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RESEARCH PAPER

Long-term effects of manures and fertilizers on chemical fractions of Fe and Mn and their uptake under rice-wheat cropping system in North-west India

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Abstract **:** In India the deficiencies of Fe and Mn are becoming very common as rice-wheat system (one of the predominant cropping systems of the country) is extended on light textured soils to feed the burgeoning population. Farm yard manure (FYM), green manure (GM) and wheat cut straw (WCS) help in release of different fractions of iron (Fe) and manganese (Mn) in the soil, when these are applied in combination with chemical fertilizers. Therefore, the present research study was conducted with a prime objective to investigate the long term effect of chemical fertilizers (NPK) alone and in combination with FYM, GM and WCS on different fractions of Fe and Mn and their interactions with each other. For this, a field experiment was in progress since 1983 with rice-wheat cropping system at Research Farm, Department of Agronomy, Punjab Agricultural University, Ludhiana. In different treatments, 50 per cent recommended dose of N was applied through chemical fertilizers (urea fertilizer with 46.4 per cent N) whereas, the remaining 50 per cent N was substituted through FYM, WCS and GM (*Sesbania aculeata*) and their biomass was added to soil on dry weight basis. Surface soil samples were collected and analyzed for basic soil parameters using standard procedures. These soil samples were also subjected to estimation of different fractions of Fe and Mn using atomic absorption spectrometer (Varian AAS-FS Model). Rice grains samples were analyzed for their Fe and Mn concentrations with Varian AAS-FS Model. The results of present study revealed that these three organic manures lowered the soil pH and EC as well as increased the organic carbon (OC) content and available NPK in soil with the application of FYM, WCS and GM in conjunction with N fertilizers as compared to alone NPK fertilizers. Significant changes were observed in the different fractions of Fe and Mn when FYM, WCS and GM were applied in conjunction with different combinations of chemical fertilizers. The broad view of results revealed that the GM, FYM and WCS applied before transplantation of rice increased the concentrations of water soluble plus exchangeable (WS+EX), amorphous iron oxide (AFeOX), crystalline iron oxide (CFeOX) and organic matter (OM) bound fractions of Fe and Mn whereas, their fractions held on specifically adsorbed (SPAD) on inorganic sites and manganese surfaces (MnOX) decreased with the incorporation of GM, FYM and WCS. Among these manures, GM (T_5) reported higher concentrations and uptake of WS+EX, SPAD, MnOX, AFeOX, CFeOX and OM bound fractions of Fe and Mn followed by FYM (T_6) whereas, higher concentrations of Fe and Mn in case of total micronutrient (TM) were reported by FYM (T_4). The increase in the WS+EX, AFeOX, CFeOX and OM bound fractions were indicative of the enhanced availability of Fe and Mn with the application of GM, FYM and WCS. The micronutrient fractions were activated differentially and the dynamics of their inter conversion from one fraction to other was accelerated due to decomposition of GM, FYM and WCS. The results further concluded that after 27 years of rice-wheat cropping system, the application of FYM, WCS and GM resulted in significantly higher content of the WS+EX- Fe and Mn in the soil with GM followed by FYM and WCS (GM>FYM>WCS) which may be ascribed to the higher supply of Fe and Mn through decomposition of organic manures.

Key Words **:** Chemical fractions, Green manure, Farm yard manure, Wheat cut straw, NPK fertilizers

