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DIFFERENTIAL RESPONSE OF MANURES IN TRANSFORMATION OF DTPA AND TOTAL ZINC AND IRON IN RICE TRANSPLANTED ON LIGHT TEXTURED SOILS OF PUNJAB

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Abstract: The present research study was conducted with a prime objective to investigate the effect of different manures on transformations of Zn and Fe in rice grown on light textured soils. To achieve these objectives, laboratory studies were conducted on the soil samples collected during *Kharif* 2009 season from an experiment on rice in the research farm of Department of Soil Science, PAU, Ludhiana. For this ten different type of manures viz. rice straw (RS), wheat straw (WS), maize straw (MW), cowpeas green manure (CGM), *Dhaincha* green manure (DGM), farm yard manure (FYM), poultry manure (PM), rice straw manure (RSM), vermi compost (VC) and biogas slurry (BGS), which were used to ameliorate Zn and Fe deficiency, helped in their transformation in the soil when these manures were incorporated before rice transplantation. The biomasses of these manures were added to soil on dry weight basis. Three soil samplings were conducted at an interval of 45 days, starting from first day of rice transplantation. Soil samples were collected and analyzed for basic soil parameters using standard procedures. These soil samples were also subjected to estimation of DTPA and total Zn and Fe fractions using atomic absorption spectrometer (Varian AAS-FS 240 Model).The results of our study reported that DTPA-Zn level decreased during different sampling times under all the manures. There was drastic reduction of DTPA-Zn during third sampling with the application of VC but it remained above the critical level of Zn. The rice crop did not show any Zn deficiency as the DTPA-Zn in all the treatments was above its critical limit (0.6 mg kg^{-1}). The higher content of DTPA-Fe was reported by PM (52.1mg kg^{-1}) followed by DGM (41.0 mg kg^{-1}) and VC (38.0 mg kg^{-1}). At the time of maximum tillering stage, Fe deficiency was reported during fourth week of paddy transplantation. With manures, the highest level of total Zn was reported by CGM (39.7 mg kg^{-1}) which was further followed by DGM (34.8 mg kg^{-1}) and BGS (32.8 mg kg^{-1}). On the other hand higher content of total Fe was reported by PM (10017 mg kg^{-1}) followed by CGM (9652 mg kg^{-1}) and DGM (9303 mg kg^{-1}). The decomposition of manures helped in release of more DTPA-Fe in the soil which was transformed to unavailable fractions under oxidized environment. This buildup of Fe was progressed nearly two times over its 1^{st} sampling with advancement of time of manure decomposition. Application of $FeSO_4$ in the soil failed to remove Fe-chlorosis in the rice plants. Our results concluded that application of manures before rice transplantation is the good practice and suitable mode to remove Fe-chlorosis in the rice plants.

Keywords: DTPA and total Zn and Fe, green manure, farm yard manure, poultry manure, vermi compost.

