among the various growth factors, zinc was recognized as one of the main limiting factors of maize crop growth and yields. This hypothesis was verified by conducting an experiment on zinc deficient soil to study the response of applied zinc through soil and foliar Zn-EDTA application at two stages of crop growth. The results revealed that soil application of ZnSO_4 @ 25 kg ha^{-1} recorded the highest grain yields (62.9 q ha^{-1}) which was at par with soil application of ZnSO_4 @ 20 kg ha^{-1} (61.5 q ha^{-1}) whereas, decline in grain yield of maize was observed at higher level of zinc soil application. Among the methods of zinc application, the combination treatment of seed fortification by 0.5 % of Zn-EDTA and two sprays of 0.2 % Zn-EDTA at 5th leaf stage and tasseling stages recorded relatively highest grain yield (59.0 q ha^{-1}) when compared to seed fortification and foliar application alone. Soil application of Zn explicitly influenced the Zn uptake by maize crop. The significantly highest Zn uptake was recorded by treatment application of ZnSO_4 @ 25 kg ha^{-1} (545 g ha^{-1}) which was at par with treatment, application of ZnSO_4 @ 20 kg ha^{-1} (532 g ha^{-1}). The accumulation of DTPA extractable Zn in the soil varied considerably within the treatments. Significant higher accumulation of DTPA extractable Zn was recorded by soil application of ZnSO_4 @ 30 kg ha^{-1} (0.43 mg kg^{-1}) which was statistically at par with soil application of ZnSO_4 @ 25 kg ha^{-1} (0.42 mg kg^{-1}). The zinc fractions did not show much variation however, treatment receiving zinc through soil application showed increased concentration of Zn fractions *versus* other methods of zinc fertilization. In general, application of 30 $\text{kg ZnSO}_4 \text{ ha}^{-1}$ recorded higher concentration but no distinct trend was observed. The highest concentration of WS-Zn (0.17 mg kg^{-1}), S-Zn (0.08 mg kg^{-1}) CA-Zn (0.25 mg kg^{-1}) was recorded by application of 30 $\text{kg ZnSO}_4 \text{ ha}^{-1}$. RES-Zn emerged as a dominant Zn fraction followed by OM-Zn. The Zn fractions were positively and significantly correlated with DTPA-Zn and Zn uptake and also exhibited positively and significantly correlated with each other.

Keywords

Foliar, Fortification,
Soil, Maize yield,
Zn fractions

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Introduction

Zinc deficiency in soil is wide spread in India, the average level of Zn deficiency in Indian

soil is about 50 % and the number is projected to increase to 63 % by 2025 (Singh, 2001). In Maharashtra the extent of Zn deficient soils ranged from 60 to 65 % (Singh, 2008). This

could be due to inherently infertile soils, soil micronutrient depletion consequent upon intensification of cultivation, less organic matter and imbalanced fertilizer use. Maize is a third most important cereal crop in India after rice and wheat. The zinc requirement of maize crop is substantially high, maize grown on soil having zinc content below the critical level is subjected to many biotic and abiotic stresses. Zinc deficiency significantly decreases net photosynthesis, stomatal conductance, maximal efficiency of photosystem-I, biomass (dry weight) and Zn concentrations in plants. Zinc-deficient plants also have a lower vascular bundle proportion coupled with a higher stomata density. These physiological and anatomical changes negatively impact the plant growth and thereby maize grain yield (Mattiello *et al.*, 2015). Bahera *et al.*, (2008) reported that Zn deficiency resulted in lower maize growth and decrease in grain yield and quality.

When it comes to human nutrition, zinc is an important mineral, contributing towards healthy human body. Some of the developing nations around the globe are highly reliant on cereal based diet, low Zn content in maize, grown on Zn deficient soil can lead to Zn deficiency in human and livestock as well. Such nation communities, having maize as their staple food are prone to the Zn deficiency induced health challenges (Jiang *et al.*, 2008). In order to reverse this trend, method of zinc application is a critical concern. Many researchers found soil application of Zn to be a better alternative of Zn nutrition whereas, some reported foliar application to be beneficial and more zinc fertilizer efficient. It was recently documented that zinc foliar application is a simple way for making quick correction of plant nutritional status, as reported for wheat (Erenoglu *et al.*, 2002) and maize (Grzebisz *et al.*, 2008). Foliar application though being efficient measure to mitigate Zn deficiency does not really take