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INTRODUCTION

In India, rice-wheat system is a dominant cropping system across the Indo-Gagnetic plains and in the foothills of Himalaya as 33 per cent of rice and 42 per cent of wheat of the country is grown under this system with the consumption of 65 per cent of total fertilizers to maintain the yield potential (Modgal, 1996). Both the rice and wheat are dominant components of Indian food security system as it is consumed as major staple food. Presently, rice-wheat cropping system in the Indo-Gangetic plains is showing sign of fatigue due to continuous cropping and use of highly analysis fertilizers in cereal-cereal system for the last three decades. The application of high analysis fertilizers went so high that it has shown its ill effects like, adverse effects on soil properties, over exploitation of natural resources, deficiency of Fe and Mn etc. Continuous application of nitrogenous fertilizers has depleted soil organic matter, resulting in inherently low in available N, P and K and available Fe and Mn which has further lowered the production potential of soil (Srivastava, 1998). The integrated plant nutrient supply system, by which we can apply the nutrients in balanced form, is emerging as the most logical concept for managing and sustaining long term soil fertility and productivity. Prasad *et al.* (1995) reported that the integrated use of GM and FYM with chemical fertilizer resulted in build up of available nutrients in soil more effectively. It ought to be desirable to encourage integrated nutrient management system by reverting to the use of FYM, crop residues incorporation (CRI) and GM in conjunction with the chemical fertilizers with the hope that such technology could bring sustainability to agriculture by maintaining the soil health with reference to available macro and micronutrients. Long term experiments on different soil types have shown that CRI increased organic carbon and available N, P, K, Fe and Mn contents in soil. Continuous use of NPK fertilizers in conjunction with organic manures brings considerable changes in available and total nutrients supply to crops. In the soil environment, these nutrients are being transferred continuously from one form to other (Singh *et al.,* 1999; Sharma *et al.,* 2004). Submergence created reduced conditions during rice growth which helped higher release of Fe and Mn in the presence of GM (Dhaliwal, 2008). The distribution of Fe and Mn among various fractions is sensitive to cultivation and management practices (Sagwan and Singh, 1993). The alternate flooding (reduced stage) in rice and upland (oxidized stage) conditions in wheat effect transformation of Fe and Mn from one chemical form to another (Manchanda *et al.,* 2006). They further reported higher level of crystalline and oxide bound cations in calcareous soils which were transformed from reducible oxides forms into exchangeable and carbonate fractions whereas, Rupa *et al.* (2002) reported transformation of DTPA-Fe fraction in two alfisols with addition of FYM. Manure applied to rice – wheat system increased WSEX-Mn and Mn specifically adsorbed on the inorganic sites whereas, Mn held on organic sites and oxide bound surfaces decreased due to their conversion to other fractions (Dhaliwal, 2008). Herencia *et al.* (2008) showed the percentage of Fe and Mn in the specific fractions with respect to the total content are as follows: WSEX-Mn>Fe; reducible- Mn>Fe; oxidizable- Mn>Fe, RES- Fe> Mn and also showed that addition of OM caused Fe to move from less soluble forms to more plant available forms and reducible and oxidizable fractions for Fe. The higher concentration of OM- Mn in the soil solution indicated that the Mn associated with OM may play a beneficial role in the release of Mn in the soil solution and its uptake in rice and wheat crops (Dhaliwal and Manchanda, 2008).

In a long term experiment Behera and Singh (2009) reported increase in the uptake of micronutrients in maize-wheat cropping system. Sekhon *et al.* (2006) reported that OM-bound concentration of Fe and Mn increased with application of FYM, which increased the yield in rice-wheat system. Herencia *et al.* (2008) reported that with addition of organic and mineral fertilization, OM-bound fractions of micronutrients increased their availability and uptake in the soil. In an inceptisol, Behera *et al.* (2008) reported that TM-Fe and Mn fractions contributed more towards its availability and plant uptake under long-term maize-wheat cropping. However, Sharma *et al.* (1992 and 2004) reported the decrease TM fractions with GM after the harvest of wheat which could be attributed to an increase in the WSEX fraction as well as micronutrient cations held on inorganic sites.