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INTRODUCTION

In India the deficiency of Zn and Fe is becoming very common as the farmers of north-eastern region have extended rice-wheat system (one of the predominant cropping systems of the country) on relatively coarse textured soils to feed the burgeoning population. This practice has caused severe deficiency of zinc (Zn) and iron (Fe) in rice and manganese (Mn) deficiency on the subsequent wheat crop. This practice has caused severe deficiency of Zn and Fe in rice. Farm yard manure (FYM), green manure (GM) and wheat cut straw (WCS) help in release of different fractions of Fe and Mn in the soil, when these are applied in combination with chemical fertilizers in the rice-wheat system (Dhaliwal and walia, 2008). Soni *et al.,* (2000) reported an increased manganese concentration in wheat grain and straw upon incorporation of green manure. Singh and Ram, (2005) reported lowest and highest uptake of Fe, by crops in control and NPK + FYM treated plots, from a 25 years long-term fertilizer experiment with a rice-wheat-cowpea system on a mollisol. Nayyar and Chhibba, (2000) suggested that the improvement in paddy yields could be due to increase in Fe and Mn with green manuring of *sesbania*. Mishra *et al.,* (2006) confirmed that application of organic manures (GM *sesbania*, FYM, wheat straw) is desirable for sustained supply of Zn to rice-wheat cropping system soils Duhan and Singh, (2002) reported that the use of organic manures increased uptake of micronutrients which may be attributed to increase in DTPA-extractable Zn and Fe in soil and to increased yield by these organic materials. Sekhon *et al.,* (2006) reported that application of organic manures resulted in increase and redistribution of Zn from non-available *forms* to readily available (water-soluble plus exchangeable) and potentially available forms in soil. Miller et al (1985) reported that the increase of organic-bound Fe may be due to chelating effects promoted by the organic matter added in treatments amended with composted urban wastes. Smith and Evans, (1977) carried out a study in a slash pine plantation treated with co-compost, and they demonstrated that this material has a variable influence on Fe concentration and decreases Mn concentration in pine foliage. Cabrera *et al.,* (1989) demonstrated noticeable increases of DTPA-extractable Fe in soils treated with MSW compost, compared with soils treated with mineral fertilizers. The higher values of DTPA-extractable Fe in FYM-treated plots could be ascribed to conversion of less soluble fractions of Fe to more plant-available fractions resulting from the addition of organic matter in the form of FYM (Shuman, 1986). Organic matter, organic residues, and manure applications affect the immediate and potential availability of micronutrient cations (Rengel, 2007). Poongothai and Mathan, (2000) in a study revealed that application of manures increased the uptake of Zn by grain and straw whereas copper application was found to have antagonistic effect on Zn, synergistic and antagonistic effect on Mn and non-significant effect on Fe. Sekhon *et al.,* (2006) observed that the addition of organic manures in the absence of inorganically applied Zn increased the water-soluble plus exchangeable, organic fraction and the manganese oxide and amorphous iron oxide fractions of Zn over their initial levels. Hellal, (2007) reported that addition of composted mixtures increased MnOX-Zn in soil, as a result Fe availability is increased in calcareous soil by high acidulation effect of compost. Herencia *et al.,* (2008) showed that percentage of Zn in the specific fractions with respect to total content are Zn and addition of OM caused Zn to move from less soluble forms to more plant available fraction which was always favoured by organic amendment. Sekhon *et al.,*(2006) reported that addition of GM to rice increased AFeOX form of Zn under rice-wheat rotation. Mandal *et al.,* (1988) observed that addition of 0.5% FYM caused a substantial increase in the contents of AFeOX bound fraction of native soil Zn with simultaneous decrease in that of CFeOX bound and Al oxides Zn fraction. Hellal, (2007) reported that addition of composted mixtures increased amorphous Fe oxide but occluded fractions did not differ significantly due to application of composted mixtures. Pal *et al.,* (1974) reported that with application of GM, FYM and WCS, the higher supply of Zn in WSEX fractions were strongly correlated with grain uptake. Agbenin and Henningsen, (2004) reported the increase in AFeOX-Fe fractions fertilized with NPK, FYM and FYM+NPK. Sekhon *et al.,* (2006) reported that OM bound fraction of Zn increased with application of FYM in rice-wheat system. Katyal and Rattan, (2003) and Sharma *et al.,* (2004) reported the decrease total fraction with GM after the harvest of wheat which could be due to an increase in the WSEX fractions as well as held on inorganic sites. Dhaliwal and Manchanda, (2008) reported that with addition of GM in rice-wheat system, WSEX-Fe fractions increased. Dhaliwal and Walia, (2008) reported that FYM, GM and WCS help in release of different fractions of Fe in the soil, when these are applied in combination with chemical fertilizers. Parsad *et al.,* (1995) reported that the integrated use of GM and FYM with chemical fertilizer resulted in build-up of available Zn and Fe in soil more effectively. Continuous use of NPK fertilizers in conjunction with organic manures brings considerable changes in available and total Zn and Fe supply to crops. In the soil environment, these nutrients are being transferred continuously from one form to other was reported by (Singh *et al.,* 1999, Sharma *et al.,* 2004). Submergence created reduced conditions during rice growth which helped higher release of Fe in the presence of GM (Dhaliwal and Manchanda, 2008). Rupa *et al.,* (2002) reported transformation of DTPA-Fe fraction in two alfisols with addition of FYM. Herencia *et al.,* (2008) reported that with addition of organic and mineral fertilization, OM-bound fractions of Zn and Fe increased their availability in the soil. Hellal, (2007) reported from his pot experiment that addition of composted mixtures increased WSEX-Fe in the soil, as a result of application of composted mixture. An increase in the availability of Fe in soil with the application of FYM and green manure in rice-wheat cropping system has previously been reported by Yadvinder-Singh *et al.*, (1992, 2000) and Yadav and Kumar, (2000). Sharma *et al.,* (2000) indicated that DTPA-extractable Fe exhibited a positive correlation with OM content in soil.