care of soil Zn depletion. Soil application of Zn fertilizer could result in accumulation of DTPA extractable Zn and various fractions of Zn (Bahera *et al.*, 2008). The soil native and applied Zn reacts with the inorganic and organic phases in the soils that influence its availability to the plant. Therefore, it is essential to study the distribution of Zn among various fractions of soil that might help to characterize chemistry of Zn in soils and possibly its availability for plant uptake. In soils, Zn exists in 5 distinct pools: (1) water soluble, (2) easily exchangeable, (3) adsorbed, chelated, or complexed, (4) associated with secondary minerals, and (5) held in primary minerals (Viets, 1962).

The present investigation therefore was designed with an intention to study the effect of zinc nutrition through soil, foliar and seed fortification in order to ensure enhanced maize grain yield and to observe zinc uptake and zinc transformation in soil.

Materials and Methods

Experimental site

An experiment was carried out on research farm of Zonal Agricultural Research Station, Sub-montane Zone, Shenda Park Maharashtra on shallow Entisol. The experiment comprised of nine treatments, replicated thrice using RBD design. The fertilizer doses of nitrogen, phosphorus and potassium were applied on the basis of soil test values following the six tier system of fertilizer application. The various treatments of zinc application treatments were coupled with fertilizer dose as per soil test value (AST) and 5 t ha⁻¹ FYM for maize crop. The treatments comprised of three levels of ZnSO₄·xH₂O. 20, 25 and 30 kg ha⁻¹, seed fortification at the rate of 5 g per 100 g seeds and 0.2 % foliar spray of Zn-EDTA at grand growth and tasseling stage of maize crop. The experiment was conducted at zinc deficient

site (0.30 mg kg⁻¹ DTPA Zn) with low organic carbon (0.31 %), available nitrogen (248 kg ha⁻¹), available P (19.7 kg ha⁻¹) and available potassium (174 kg ha⁻¹).

Collection of soil samples

The soil samples were collected with the help of screw auger at 15 cm depth before and after harvest of the crop. The subsamples were collected from 4 randomly selected positions in each treatment plot and mixed thoroughly to obtain representative soil sample for each treatment. The samples were air dried, ground in wooden pestle-mortar and passed through 2 mm sieve.

Plant and soil analysis

The samples were analysed by following standard methods of analysis viz., organic carbon Walkley and Black (1934), Available N: Subbaih and Asija (1956), Olsen's P: Olsen *et al.*, (1954), Available K: Hanway and Heidel (1952), DTPA-extractable Zn: Lindsay and Norvell (1978).

To study the uptake of major nutrient and Zn, the grain and straw samples were collected from each plot at the time of harvest of maize. These samples were thoroughly washed and dried in oven at 50°C for 72 h, ground in a stainless steel Wiley mill, and digested in a di-acid mixture of HNO₃ and HClO₄ (Jackson 1973).

Sequential fractionation methods

The different fractions of Zn were analysed by following the sequential fraction method by Ma and Uren (1995). Soil sample weighing 5 g was taken for Zn fractionation. The sample was washed with 20 mL of double distilled water after each fractionation step. The fractionation steps involved are abridged as under in tabular form (Table.6).

The total concentration of Zn was determined after digestion of the soil with H₂SO₄-HClO₄-HNO₃-HF mixture. The concentration of zinc was determined by means of an atomic absorption spectrometry with a flame (air-acetylene) atomization (Thermo Scientific India Ltd.). A zinc hollow cathode lamp was operated at 10 mA current. The integrated absorbance signal of zinc was measured at 213.9 nm with a slit width of 0.2 nm using deuterium background correction.

