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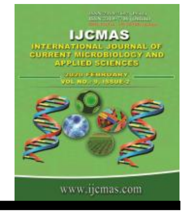

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Establishment of Critical Limits of Zinc in Soils Using Multi-extractants for Paddy Crop Grown in Central India

Rakesh Dhakad*, G. S. Tagore, B. L. Sharma, H. K. Rai and G. D. Sharma*

Department of Soil Science and Agricultural Chemistry, JNKVV, Jabalpur, Madhya Pradesh, India
**Department of Soil Science and Agricultural Chemistry, College of Powarkeda, JNKVV, Jabalpur Madhya Pradesh, India*

**Corresponding author*

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A B S T R A C T

Field experiments were conducted during *Kharif* season 2015-16 at twenty farmer's field to refine the critical limit of Zinc in soils for rice crop grown in Mandla district of Madhya Pradesh. The soils of study sites varied in available Zn from 0.12 to 2.17 mg kg^{-1} and classified in three groups i.e., deficient (<0.60 mg Zn kg^{-1}), marginal (>0.60 to <1.2 mg Zn kg^{-1}) and adequate (>1.2 mg Zn kg^{-1}). The soils were clayey, neutral to slight alkaline in reaction and low in organic carbon. The Zn treatments (0, 2, 4, 6 and 8 kg Zn ha^{-1} through $ZnSO_4 7H_2O$ and 60 kg N, 60 kg P_2O_5 and 40 kg K_2O through urea, single super phosphate (SSP) and muriate of potash, respectively were applied at the time of sowing in a factorial RBD and 60 kg N ha^{-1} was applied at tillering stage. The rice MTU-1010 variety was sown @ 80 kg seed ha^{-1} at 22.5 cm row to row spacing and harvested at maturity (120 DAS). The findings suggested that the increasing levels of Zn addition significantly increased the grain yield over control and optimum was at 6.0 kg Zn ha^{-1}. The grain yield was identical at 6.0 and 8.0 kg Zn ha^{-1}. In field situation, the critical limit of Zn was calculated to be 0.62 mg kg^{-1} using Cate and Nelson statistical method and gave a predictability value of 53 per cent. Critical limits of Zn in soil for rice calculated to be 1.12 mg kg^{-1} by NH_4HCO_3 DTPA, 0.57 mg kg^{-1} by NH_4OAC, 0.88 mg kg^{-1} by EDTA $(NH_4)_2$ CO_3 and 0.31 mg kg^{-1} by 0.05 N HCl + 0.025 N H_2SO_4. Critical levels of Zn were found to be 12.7 mg kg^{-1} for paddy grain. In study area, paddy crop responded to Zn application. Hence, the application of 6 kg Zn ha^{-1} in soil through $ZnSO_4 7H_2O$ will enhance the productivity of rice.

Introduction

Rice is one of the most important global staple food crops and is a primary food source for more than one third of the global population (Prasad *et al.*, 2010). Nutritionally, the grain comprises 80% starch, 7.5% protein, 0.5% ash and 12% water. In Asia, India has the largest area under rice cultivation (44.3 million ha) accounting for 29.4 per cent of the global rice area. Though the productivity level in India is low (2.04 t ha^{-1}) as compared to Japan (6.25 t ha^{-1}), China (6.24 t ha^{-1}) and Indonesia (4.25 t ha^{-1}) which can be attributed to either insufficient fertilizer use or imbalanced fertilization and are strongly related with nutrient depletions (Chaudhary *et al.,* 2007).

Zinc is one of the essential plant micronutrient and its importance for crop productivity is similar to that of major nutrients (Rattan *et al.,* 2009). Zinc is required for large number of enzymes and plays an essential role in DNA transcription. It is a constituent of several enzymes with role in carbohydrate and protein synthesis, maintaining the integrity of membranes, regulating auxin synthesis and in pollen formation. Zinc leads to the formation of indole acetic acid from tryptophane, which is found in plants and in the activity of dehydropeptidase and glycoglycine dipeptidase, which play a specific role in the protein metabolism.

It is required by rice in small quantity, but its deficiency has an adverse effect on healthy crop growth and yield may be reduced up to 30 percent. Almost 50% of the world soils in cereal growing areas are Zn deficient (Gibbson, 2006). In India 49% soils are potentially deficient in Zn (Singh, 2008), while 60% soils in Madhya Pradesh were found Zn deficient (Shukla and Tiwari 2016). Availability of Zn in soils for plants is a function of soil properties. Zinc fertilizers are used for the prevention of Zn deficiency and biofortification of cereal grains (Alloway, 2009). Zn use efficiency is hardly 1 to 5%. Imbalanced, blanket use and inadequate use of chemical fertilizers in intensive cropping systems is the main cause for stagnation in productivity, insecurity in food and environmental hazards. Under deficient condition the crops are likely to respond more to application of zinc.