Consequently, the present research study was conducted with a prime objective to investigate the effect of different manures on transformations (distribution) of DTPA and total Zn and Fe in soil.

MATRIALS AND METHODS

Selection of Experimental Site

Laboratory studies were conducted during *Kharif* 2009 on the soil samples collected through three samplings from an experiment on rice in the research farm of Department of Soil Science, PAU, Ludhiana. The experimental field lies in the central zone of Punjab situated at $30^0 56'$N latitude and $75^0 52'$E longitude with a mean elevation of 247 m above mean sea level. The manures treatments were replicated thrice. Ten different type of manures viz. rice straw (RS), wheat straw (WS), maize straw (MW), cowpeas manure (CGM), *Dhaincha* manure (DGM), farm yard manure (FYM), poultry manure (PM), rice straw manure (RSM), vermi compost (VC) and bio gas slurry (BGS) were incorporated in the experimental field one week ahead of rice transplantation. One week after incorporation of these manures, rice plants were transplanted with application of recommended nutrients on soil test basis. Irrigation was scheduled at weekly interval. Ferrous sulphate (FeSO4.7H2O) was applied @ of 25 kg ha^{-1} to overcome the Fe deficiency. The objective of the research study was that the incorporation of these manures may help in transformation of Zn and Fe in the soil to ameliorate their deficiency. These ten types of manures with their different levels were incorporated in the experimental field one week ahead of rice transplantation are reported in Table 1.

Table 1: Levels of different manures incorporated before rice transplantation

Sr No.	Manures applied	Abbreviation used	Levels of manure added
1	Rice straw	RS	20 t ha^{-1}
2	Wheat straw	WS	20 t ha^{-1}
3	Maize straw	MS	20 t ha^{-1}
4	Cowpeas green manure	CGM	15 t ha^{-1}
5	*Dhaincha* green manure	DGM	15 t ha^{-1}
6	Farm yard manure	FYM	15 t ha^{-1}
7	Poultry manure	PM	15 t ha^{-1}
8	Rice straw manure	RSM	15 t ha^{-1}
9	Vermi compost	VC	15 t ha^{-1}
10	Biogas slurry	BGS	15 t ha^{-1}

Collection of Soil Samples

Bulk soil sample was collected from the experimental field to investigate the initial nutrient status of soil. Soil samples were collected from 0-15 cm soil depth from all the replications after rice transplantation in June 15, 2009. Three soil samplings (1^{st} August, 15^{th} September and 1^{st} November) were conducted at an interval of 45 days, starting from day of rice transplantation. These soil samples were mixed thoroughly, air dried in shade and crushed to pass through 2 mm sieve and stored in sealed plastic jars for further chemical analysis.

Analysis of soil samples for DTPA-extractable Zn and Fe

The DTPA-extractable Zn and Fe content in the soil samples taken during growth period of rice, were determined from 1:2 soil-extractant ratio using DTPA-TEA buffer (0.005 M DTPA + 0.001 M $CaCl_2$ + 0.1 M TEA, pH 7.3) and concentration of Zn and Fe were measured on atomic absorption spectrophotometer (Lindsay and Norvel, 1978).