Results and Discussion

Yield

The yield data depicted in table 1 revealed that ZnSO₄ application through soil had recorded in general, higher grain yield of maize when compared to other method of zinc fertilization but at higher level of ZnSO₄ soil application the yield was found to be decline

When it was compared amongst the foliar application methods, combination treatment of seed fortification and Zn-EDTA spray at 5th leaf stage and tasseling stage emerged as promising approach of Zn fertilization. The treatment AST + ZnSO₄ soil application @ 25 kg ha⁻¹ recorded the highest grain yields (62.9 q ha⁻¹) which was at par to soil application of ZnSO₄ @ 20 kg ha⁻¹ (61.5 q ha⁻¹) and was significantly superior over AST + 5 t FYM ha⁻¹ (56.4 q ha⁻¹).

The lowest yield was recorded by control (8.3 q ha⁻¹). Similar pattern was observed in straw yields. This result clearly showed that there was a spectacular response for applied Zn when the Zn status was below critical limit. The results are in conformity with that of Durgude *et al.*, (2014) who reported higher yield of maize with soil and foliar application of Zn and Fe. Panneerselvam and Stalin (2014) studied Zn response in maize crop on Zn deficient site and found that the maize

yield significantly improved due to application of Zn whereas, there no or declining response to higher levels of Zn application.

Nutrient uptake

In general higher uptake of nutrients was observed with higher level of Zn application. The treatment AST + ZnSO₄ soil application @ 25 kg ha⁻¹ recorded highest uptake of nutrients (195, 31, 176 kg N, P, K ha⁻¹) which was at par with AST + ZnSO₄ soil application @ 20 kg ha⁻¹ (191, 31, 172 kg N, P, K ha⁻¹) and significantly superior over AST + 5 t FYM ha⁻¹ (162, 26, 146 kg N, P, K ha⁻¹) and AST + water spray (154, 25, 140 kg N, P, K ha⁻¹). The Zinc uptake was higher in the treatments receiving Zn nutrition through soil application when compare to treatment receiving through foliar or combine treatment of foliar and seed fortification.

Significant higher value of Zn uptake was observed in treatment AST + ZnSO₄ soil application @ 25 kg ha⁻¹ (532 g ha⁻¹) which was at par with AST + ZnSO₄ soil application @ 25 kg ha⁻¹ (532 g ha⁻¹) and significantly superior over AST + Water spray (338 g ha⁻¹).

Amongst the different treatment foliar application the combine treatment of foliar and seed fortification recorded higher uptake of Zn (507 g ha⁻¹) followed by treatment foliar spray of Zn EDTA @ 0.2 % at grand growth and tasseling stages of crop growth (474 g ha⁻¹). The foregoing results are in close agreement to that of Durgude *et al.*, (2014) who reported higher uptake of nutrients with higher level of Zn application.

They observed that the uptake of Zn is higher in case of soil application of Zn when compared to foliar application. Further, their data also revealed that the highest level of ZnSO₄ application through soil recorded slightly lower uptake of phosphorus. This

could be the antagonistic interaction of Zn and P in the soil system. Similarly, Das *et al.*, (2005) reported that the amount of P and Zn in soils showed an increase with their separate applications either as soil or foliar spray while that of the same value significantly decreased both in soils and plants due to their combined applications, suggesting a mutual antagonistic effect between Zn and P affecting each other's availability in soil and content in the stevia plant.

Soil properties

The data pertaining to soil properties and nutrient status presented in table 2 revealed that the soil properties after harvest of the crop *viz.* pH, EC and organic carbon content of the soil were not altered by the application of different treatments. Similarly, the available nutrient N, P, K was not influence by the different treatments. However, a slightly lower value of available P (22 kg ha⁻¹) was observed in treatment receiving higher Zn i.e. 30 kg ZnSO₄ ha⁻¹.

The DTPA extractable Zn showed a spectacular difference between the foliar application and soil application method of Zn fertilization. The treatment AST+ ZnSO₄ soil application @ 30 kg ha⁻¹ recorded significantly highest values of DTPA extractable Zn (0.43 mg kg⁻¹) which was at par with ZnSO₄ soil application @ 25 (0.42 mg kg⁻¹) and 20 kg ha⁻¹ (0.42 mg kg⁻¹) whereas, significantly superior over all other treatments.

In general soil application of ZnSO₄ proved to be most efficient nutrient management practice to enhance the Zn content in the soil.