Critical levels means a level below which the crops will readily respond to its application. This level varies with crops, soil and the extractants used. Zinc application is usually made on the basis of the soil fertility class, thus the crop response to added Zn is not always obtained (Rahman *et al.,* 2007). Critical zinc for rice was (0.74 ± 0.18 mg kg^{-1}) across the soils and agro-ecological regions of India (Rattan *et al.,* 2008). The critical limits are quite often employed for a wide variety of soils and crops, even though these critical limits may be different not only for soils, crop species but also for different varieties of a given crop (Singh and Agrawal, 2007). Soils with DTPA-Zn less than critical limit gave 82.7% more yield when Zn was applied at 5 mg kg^{-1} and soils with DTPA-Zn more than critical limit recorded only 34.8% yield increase in Meghalaya soils (Singh *et al.,* 1999).

The general critical limit of Zn in soil and crops fall in the range of 0.6-1.0 mg kg^{-1} (DTPA-extractable) and 10-20 mg kg^{-1} in dry matter respectively (Katyal and Rattan, 2003) but it vary with soils and crops. For clear prediction of possible deficiencies, their critical limits must be refined with reference to the soil and crop characteristics, respectively as they vary in their Zn supplying capacity and use efficiency. In earlier, most of the studies of critical limits have been conducted in pot, which are entirely different than field conditions. In study area where of rice is predominant and intensively cultivated and critical limit for zinc has not been fixed so far. Therefore, the present investigation was undertaken under field condition to refine the critical limit of zinc in soil for rice for making Zn application more rational.

Materials and Methods

Description of study area

Geographically, the Mandla district is located in the east-central part of the Madhya Pradesh covering an area of 8771 sq km and consists of a rugged high tableland in the eastern part of the Satpura hills. Thus the climate of this district is characterized by hot summer season and general dryness except in the southwest monsoon season. May is the hottest month with the mean daily minimum temperature at 41.3 ^{0}C and the mean daily minimum at 24 ^{0}C. Paddy, Maize, Kodo and Kutki is an important crops during *Kharif* season and Wheat, Pea, Chickpea, Lentil and Mustard crops during *Rabi* season in tribal areas of district.

Zinc status and distribution in soil of different villages of Mandla district

Survey, collection of soil samples for selecting sites

Seventy five surface soil samples (0-15cm) were collected from different tribal villages (Bilnagari Mal, Bhvera Mal, Chikhali and Chargaon Kalan) of Bijadandi block of Mandla district in Madhya Pradesh, India (Table-1 and Fig-1).

Selection of sites for experimentation

The initial soil samples were analysed for available zinc (0.005 M DTPA) as given in table-1 indicated that the soil pH varied from 5.40 to 7.80 with a mean value of 6.73. The organic carbon content of soil samples ranged from 3.0 to 9.20 g kg^{-1} with a mean value of 6.01 g kg^{-1}. In general, soils were low to medium in organic carbon content and more than 25 per cent soils were found low in organic carbon. The available N, P and K status of soils ranged from 145 to 410 kg ha^{-1}; 7.0 to 31.80 kg ha^{-1} and 150 to 614 kg ha^{-1} with a mean value of 298.50 kg ha^{-1} ; 15.14 kg ha^{-1} and 320.30 kg ha^{-1}, respectively. The value of S was ranged from 1.61 to 31.63 mg kg^{-1} with a mean value of 15.95 mg kg^{-1}. The results are in agreement with earlier work of Tagore *et al.*, (2015). The DTPA-extractable Zn ranged from 0.21 to 2.17 mg kg^{-1}. Variations in soil pH, lime, organic matter amount of phosphorus and zinc can significantly affect the Zn bioavailability (Adiloglu and Adiloglu, 2006).

Details of the experimentation

Field experiments were conducted during *Kharif* season 2015-16 at twenty farmer's field to find out the effect of Zn levels (0.0, 2.0, 4.0, 6.0 and 8.0 kg Zn ha^{-1}) on yield, Zn content and their uptake by rice grown on selected sites with standard agronomic practices. The soils of study sites varied in available Zn from 0.12 to 2.17 mg kg^{-1} and classified in three groups i.e., deficient (<0.60 mg Zn kg^{-1}), marginal (>0.60 to <1.2 mg Zn kg^{-1}) and adequate (>1.2 mg Zn kg^{-1}).