Analysis of Soil Samples for total Zn and Fe

For total elemental analysis of Zn and Fe, a 0.5 gm sample of soil was digested with 5 ml of hydrofluoric acid (HF), 1.0 ml of perchloric acid ($HClO_4$) and 5-6 drops of nitric acid (HNO_3) in a 30 ml capacity platinum crucibles (Page *et al.,* 1982). When the soil became completely dry in the crucible the residue in the crucible was completely dissolved in 5ml of 6N HCl. The contents of the crucible were transferred to 100 ml volumetric flask with double distilled water. The digests were analyzed for total Zn and Fe after appropriate dilutions. The results of the elemental analysis were reported on an oven-dry weight basis. After proper dilution with double distilled water, the Zn and Fe contents in digests were estimated by using atomic absorption spectrophotometer (Varian AAS FS 240 Model).

Initial fertility status of experimental field

Soil samples collected from study site were subjected to laboratory analysis to determine their initial physico-chemical characteristics (Table 2). The results of the study revealed that soils at the study sites were light in texture (loamy sand) and slightly alkaline in nature. Higher EC value of 0.18 dS m^{-1} was observed in experimental soils. Low, medium and low levels were reported in available N (85 kg ha^{-1}), P (12.2 kg ha^{-1}) and K (124.8 kg ha^{-1}) respectively. The organic carbon (OC) was reported low (0.18 %). The DTPA- extractable concentrations of Zn (0.52 mg kg^{-1}) and Fe (3.75 mg kg^{-1}) fall below their critical level of 0.6 mg kg^{-1} and 4.5 mg kg^{-1} respectively.

Table 2: Physico-chemical analysis of experimental soil before start of experiment

Sr No.	Physico-chemical properties	Magnitude
1	Texture	Loamy sand
2	pH (1:2 :: soil : water)	7.32
3	EC (dSm^{-1})	0.18
4	Organic carbon (%)	0.18
5	Available N (kg ha^{-1})	85.8
6	Available P (kg ha^{-1})	12.2
7	Available K (kg ha^{-1})	124.8
8	Available Zn (mg kg^{-1})	0.52
9	Available Fe (mg kg^{-1})	3.75

Statistical analysis

The statistical analysis of data was done by the method described by Panse and Sukhatame, (1985).

RESULTS AND DISCUSSION

Build up of DTPA- Zn and Fe in soil with incorporation of different manures

The results presented in Table 3 reported that DTPA-Zn level decreased during different sampling times under all the manures. There was drastic reduction of DTPA-Zn during third sampling with the application of manures in general and VC in particular. The rice crop did not show any Zn deficiency as the DTPA-Zn in all the treatments varied from 0.8 to 4.9 mg kg^{-1}. Poultry manure, DGM and BGS reported higher levels of DTPA-Zn during third sampling which were to the tune of 4.9, 2.8 and 2.7 mg kg^{-1} respectively. Different workers reported decrease in DTPA-Zn during rice cultivation but in our study Zn deficiency is rarely observed on rice plants due to release of Zn by manures. The results of our study showed that this deficiency of Zn is controlled by the manures during their decomposition. The minimum DTPA-Zn was reported in control (0.8 mg kg^{-1}) but it was higher than its critical level (0.6 mg kg^{-1}). The different manures released different contents of Zn in the soil but application of green manures viz. DGM and CGM proved the best sources to provide Zn in the soil. Green manuring application to soil is economically viable as other manures viz. RS, WS, MS, FYM, VC and RM required in large quantity to meet out the crop requirement.

Table 3: DTPA-extractable Zn and Fe concentrations during first, second and third sampling

		Soil Samling					
		1^{st}	2^{nd}	3^{rd}	1^{st}	2^{nd}	3^{rd}
		Zn (mg kg^{-1})			Fe (mg kg^{-1})		
1	Control	9.5	8.4	0.8	12.5	20.9	32.3
2	Rice straw	12.6	11.1	1.1	13.0	24.6	34.6
3	Wheat straw	12.9	11.5	1.1	14.5	32.0	29.8
4	Maize straw	12.5	11.6	1.8	12.8	23.2	31.2
5	Farm yard manure	19.8	16.0	2.8	10.1	26.0	32.1
6	Vermicompost	21.8	16.9	1.0	12.5	31.5	38.0
7	Rice manure	14.5	14.3	1.3	13.0	30.3	32.0
8	Poultry manure	24.0	17.7	4.9	11.9	37.3	52.1
9	*Dhaincha* green manure	17.8	14.0	2.8	11.3	26.1	41.0
10	Cowpeas green manure	17.2	13.0	2.7	12.7	21.1	36.2
11	$FeSO_4$ (Soil)	12.5	9.6	2.7	11.0	19.7	26.2
12	Biogas slurry	20.5	9.1	2.7	13.5	27.4	34.3
CD (0.5)		12.3	8.7	2.8	10.4	12.6	18.9