The finding is in close agreement with those by reported by Durgude *et al.*, (2014), Bahera *et al.*, (2008). Priyanka *et al.*, (2017) reported that the treatment receiving soil Zn + FYM resulted in higher accumulation of DTPA-Zn

Zinc fraction

The data on Zn fractions, illustrated in table 3 revealed that the method of zinc application did not influence the concentration zinc fractions to the major extent. However, slight difference in the concentration Zn fractions could be observed when Zn soil application and foliar application method was being compared. The treatment AST + ZnSO₄ soil application @ 30 kg ha⁻¹ recorded significantly higher values for water soluble-Zn (0.17 mg kg⁻¹) which was statistically at par to other treatment except control and without Zn treatments. Sorbed-Zn (S-Zn) showed statistically non-significant relationship between all the treatments however, higher concentration S-Zn was observed in treatment AST + ZnSO₄ soil application @ 30 kg ha⁻¹ (0.08 mg kg⁻¹).

Zn associated with easily reducible Mn (ERMn-Zn) found to be significantly highest in treatment AST + ZnSO₄ soil application @ 25 kg ha⁻¹ (0.31 mg kg⁻¹) which was at par with all other treatments except control (0.22 mg kg⁻¹). Zinc associate with carbonate (CA-Zn) recorded significant highest value by treatment AST + ZnSO₄ soil application @ 30 kg ha⁻¹ (0.25 mg kg⁻¹) which was found to be superior over treatments receiving foliar Zn application and control while statistically at par with other soil application treatments.

In case of Zn associated with organic matter (OM-Zn) no statistical difference was noticed amongst the various treatments however, significant higher concentration was recorded by treatment AST + ZnSO₄ soil application @ 30 kg ha⁻¹ (0.51 mg kg⁻¹) over control (0.40 mg kg⁻¹). This might be due to common application of organic manure (5 t ha⁻¹) received by all treatments except control. Zn associated with Fe and Al oxides (FeOx-Zn) showed similar trend to that of OM-Zn with non-significant but highest value recorded by

AST + ZnSO₄ soil application @ 30 kg ha⁻¹ (0.43 mg kg⁻¹). The residual Zn (RES-Zn) fraction was found to be significant highest in treatment AST + ZnSO₄ soil application @ 30 kg ha⁻¹ (33.66 mg kg⁻¹) which was at par with foliar, seed fortification, combination treatment of foliar and fortification and other level of Zn soil application but superior over control and without Zn treatments.

Though not very sizeable, there is slight increase in concentration of various Zn fractions in treatments receiving soil application of Zn, viewing this, it could be concluded that soil Zn application is advantageous towards accumulation of Zn. The results are in agreement Bahera *et al.*, (2008) who reported increased concentration of some of the Zn fractions due to soil application of Zn combined with NPK fertilizer. Nadaf and Chidanandappa, (2015) studied the effect of Zn and boron application on distribution of Zn fraction, they reported that application of 10 kg and 20 kg ZnSO₄ ensued significant increase in concentration of Zn fractions.

The Res-Zn contributed towards major fraction of total Zn (Priyanka *et al.*, 2017). The values of total Zn content enable better depiction of Zn accumulation in the soil. The highest significant value of total Zn content to the tune of 35.40 mg kg⁻¹ was recorded by treatment AST + ZnSO₄ soil application @ 30 kg ha⁻¹ over all foliar, seed fortification, combination treatment and without Zn treatment while, the lowest value was recorded by control treatment (25.99 mg kg⁻¹). The results are in accordance to that of Bahera *et al.*, (2008) who found that the treatment receiving NPK fertilizer coupled with Zn soil application recorded highest total Zn content in the soil. Priyanka *et al.*, (2017) also reported higher values of total Zn in treatment receiving soil Zn + NPK + S in maize-wheat cropping system.