The study of various fractions of Fe and Mn present in soil and conditions under which these become available to plants is pre- requisite in assessing their availability to plants. It is important to know the relationship between different chemical fractions of micronutrients in the soil and their uptake by the crop. Under continuous rice-wheat cropping system, micronutrients are generally considered to be present in association with soil solution, organic and inorganic solid phases and this association is often referred to as speciation (Bahera *et al.,* 2009), thus forming their various chemical fractions such as water soluble plus exchangeable (WSEX), specifically adsorbed (SPAD), and those associated with free calcium carbonate ($CaCO_3$), oxide surfaces, soil organic matter and minerals (Lyenger *et al.,* 1981). With these observations, the present study is aimed at an experiment on the long term basis with graded levels of N, P, K in combination with organic manures (FYM, GM and WCS) in rice - wheat system on various fraction of Fe and Mn in soil. So, the cherished and sole objectives of the present study were to investigate the long-term effect of FYM, WCS, GM and N fertilizers on the transformation of Fe and Mn fractions and to work out relationships between various fractions and their uptake in rice-wheat cropping sequence.

MATERIALS AND METHODS

Location of the experimental site:

Surface soil samples collected from 0-15 cm in an on-going long-term experiment on rice-wheat sequence is in progress since 1983 at Research Farm area of Department of Agronomy, Punjab Agricultural University, Ludhiana, under "All India Co-ordinated Research Project on Cropping Systems". Ludhiana is situated at the latitude of $30^0$54'N and longitude of $75^0$48'E at an altitude of 247 m above sea level (MSL) and it represents agro-ecological zone No.4 in the Punjab state.

Weather parameters of experimental site:

The Ludhiana has hot moist, semi-arid with alluvial, medium available water holding capacity. This climate zone (Zone-4) of Ludhiana is classified under hot moist and semi-arid sub-tropical class. The mean values of minimum and maximum temperature recorded in 2008 during growing season of rice and wheat ranged from 27.1^{0}C–34.1^{0}C and 8.6^{0}C-27.6^{0}C, respectively. The value of mean minimum to maximum relative humidity during growing season of rice and wheat ranged from 69- 89 per cent and 38-95 per cent, respectively. The average sunshine hours during growing season of wheat ranged from 5.1- 6.1 hours/day. The cumulative rainfall ranged from 152.7-392.8 mm and 0.4-13.9 mm during growing season of rice and wheat, respectively.

Six out of 14 different treatments combinations were selected for the present investigation in the on going long term experiment and these six treatment combinations consisted of addition of NPK fertilizers alone and in conjunction with FYM, wheat cut straw (WCS) and GM as mentioned in Table A. Recommended nutrients *viz*., N, P and K for rice were added @ 120 kg, 30 kg and 30 kg ha^{-1}, respectively. *Dhaincha* (*Sesbania aculeata*) as GM crop was raised during summer by applying phosphorus dose of succeeding rice crop. *In situ Sesbania aculeata* was grown during the last week of April after harvest of wheat crop. After two months, the green manure was incorporated in the field, followed by puddling with disc plow. The quantities of FYM, GM and WCS were added on laboratory test basis so that 50 per cent N was contributed by these manures.

The surface (0-15) cm soil samples from each treatment were taken using a five cm diameter auger after harvest of rice crop. 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 analysis. Soil texture was determined by standard international pipette method (Day, 1965). Soil pH was determined by the procedure given by Jackson (1973) whereas, EC was determined with method of Richard (1954). Rapid titration method (wet digestion method) was used for organic carbon determination (Walkley and Black, 1964). Available nitrogen, phosphorus and potassium were determined by the standard methods (Subbiah and Asija, 1956; Olsen *et al.,* 1950; Merwin and Peech, 1954), respectively. For determining micronutrients (DTPA-extractable Fe and Mn content, soil samples were taken at harvesting of rice and micronutrients 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 these micronutrients was measured on an atomic absorption spectrophotometer (Lindsay and Norvel, 1978). For estimation of micronutrients (Zn and Fe) content in grain, 0.5 g grain sample was digested using diacid mixture (HNO_3: $HClO_4$:: 4:1) as per method (Page *et al.,* 1982). After proper dilution with double distilled water, the micronutrient content in digested materials was estimated by using an atomic absorption spectrophotometer (Varian AAS-FS Model).