The soils are clayey, neutral to slight alkaline in reaction and low to medium in organic carbon. The Zn treatments (0, 2, 4, 6 and 8 kg Zn ha^{-1} through $ZnSO_4 7H_2O$) were applied at the time of sowing in a factorial randomised block design. The basal dose of 60 kg N, 60 kg P_2O_5 and 40 kg K_2O were applied through urea, single super phosphate (SSP) and muriate of potash respectively at the time of sowing and 60 kg N ha^{-1} was applied at tillering stage. The rice MTU-1010 variety was sown @ 80 kg ha^{-1} at 22.5 cm row to row spacing and harvested at maturity (120 DAS).

Soil sample preparation and their chemical analysis

From each experimental site, representative surface (0-15 cm) soil samples were collected before and after harvest of rice crop. The experimental soil (0-15 cm depth) samples were air dried and crushed with wooden pestle and mortar and sieved through 2 mm sieve. Initial and post harvest data thus obtained are given in Table-1. Organic carbon of the soil was analyzed by Walkley and Black (1934) method. Soil pH was measured in soil: water: (1:2.5) suspension. Electrical conductivity was determined by following standard protocol (Jackson, 1973). Macronutrients were analsyed using standard method described by (Jackson 1973). Available zinc content in soil samples was extracted with 0.005M DTPA (Diethylene triaminepenta acetic acid) -TEA (pH 7.3) in 1:2 ratio (Soil: Extractant) following the method of Lindsay and Norvell (1978) and the concentration of Zn in the extracted solution was estimated with the help of Atomic Absorption Spectrophotometer (AAS).

Chemical analysis of plant samples

Grain and straw yield from each plot were recorded and grain and straw samples were analyzed for Zn content. The plant samples were digested in a di-acid mixture of nitric and perchloric acid (4:1) and Zn content in digestate was determined using Atomic Absorption Spectrophotometer. The uptake was estimated by multiplying the Zn content in grain and straw with their yield.

Estimation of critical limit

For establishing the critical limit of available Zn (DTPA extractable) the method of Cate and Nelson (1971) was used. The Bray's per cent yield was calculated as per the formula given in Bray's percent Yield =Yield without zinc/ Optimum yield with zinc x 100. In the graphical version, horizontal and vertical lines were positioned to maximise number of points in the first and third quadrant to obtain the critical value. This was verified statistically from the total variance (R^2) of observed values with postulated critical values, where the R^2 peaks at the critical value.

Results and Discussion

Considering critical value of Zn in soils (0.60 mg kg^{-1}), 45, 30 and 25 percent soils were grouped into deficient, marginal and adequate classes, respectively (Table-2). Grain and straw yield of paddy significantly increased with the application of 2, 4, 6 and 8 kg Zn ha^{-1} over control (RDF). The maximum yield of grain and straw was recorded with 8 kg Zn ha^{-1} application, which was at par to 6 kg Zn ha^{-1} as soil application. The variations in yield of rice in different soils were due to difference in ability of soils to supply zinc to the crop. Data revealed that the response in grain yield per cent with increasing levels of applied Zn in soils ranged from 11.12 (S-12) to 76.26(S-13) per cent. However, at higher Zn levels (6.0 and 8.0 kg Zn ha^{-1}) the response was not much more over RDF.

The positive effect of Zn might be due to its beneficial effect on metabolism (Rashid and Fox 1992). Naik and Das (2010) reported that the application of zinc to low land rice soil of West Bengal resulted the 37.8% and 20.9 % increase in grain and straw yield of rice, respectively over the control. Significant yield increase was observed by Muthukumararaja and Sriramachandrasekharan (2012) when an application of 5 and 7.5 mg Zn kg^{-1} was done in a soil with DTPA-Zn 0.86 mg kg^{-1} in India. Fageria *et al.*, 2011 reported DMY increase to occur in an Inceptisol after applying 5 mg Zn kg^{-1}. Kandali *et al.,* 2014 reported a significant increase in straw yield when 4.2 mg Zn ha^{-1} was applied in a soil with DTPA-Zn 0.55 mg Zn kg^{-1}. The lack of response of plants grown in the six soils is justified by Dobermann and Fairhust (2000) who concluded that soils with zinc above 0.8 mg Zn kg^{-1} were not expected to give any response. Other researchers, Fageria *et al.*, 2011 reported a no significant effect between 5 and 120 mg Zn kg^{-1} rates when Zn was applied in an acidic soil with 1.4 mg Zn kg^{-1} which supports the no yield increase in the treatments that received 5 and 10 mg Zn kg^{-1} application rates.