Table.1 Grain yields, straw yields and nutrient uptake as influenced by different Treatments on maize crop

S. No	Treatments	Grain Yield (q ha ⁻¹)	Straw yield	Nutrient uptake			
				N	P	K	Zn
				(kg ha ⁻¹)			(g ha ⁻¹)
T1	Control	8.3	9.8	26	4	23	47
T2	Fert. As per soil test + water spray	49.8	59.6	154	25	140	338
T3	AST + 5 t FYM ha ⁻¹	52.1	62.5	162	26	146	396
T4	AST + Seed fortification with Zn-EDTA @0.5 %	56.7	68.9	176	28	159	442
T5	AST + 0.2% Zn-EDTA spray at 5 th leaf stage and tasseling stage	58.7	70.1	182	29	164	474
T6	Combination of T4 and T5	59.0	70.5	183	30	165	507
T7	AST + ZnSO ₄ soil Appl. 20 kg ha ⁻¹	61.5	74.3	191	31	172	532
T8	AST + ZnSO ₄ soil Appl. 25 kg ha ⁻¹	62.9	74.9	195	31	176	545
T9	AST + ZnSO ₄ soil Appl. 30 kg ha ⁻¹	56.4	67.6	175	28	158	518
SE_±		1.89	2.32	6.40	1.03	5.78	20.6
CD 0.05		5.66	6.97	19.18	3.09	17.32	61.7

Table.2 Soil properties and available nutrient status as influenced by different Treatments on maize crop

S. No	Treatments	pH	EC dsm ⁻¹	OC (%)	Available Nutrients			
					N	P	K	DTPA- Zn
					(kg ha ⁻¹)			(mg kg ⁻¹)
T1	Control	7.1	0.18	3.3	240	19	181	0.30
T2	Fert. As per soil test + water spray	7.2	0.17	3.6	261	26	211	0.35
T3	AST + 5 t FYM ha ⁻¹	7.1	0.17	3.8	272	26	214	0.36
T4	AST + Seed fortification with Zn-EDTA @0.5 %	7.1	0.17	3.6	262	26	211	0.36
T5	AST + 0.2% Zn-EDTA spray at 5 th leaf stage and tasseling stage	7.2	0.18	3.6	263	26	211	0.36
T6	Combination of T4 and T5	7.2	0.17	3.6	263	26	212	0.37
T7	AST + ZnSO ₄ soil Appl. 20 kg ha ⁻¹	7.1	0.17	3.5	263	25	210	0.42
T8	AST + ZnSO ₄ soil Appl. 25 kg ha ⁻¹	7.2	0.18	3.7	266	24	210	0.42
T9	AST + ZnSO ₄ soil Appl. 30 kg ha ⁻¹	7.1	0.17	3.5	263	22	211	0.43
CD 0.05		NS	NS	NS	10.3	4.52	12.9	0.055

Table.3 Zinc fractions as influenced by different treatments on maize crop

	WS-Zn	S-Zn	ERMn-Zn	CA-Zn	OM-Zn	Fe-OX-Zn	RES-Zn	T-Zn
mg kg⁻¹								
T1	0.10	0.05	0.22	0.15	0.40	0.34	24.70	25.99
T2	0.13	0.08	0.28	0.17	0.48	0.36	29.14	30.63
T3	0.13	0.09	0.26	0.18	0.48	0.38	29.68	31.20
T4	0.14	0.06	0.25	0.18	0.49	0.39	29.97	31.48
T5	0.14	0.07	0.23	0.17	0.50	0.40	29.86	31.37
T6	0.16	0.07	0.25	0.18	0.50	0.40	30.05	31.60
T7	0.16	0.07	0.28	0.22	0.52	0.42	31.19	32.86
T8	0.15	0.09	0.31	0.23	0.51	0.43	31.78	33.50
T9	0.17	0.08	0.30	0.25	0.51	0.43	33.66	35.40
CD 0.05	0.027	NS	NS	0.059	0.097	0.078	3.693	3.636

WS-Zn: Zn in soil solution	CA-Zn: Zn associated with carbonate	RES-Zn: residue Zn
SORB-Zn: Sorbed Zn	OM-Zn: Zn associated with organic matter	T-Zn : Total Zn
ERMn-Zn: Zn associated with easily reducible Mn	FeOx-Zn: Zn associated with Fe and Al oxides	

Table.4 Correlation between yield, uptake, soil properties and available nutrient and Zn fraction