The results of our study presented in Table 3 reported that the concentration of DTPA-Fe increased starting from 1^{st} sampling upto 3^{rd} sampling. Higher content of DTPA-Fe was reported by PM (52.1mg kg^{-1}) which was followed by DGM (41.0 mg kg^{-1}) and VC (38.0 mg kg^{-1}). Iron deficiency was reported during fourth week of paddy transplantation at maximum tillering stage and after that the deficiency symptoms of Fe disappeared. This may be due to decomposition of manures helped in buildup of Fe in the soil. So the Fe release was progressed 2-3 folds with advancement of time of manure decomposition. Our results further reported that application of manures before rice transplantation is suitable mode to remove Fe-chlorosis in the paddy crop.

Application of Fe in the soil which is not generally recommended, improved Fe deficiency to some extent. Among different manuring crops, DGM and CGM are the best sources for removal of Fe-chlorosis from the plants. Manures like RS, WS and MS release Fe in the soil at low rate due to slow rate of decomposition. The DTPA-Fe concentration varied from 12.0 to 13.0, 19.7 to 37.3 and 21.7 to 52.1 mg kg^{-1} during first, second and third sampling respectively. Green manure (DGM and CGM) application apart from release of Fe in the soil, helped in the improvement of physical environment of the soil. The soil application of $FeSO_4$ reported equivalent amount of Fe compared to the control. The buildup of DTPA-Fe by different manures varied marginally over time. So only their average contents are reported in the Table 3. It is evident that green manure treatments maintained increased level of DTPA-Fe after the submergence was terminated. In comparison to BGS, VC and FYM yielded very low levels of DTPA-Fe which were hardly different from no-manure application treatment. While the seedling growing in straw treated plots (RS, WS and MS) were comparatively not free from Fe-chlorosis, which further exhibited nitrogen deficiency which could be alleviated by the application of nitrogen fertilizers.

The variation in different organic manures regarding their buildup of DTPA-Fe can be attributed to their effect on the redox-potential and pH which are considered to be associated with mobilization and solublization of soil Fe. Since green manures exert a pronounced effect on redox-potential and pH, consequently the buildup of Fe was favoured. In contrast, FYM, RM and VC which are stabilized manures, are reported to change the electrochemical potential properties of soil, with the result the Fe transformation leading to its increased availability remains unaffected. This increase in DTPA-Zn and Fe contents may be ascribed to reduction in the redox-potential of the soil with the addition of CGM, DGM, MS,WS and RS, which led to more release of soil micronutrients in available form as compared to the application of chemical fertilizers alone (Mishra *et al.,* 2008). The DTPA-extractable Fe contents of soil contrary to other nutrients increased appreciably over its initial value of 4.28 mg kg^{-1}. The increase in Fe status of soil over its initial status may be due to the induced submerged conditions and lowering of pH of the soil during rice growing season, thereby resulting in an increase in the soluble Fe^{2+} ions in the soil (Poongothai and Mathan, 2000). Different workers reported the same results under rice–wheat system practiced on coarse textured soils (Rupa *et al.,* 2002; Singh and Ram, 2005).

Build up of total Zn and Fe in soil with incorporation of different manures

The data reported for total Zn indicated that the Zn in soil increased significantly during 1st, 2nd and 3rd sampling in all the manure treatments over control (Table 4). The concentration of total Zn ranged from 19.3-32.8 mg kg^{-1}. Under all the manures, the highest level of total Zn was reported by CGM (39.7 mg kg^{-1}) which was further followed by DGM (34.8 mg kg^{-1}) and BGS (32.8 mg kg^{-1}).