Table.1 Details of experimental sites and initial fertility status

ID	Name of farmers	Location	Lat (DD)	Long (DD)	Zn ($mgkg^{-1}$)	pH	EC (dSm^{-1})	OC ($g\ kg^{-1}$)	N ($kgha^{-1}$)	P ($kgha^{-1}$)	K ($kgha^{-1}$)	S ($mgkg^{-1}$)
1	Shri Suresh Kumar	Chikhali	23.07156	80.22461	2.17	6.50	0.14	3.90	188.00	9.00	485.00	4.72
2	Shri Gariba marko	Chikhali	23.07672	80.21856	0.12	6.90	0.27	5.70	275.00	15.30	340.00	30.07
3	Shri Bhuvan lal	Chikhali	23.07064	80.24361	0.43	6.50	0.12	9.20	410.00	31.80	205.00	30.46
4	Shri Roop Singh 1	Chargaon kala	23.07361	80.22867	0.90	7.00	0.05	5.60	267.00	11.40	250.00	31.63
5	Shri Indar Singh	Poniya mal	23.07167	80.24598	0.47	7.70	0.41	6.20	296.00	29.40	280.00	5.21
6	Shri Pohat Singh Yadav	Bhavera Raiyat	23.07444	80.2265	1.00	6.30	0.08	6.20	296.00	7.10	250.00	8.05
7	Shri Shankar lal	Bhavera Raiyat	23.07775	80.23525	0.15	5.40	0.13	4.90	332.00	22.30	384.00	12.50
8	Shri Tilak Singh	Bhavera Raiyat	23.06956	80.24883	0.34	6.40	0.18	8.10	389.00	12.90	614.00	17.78
9	Shri Javahar singh	Bhavera Raiyat	23.08783	80.24067	0.22	6.90	0.26	4.20	346.00	15.70	207.00	16.53
10	Shri Nokhelal	Bhavera Raiyat	23.07042	80.24656	0.51	6.80	0.36	3.00	145.00	15.70	587.00	12.84
11	Shri Tibari Singh	Chargaon kala	23.07464	80.22389	1.07	7.30	0.06	6.50	310.00	10.60	212.00	9.41
12	Shri Hunkar Singh	Chargaon kala	23.07342	80.22361	1.27	6.50	0.09	7.20	346.00	7.40	184.00	12.15
13	Shri Gyanprasad	Chargaon kala	23.06683	80.22806	1.43	7.60	0.12	7.40	354.00	18.40	230.00	14.06
14	Shri Ramlakhan shahu	Chargaon kala	23.08653	80.23378	0.27	6.90	0.15	7.70	368.00	11.40	457.00	24.37
15	Shri Roop Singh 2	Chargaon kala	23.07042	80.25581	0.32	6.40	0.27	5.00	239.00	19.20	211.00	20.68
16	Shri Rampal	Chargaon kala	23.06942	80.22606	1.66	7.80	0.24	5.00	239.00	11.40	411.00	14.41
17	Shri Ashok Singh	Bilnagari mal	23.06889	80.22639	1.83	6.20	0.16	4.20	203.00	20.40	273.00	18.14
18	Shri Bhagavat Singh	Bilnagari mal	23.08556	80.244	0.61	6.30	0.13	4.50	217.00	12.50	375.00	26.06
19	Shri Keshav lal	Bilnagari mal	23.09189	80.24183	0.71	6.30	0.10	7.70	368.00	10.60	150.00	1.61
20	Shri Ashok Singh	Bilnagari mal	23.07778	80.24464	0.83	6.80	0.17	8.00	382.00	10.20	301.00	8.39
Minimum					**0.12**	**5.40**	**0.05**	**3.00**	**145.00**	**7.10**	**150.00**	**1.61**
Maximum					**2.17**	**7.80**	**0.41**	**9.20**	**410.00**	**31.80**	**614.00**	**31.63**
Mean					**0.82**	**6.73**	**0.17**	**6.01**	**298.50**	**15.14**	**320.30**	**15.95**

Table.2 Summary of chemical extractants used to determine available soil micronutrients