	WS-Zn	S-Zn	ERMn-Zn	CA-Zn	OM-Zn	FeOx-Zn	RES-Zn
Grain Yield	0.849**	0.555	0.536	0.554	0.954**	0.783*	0.858**
Straw yield	0.833**	0.537	0.524	0.525	0.942**	0.752*	0.841**
Zn uptake	0.933**	0.546	0.587	0.692*	0.984**	0.900**	0.925**
pH	0.322	0.256	0.075	-0.036	0.352	0.279	0.233
EC dSm⁻¹	-0.233	-0.100	-0.391	-0.202	-0.135	0.018	-0.276
OC (%)	0.258	0.685*	0.272	0.122	0.442	0.296	0.387

*= significant at 0.05 level, **= significant at 0.01 level

WS-Zn: Zn in soil solution	CA-Zn : Zn associated with carbonate	RES-Zn: residue Zn
SORB-Zn: Sorbed Zn	OM-Zn: Zn associated with organic matter	
ERMn-Zn: Zn associated with easily reducible Mn	FeOx-Zn: Zn associated with Fe and Al oxides	

Table.5 Inter-correlation between the Zn fractions, DTPA extractable Zn and total Zn

	WS-Zn	S-Zn	ERMn-Zn	CA-Zn	OM-Zn	Fe Ox-Zn	RES-Zn	DTPA Zn	T-Zn
WS	1								
S-Zn	0.407	1							
ERMn-Zn	0.617	0.704*	1						
CA-Zn	0.751*	0.533	0.847**	1					
OM-Zn	0.911**	0.528	0.610	0.725*	1				
Fe-OX-Zn	0.894**	0.528	0.703*	0.895**	0.918**	1			
RES-Zn	0.922**	0.616	0.761*	0.868**	0.922**	0.923**	1		
DTPA Zn	0.868**	0.608	0.853**	0.957**	0.881**	0.962**	0.943**	1	
Total Zn	0.922**	0.619	0.767*	0.874**	0.923**	0.927**	1.000**	0.948**	1

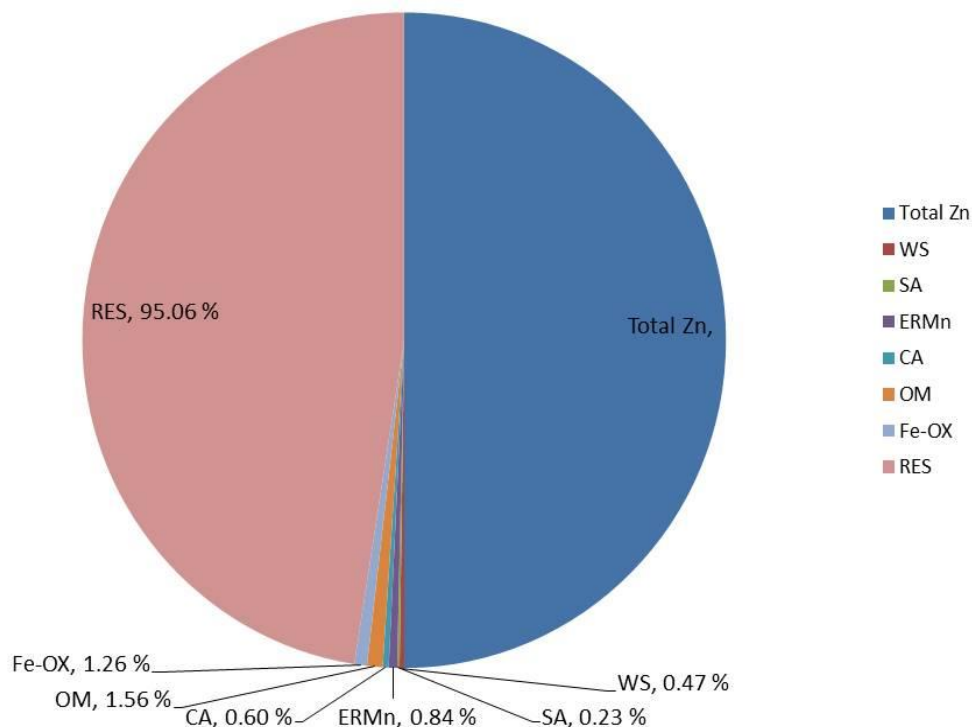
*= significant at 0.05 level, **= significant at 0.01 level