Table 4: Total Zn and Fe concentrations during first, second and third sampling

Sr No.	Treatments	Soil Sampling					
		1st	2nd	3rd	1st	2nd	3rd
		Zn (mg kg^{-1})			Fe (mg kg^{-1})		
1	Control	19.3	27.2	30.7	3439	4165	5198
2	Rice straw	26.3	65.5	72.0	5279	6848	7880
3	Wheat straw	27.9	66.9	73.4	6510	7405	8438
4	Maize straw	25.3	57.1	70.6	5105	7977	9010
5	Farm yard manure	22.5	59.8	83.4	6709	7677	8709
6	Vermicompost	27.8	66.2	89.7	5924	8186	9219
7	Rice manure	26.7	46.7	73.2	7653	8059	9092
8	Poultry manure	24.9	46.8	80.4	5453	8984	10017
9	*Dhaincha* green manure	34.8	81.7	95.2	5589	8271	9303
10	Cowpeas green manure	39.7	86.4	97.0	5882	8620	9652
11	$FeSO_4$ (Soil)	24.6	49.5	63.0	5840	8028	9061
12	Biogas slurry	32.8	96.0	109.5	5523	7554	8587
CD (0.5)		16.8	34.6	45.8	1278.6	1732.4	1956.5

During the 1st sampling, the three straw based manures namely MS, WS and MS reported total Zn varying from 25.3-27.9 mg kg^{-1}. Interestingly, during 2nd and 3rd sampling BGS reported higher concentration of total Zn (96.0 mg kg^{-1} and 109.5 mg kg^{-1} respectively) which was followed by CGM (86.4 mg $kg^{-1}$and 97.0 mg kg^{-1} respectively) and DGM (81.7

mg $kg^{-1}$and 95.2 mg kg^{-1} respectively). Compared to other manures, lower total Zn content was reported by RS (72.0 mg kg^{-1}), WS (73.4 mg kg^{-1}), MS (70.6 mg kg^{-1}) and RM (73.2 mg kg^{-1}) during 3rd stage of sampling which may be due to slow decomposition rate of freshly added straw. Even under the effect of other manures, the Zn concentration further decreased during 2nd and 3rd sampling.

The results of our study presented in Table 4 reported that the concentration of total Fe increased starting from 1st sampling upto 3rd sampling. Higher content of total Fe was reported by PM (10017 mg kg^{-1}) which was followed by CGM (9652 mg kg^{-1}) and DGM (9303 mg kg^{-1}). Iron deficiency appeared during 4th week after paddy transplantation which later disappeared due transformation of total Fe to DTPA-Fe fraction (52.1 mg kg^{-1}). Our results concluded that application of manures before rice transplantation is the only suitable mode to remove Fe-chlorosis in the paddy crop. Further, it is interesting to note that incorporation of manures resulted in build-up of total Zn and Fe in soil. This may be narrated to the higher release of total Zn and Fe in soil. This increase in total Zn and Fe contents may be ascribed to increase in the redox-potential of the soil with the addition of manures, which led to more addition of Zn and Fe in total form. The Total Fe contents of soil contrary to Zn, other nutrients increased appreciably over control. The increase in total Fe status of soil over its initial status may be due to the induced unsubmerged conditions due to transplantation of rice in the completely sandy soil, thereby resulting in an increase in the insoluble Fe in the soil (Herencia *et al.,* 2008). These results were reported by Dhaliwal and Manchanda, (2008) and Sekhon *et al.,* (2006) under rice-wheat system practiced on coarse textured soils.

CONCLUSIONS

The Zn and Fe concentrations were activated differentially and the dynamics of their inter conversion from one fraction to other was accelerated due to decomposition of added manures. The results further concluded that the incorporation of FYM, GM, PM and BGS in the soil before rice transplantation resulted in significantly higher content of the DTPA and total Zn and Fe in the soil which may be ascribed to the higher release of Zn and Fe through decomposition of organic manures. To sustain the productivity of rice in rice-wheat system in loamy sand soil of Punjab it is imperative to apply manures before paddy transplantation. The increase in DTPA-extractable and total Zn and Fe may be attributed to chelating action of organic compounds released during decomposition of manures. The organic compounds released during decomposition of manures enhanced the availability of Zn and Fe by preventing fixation, oxidation, precipitation and leaching.

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