S. No.	Extractants	Soil: Solu. Ratio	Shaking period	Reference
1	0.005M DTPA-$CaCl_2$ (pH 7.3)	1:2	2 hours	Lindsay and Norvell (1978)
2	1M NH_4HCO_3+0.005M DTPA (pH 7.6)	1:2	15 minutes	Soltanpour and Schwab (1977)
3	0.01M EDTA+1M $(NH_4)_2CO_3$(pH 7.0)	1:2	30 minutes	Trieweiler and Lindsay(1969)
4	1N CH_3 $COO.NH_4$ (pH 6.8)	1:20	2 hours	Lyman and Dean (1942)
5	0.05 N HCl+0.025 N H_2SO_4 (6.5)	1:5	30 minutes	Mehlich-1 (1953)

Table.3 Response of Zn application on yield at optimum dose of Zn 6.0 kg Zn ha^{-1}

Soil	DTPA extractable Zn ($mgkg^{-1}$)	Grain yield (t ha^{-1})			Straw yield (t ha^{-1})		
		Zn-	Zn+	Res. (%)	Zn-	Zn+	Res. (%)
S-1	0.47	2.19	2.54	15.98	5.49	7.48	36.20
S-2	0.12	1.93	2.39	23.83	3.84	5.25	36.60
S-3	1.00	2.28	3.00	31.39	4.67	5.92	26.70
S-4	0.90	2.70	3.40	25.96	5.14	7.17	39.47
S-5	2.17	2.06	3.11	50.73	4.41	6.03	36.84
S-6	0.43	2.28	2.69	17.66	5.46	7.30	33.68
S-7	1.27	2.34	3.22	37.41	6.40	8.54	33.32
S-8	0.34	2.18	2.90	32.82	4.93	6.11	23.95
S-9	0.22	3.95	5.01	26.92	8.02	9.07	13.14
S-10	0.71	2.91	4.77	64.03	5.25	7.81	48.70
S-11	0.27	2.36	2.99	27.02	7.26	8.45	16.49
S-12	0.51	2.70	3.00	11.12	7.41	9.35	26.14
S-13	1.43	2.31	4.07	76.26	8.19	9.81	19.78
S-14	1.07	3.16	5.10	61.56	7.69	9.97	29.55
S-15	0.32	2.61	3.35	28.22	4.28	6.32	47.55
S-16	0.61	3.06	3.43	11.86	4.97	6.71	34.94
S-17	1.83	1.79	2.81	56.98	4.95	6.71	35.53
S-18	1.66	2.33	3.40	45.78	4.34	7.11	63.62
S-19	0.15	2.49	3.02	21.42	4.74	7.35	55.04
S-20	0.63	2.57	3.64	41.76	5.13	6.71	30.80