WS-Zn: Zn in soil solution	CA-Zn : Zn associated with carbonate	RES-Zn: residue Zn
SORB-Zn: Sorbed Zn	OM-Zn: Zn associated with organic matter	T-Zn: Total Zn
ERMn-Zn: Zn associated with easily reducible Mn	FeOx-Zn: Zn associated with Fe and Al oxides	

Table.6 Sequential fractionation methods

Form/association	Step	Operational definition
Zn in soil solution (WS)	1	Distilled water, 1:5, shaking 2 h
Sorbed (SORB)Zn	2	1% NaCaHEDTA in 1 M NH ₄ OAc, pH 8.3, 1 : 10, shaking 2 h
Zn associated with easily reducible Mn(ERMn)	3	0.2% quinol in 1 M NH ₄ OAc, pH 7. 0, 1:10, shaking 2 h
Zn associated with carbonate (CA)	4	0.5 M Na/H acetate, pH 4.74, 1 : 10, soaking 15 h/shaking 3 h
Zn associated with organic matter (OM)	5	5mL 30% H ₂ O ₂ , pH 4.74, digested twice at 85°C, and extracted as for carbonate fraction
Zn associated with Fe and Al oxides (FeOx)	6	0.175 M (NH ₄) ₂ C ₂ O ₄ -0.100M H ₂ C ₂ O ₄ , pH 3.25, 1 : 10, soaking 15 h/shaking 2 h
Residue (RES)	7	Total minus sum of the extractable amounts

Fig.1 Average percent contribution of different zinc fractions to total zinc



Relationships among yield, uptake, soil properties and Zinc fraction

Relationship between yield, uptake, soil properties and zinc fractions is presented in table 4. The grain yield of maize showed positive and significant correlation coefficient with WS-Zn ($r = 0.849^{**}$), OM-Zn ($r = 0.954^{**}$), Fe-Ox-Zn ($r = 0.783^*$), Res-Zn ($r = 0.858^{**}$) whereas, S-Zn, ERMn-Zn and CA-Zn revealed positive but non-significant relationship with yield. The straw yield revealed almost resembling relationship with all Zn fractions the way it was noticed in grain yield. The zinc uptake exhibited positive and significant correlation with all fractions *viz.* WS-Zn ($r = 0.933^{**}$), CA-Zn ($r = 0.692^*$), OM-Zn ($r = 0.984^{**}$), FeOx-Zn ($r = 0.900^{**}$) and RES-Zn ($r = 0.925^{**}$) while the S-Zn and ERMn-Zn showed non-significant but

positive relationship. Nadaf and Chidanandappa, (2015) in their study confirmed that the various Zn fractions contributed directly or indirectly to the Zn uptake in groundnut. Similarly, Bahera *et al.*, (2008) showed that different fractions of Zn were not correlated with Zn uptake but through the path coefficient analysis it was revealed that the OM-Zn and SORB-D-Zn contributed directly towards the uptake of Zn. The correlation study amongst the Zn fraction and soil properties showed that pH was positively but non-significantly correlated with Zn fractions while EC is negatively and non-significantly correlated. The organic carbon content in soil exhibited positive and significant correlation coefficient with SORB-D-Zn (0.685^*) and positive relation with other Zn fractions. The results are symptomatic that increase in organic matter

could tend to increase in the concentration of Zn fractions particularly SORBD-Zn. These results are in close agreement with those of Okoli *et al.*, (2016) who reported identical relationship of soil properties with Zn fractions.

Inter-correlation among Zn fraction, DTPA Zn and Total Zn

The data presented in table 5 divulged that the different fractions of Zn are not only positively correlated with each other but most of them exhibited significant correlation coefficient. A significant and positive correlation between ERMn-Zn and S-Zn ($r = 0.704^*$), CA-Zn with WS-Zn ($r = 0.751^*$) and ERMn-Zn ($r = 0.847^{**}$), OM-Zn with WS-Zn ($r = 0.911^*$) and CA-Zn ($r = 0.725^*$), FeOx-Zn with WS-Zn ($r = 0.984^{**}$), ERMn-Zn ($r = 0.703^*$), CA-Zn ($r = 0.895^{**}$) and OM-Zn ($r = 0.918^{**}$), RES-Zn with WS-Zn ($r = 0.922^{**}$), ERMn-Zn ($r = 0.761^*$), CA-Zn ($r = 0.868^{**}$), OM-Zn ($r = 0.922^{**}$) and FeOx-Zn ($r = 0.923^{**}$) was observed. The results suggest that there is a dynamic equilibrium amongst the different soil Zn fractions (Bahera *et al.*, 2008), Nadaf and Chidanandappa (2015) and Spalbar *et al.*, (2017). The soil DTPA extractable Zn after harvest of maize crop divulged significant and positive correlation coefficient with all the fractions except SA-Zn. DTPA-Zn showed significant and positive correlation with WS-Zn ($r = 0.868^{**}$), ERMn-Zn ($r = 0.853^{**}$), CA-Zn ($r = 0.957^{**}$), OM-Zn ($r = 0.881^{**}$) and FeOx-Zn ($r = 0.962^{**}$) and RES-Zn ($r = 0.943^{**}$). The results suggest that the soil Zn fractions are in equilibrium as earlier suggested by Viets (1962). The results are in accordance to Nadaf and Chidanandappa (2015) who reported positive and significant correlation among Zn fractions and DTPA-Zn whereas, they found RES-Zn to be negatively and significantly correlated with DTPA-Zn. The reason for this ambiguity is unknown. But the present results

agree with Priyanka *et al.*, (2017) and Bahera *et al.*, (2008). The results are indicative of soil Zn fractions contribution to DTPA extractable Zn Verma and Subehia (2005). The total Zn concentration in soil after harvest of maize revealed positive and significant correlation with all the fraction of Zn. The correlation coefficient among T-Zn and different Zn fractions are viz. WS-Zn ($r = 0.922^{**}$), ERMn-Zn ($r = 0.767^*$), CA-Zn ($r = 0.874^{**}$), OM-Zn ($r = 0.923^{**}$) and FeOx-Zn ($r = 0.927^{**}$) and RES-Zn ($r = 1.0^{**}$). Positive and significant correlation among total Zn and different Zn fractions were reported by with Priyanka *et al.*, (2017).

Percent contribution of Zn fractions to total Zn

To average percent contribution of various Zn fractions is illustrated in figure 1. The major portion of total Zn is contributed by RES-Zn (95 %). Residual Zn is associated with mineral fractions of soil, higher RES-Zn could be due to less removal of applied Zn. The higher concentration of Zn as residual fraction indicates its greater tendency to become unavailable in the soil. The results corroborate the finding of Priyanka *et al.*, (2017), Behera *et al.*, (2008), Nadaf and Chidanandappa (2015). The least portion of T-Zn, among fractions was constituted by SORBD-Zn (0.23 %) followed by water soluble (0.47 %) and CA-Zn (0.60 %). Spalbar *et al.*, (2017), Ramzan *et al.*, (2014) reported WSEX-Zn to be least among Zn fractions. The organic matter bound Zn constituted 1.56 % of total Zn while the Zn associated with Fe and Al oxides (FeOx-Zn) and Zn associated with easily reducible Mn (ERMn-Zn) constituted 1.26 % and 0.84 % respectively. The influence of organic matter can be attributed to formation of organo-zinc complexes which produces buffer zone for Zn (Udom *et al.*, 2004). In this case, each treatment received FYM at 5 t ha⁻¹ except

control which might have influenced the soil buffering capacity for Zn. The organic matter content influence the overall transformation of Zn hence the control treatment exhibited lower concentration of Zn in all forms. Similar results were reported by Spalbar *et al.*, (2017), Ramzan *et al.*, (2014).

The results of this study reveals that the soil application of 25 kg ZnSO₄ ha⁻¹ recorded higher maize grain yield whereas, at higher level of Zn the yield tends to decline. The soil DTPA extractable Zn and various Zn fractions were found to be improved with soil applied Zn. Residual zinc was the dominant fraction of Zn. The correlation studies revealed that most of the Zn fractions were positively and significantly correlated with DTPA-Zn and Zn uptake. Zinc fractions also exhibited positive and significant inter-correlations suggesting dynamic equilibrium between them.

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