Fig.1 Location of experiments

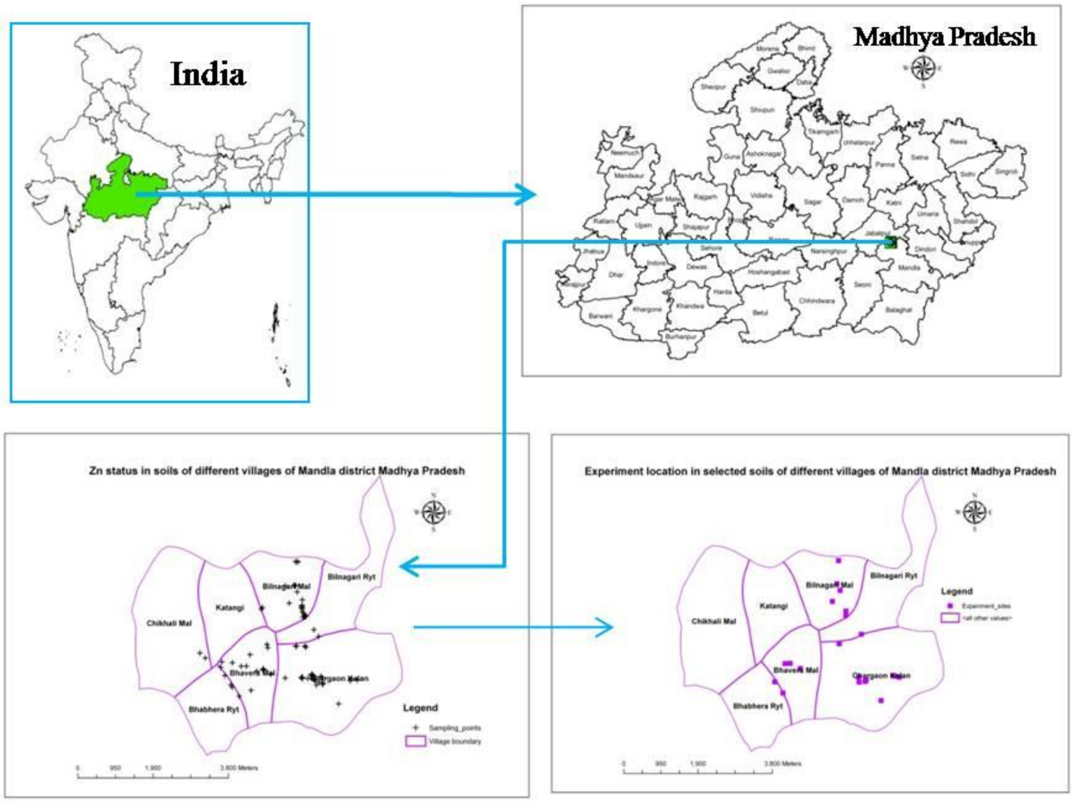

Fig.2

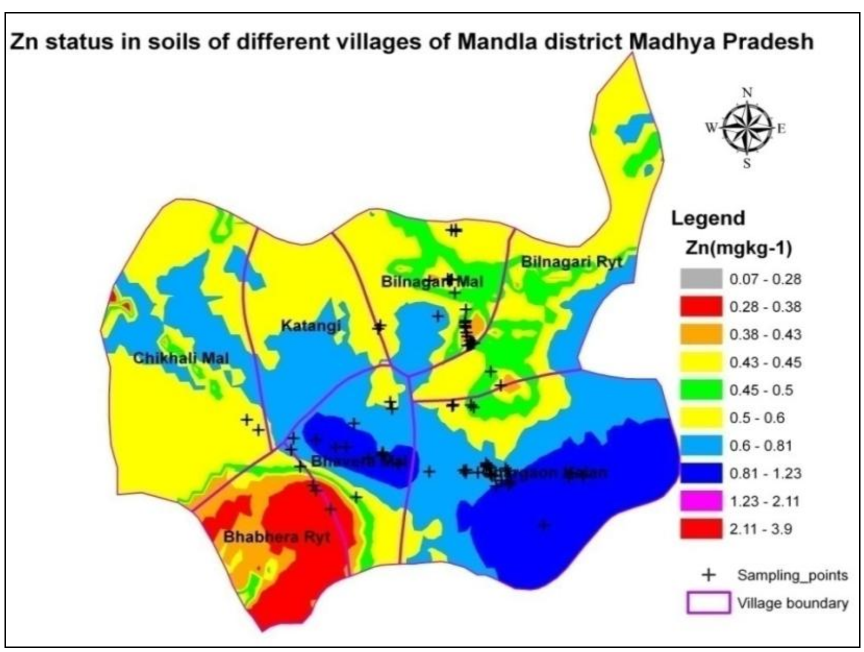

Fig.3.1 to 3.5 scattered diagram for critical limits of Zn in soil for paddy grown in soils of Mandla district using different extract ants and Fig. 3.6 to 3.7 scattered diagram for critical limits of Zn in rice grain and shoot of paddy.

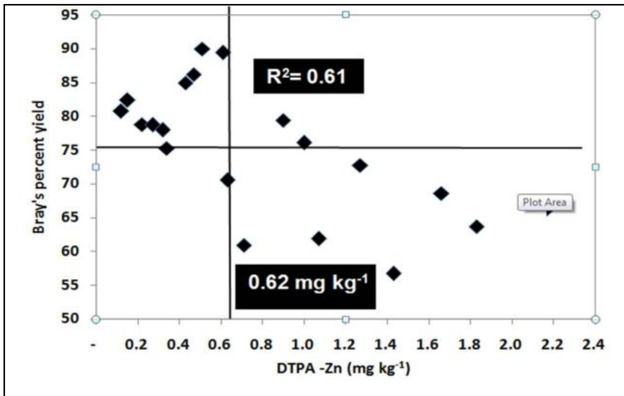

Fig. 3.1: Relationship of Bray's percent yield of rice with DTPA extractable zinc in soil

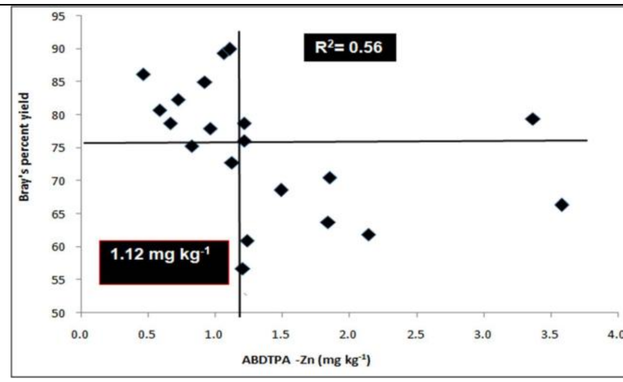

Fig 3.2: Relationship of Bray's percent yield of rice with NH_4HCO_3-DTPA extractable zinc in soil

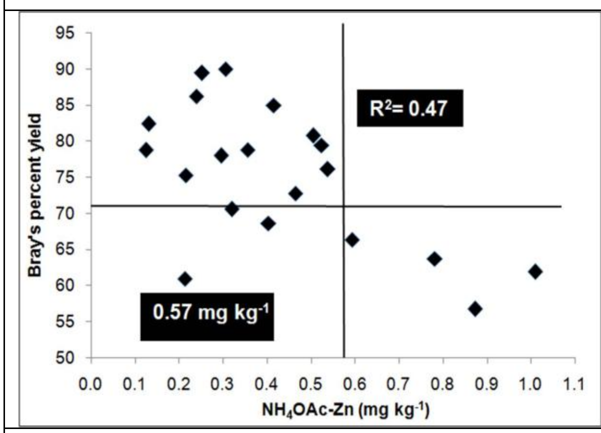

Fig3.3: Relationship of Bray's percent yield of rice with NH_4OAc extractable zinc in soil

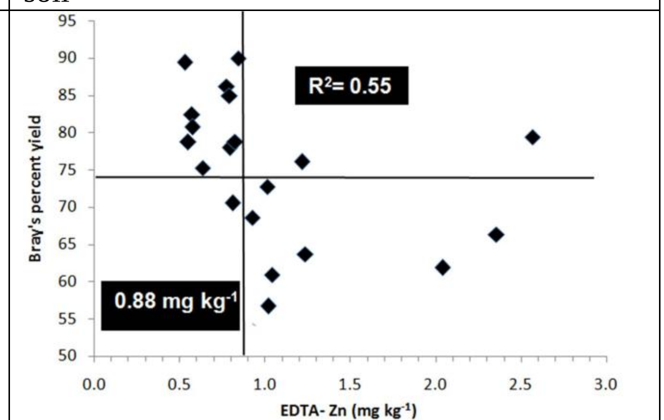

Fig 3.4: Relationship of Bray's percent yield of rice with $(NH_4)_2CO_3$ extractable zinc in soil

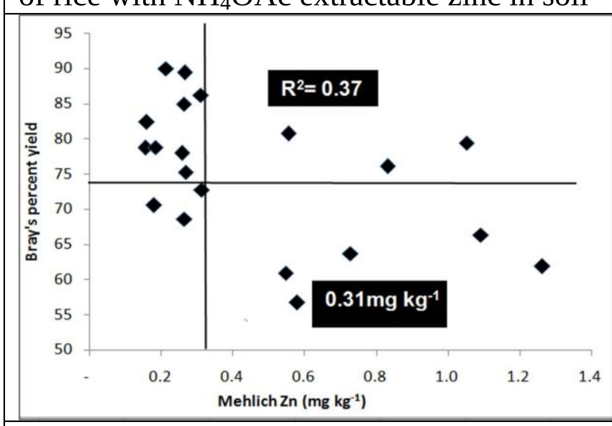

Fig 3.5: Relationship of Bray's percent yield of rice with Mehlich-1 extractable zinc in soil

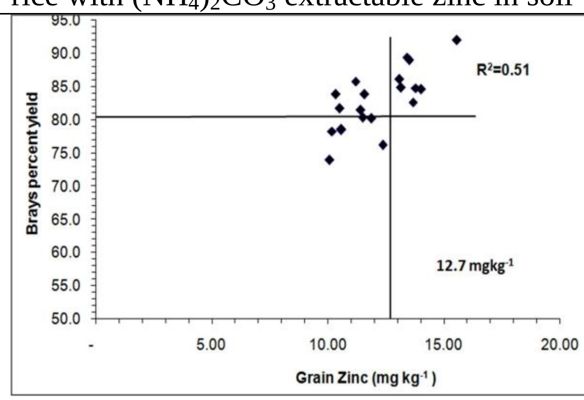

Fig.3.6: B Relationship of Bray's percent yield with zinc concentration in rice grain

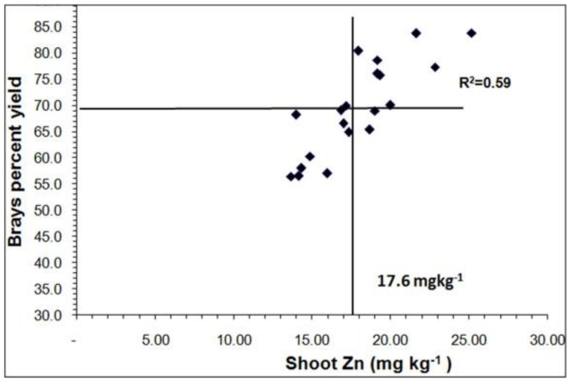

Fig.3.7: B Relationship of Bray's percent yield with zinc concentration in shoot of rice

Rasavel and Ravichandran (2012) observed a similar trend in an alkali soil with DTPA-Zn of 0.21 mg kg^{-1} at Tamil Nadu, India. The grain yield increase can be explained by the fact that Zn controls enzymes related to reproduction (Rahman *et al.*, 2007, Fageria *et al.*, 2011). The decrease in yield due to application of Zn at 10 mg Zn kg^{-1} suggests that Zn may approach the toxic levels when high rate of Zn is applied in soils with Zn above 3.0 mg kg^{-1} in soil. Sakal *et al.*, 1982 reported yield decrease when 5 and 10 mg Zn kg^{-1} were applied in calcareous soil with high levels of Zn.

Critical limits of Zn in soil for paddy grown in Mandla district using different extract ants

The DTPA-$CaCl_2$ extractable zinc was highly correlated as it gave maximum values of correlation coefficients with Bray's per cent yield (r= 0.539**) and Zn uptake (r=0.533**). The amount of zinc extracted by NH_4HCO_3 – DTPA was also correlated significantly with Bray's yield (r=0.445**) and Zn uptake (r=0.503**) by rice crop. Further, the relationships between zinc extracted by ammonium acetate and Zn uptake (r=0.483*) was found significant. Similarly EDTA-$(NH_4)_2CO_3$ extractable zinc and Mehlich-1 correlated with Bray's yield and zinc uptake by rice crop but non-significant.

The scatter diagrams for Bray's yield versus soil zinc by different methods are presented in (Fig.3.1 to 3.5). Critical limits were calculated to be 0.62 $mgkg^{-1}$ by DTPA-$CaCl_2$,, 1.12 mg kg^{-1} by NH_4HCO_3 DTPA, 0.57 mg kg^{-1} by NH_4OAC, 0.88 mg kg^{-1} by EDTA $(NH_4)_2 CO_3$ and 0.31 mg kg^{-1} by 0.05 N HCl + 0.025 N H_2SO_4. These values are close to critical level of Zn for soils (0.83 mg kg^{-1}) as observed by Rahman *et al.*, (2007), Muthukumararaja *et al.*, (2012). Result showed the critical levels of Zn were found to be 12.7 mg kg^{-1} for rice grain (Fig 3.6). However, critical limit of DTPA-extracted Zn and plant Zn was 0.76 mg kg^{-1} soil and 21.5 mg kg^{-1} reported by Sakal *et al.*, (1984) for rice in Sub-Himalayan hill and forest soils of India. The critical limits of Zn in plants indicates deficiency as suggested by Dobermann *et al.*, (2000) are :< 10 mg kg^{-1} definite Zn deficiency, 10–15 mg kg^{-1} very likely,15–20 mg kg^{-1} likely and >20 mg kg^{-1} unlikely (sufficient). In most crop species leaf sufficiency range for Zn 15 to 50 $mgkg^{-1}$ in the dry matter of mature plants and in most cases 15 $mgkg^{-1}$ Zn is considered as critical value (Benton, 2003). For better Zn nutrition of human being, cereals grains should contain around 40-60 mg Zn kg^{-1}; however the current situation is 10 to 30 mg kg^{-1} Zn (Cakmak 2008). Dobermann and Fairhust (2000). They suggested that zinc concentration in rice tissues between 10 to 20 mg kg^{-1} as deficient. This phenomenon was expected since these soils had low levels of Zn concentration and resulted in plants with relatively low grain yields which were accompanied with low Zn concentration in the Zn without treatment. The critical concentration of Zn in rice shoots was approximated to be 17.6 mg kg^{-1} (Fig-3.7). This critical concentration is close to the lower level of the optimum range of 25-50 mg kg^{-1} reported by Dobermann and Fairhust (2000) as well as the lower level of the sufficiency range of 20-160 mg kg^{-1} reported by Campbell 2000.

It is concluded that in study area, the critical limit of Zn was analysed to be 0.62 mg kg^{-1} for rice in field situation, hence, paddy crop will be responded to 6 kg Zn ha^{-1} in soil through $ZnSO_4 7H_2O$.

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