The soil of the experimental field was classified as *Tolewal* loamy sand with EC 0.32 dS m^{-1}, pH 8.15, low in organic carbon, available N, P and K. During the year 2002-03 the DTPA-extractable Fe and Mn levels were 9.40 and 9.06 mg kg^{-1}soil, respectively whereas, during 2008-09 these values were elevated to 9.80 and 9.58 mg kg^{-1}soil, respectively in 0-15 cm depth. The experiment was designed in a Randomized Block Design.

Sequential extraction of soil samples:

The processed soil samples were used to fractionate Fe and Mn into following chemical forms as per sequential procedure described below.

Water soluble plus exchangeable fraction (WSEX):

Five grams of soil was shaken with 20 ml of 0.005 M Pb $(NO_3)_2$ in 100 ml centrifuge tubes for fifteen minutes at 25^{0}C in orbital shaker and mixture was centrifuged for ten minutes at

Table A : Different treatments combinations of manures and fertilizers

Treatments	Rice	Wheat
T_1	No fertilizer, No manure	No fertilizer, No manure
T_2	100 % NPK (Fert.)	100 % NPK (Fert.)
T_3	50% NPK (Fert.) + 50 % N (FYM)	100 % NPK (Fert.)
T_4	50 % NPK (Fert.) + 50 % N (WCS)	100 % NPK (Fert.)
T_5	50 % NPK (Fert.) + 50 % N (GM)	100 % NPK (Fert.)
T_6	100 % NPK (Fert.) + 50 % N (FYM)	100 % NPK (Fert.)

6000 rpm. The supernatant filtered, separated and stored for analysis (Manchanda *et al.,* 2006). The sequential extraction continued in the residue of the soil sample.

Specifically adsorbed (SPAD):

The soil residue from water soluble plus exchangeable fraction was shaken with 20 ml of 0.05M Pb $(NO_3)_2$ for 2 hours at 25^{0}C in orbital shaker and the sample was, thereafter, centrifuged for ten minutes at 6000 rpm and the supernatant was filtered (Iwasaki *et al.,* 1993). The sequential extraction continued in the remaining of the soil sample.

Mn-oxide bound fraction (MnOX):

To the residue of SPAD, soil sample 20.0 ml of 0.1 mol L^{-1} $NH_2OH.HCl$ (hydroxylamine hydrochloride), at pH 2.0 were added and the mixture was shaken for 30 minutes, centrifuged and filtered. The separated supernatant was stored for analysis (Chao, 1972).

Amorphous Fe-oxides bound (AFeOX):

To the MnOX bound fraction free soil sample 20.0 ml of $NH_2OH.HCl$ (hydroxylamine hydrochloride) 0.1 mol L^{-1} plus HCl 0.25 mol L^{-1}, at pH 1.3 were added, and the mixture was shaken for 30 min at 25°C in orbital shaker, centrifuged and filtered; the separated supernatant was stored for analysis (Chao and Zhou, 1983).

Crystalline Fe-oxides bound (CFeOX)

To the AFeOx free soil sample 20.0 ml of 0.25 M $NH_2OH.HCl$ +0.25 M HCl + ascorbic acid 0.01 mol L^{-1}, at pH 1.21 were added, the mixture was heated with boiling water (100°C) in a beaker placed on hot plate for 30 minutes, shaking from time to time; thereafter centrifuged and filtered; the separated supernatant was stored for analysis (Manchanda *et al.,* 2006) The sequential extraction continued in the remaining of the soil sample.

Organically bound fraction (OM):

To the CFeOX free soil sample was shaken with 20 ml of 1 per cent $Na_4P_2O_7$ for one hour at 25^{0}C in orbital shaker and mixture was centrifuged for ten minutes at 6000 rpm the supernatant filtered, separated and stored for analysis (Raja and Lyengar, 1986).

Total micronutrient (TM):

For total elemental analysis of Fe and Mn a 0.5 g 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 Fe and Mn after appropriate dilutions. The results of the elemental analysis were reported on an oven-dry weight basis.

Plant analysis:

The grain samples of rice were collected from each plot at physiological maturity and dried in hot air oven at 65^{0}C for 3 days. Dried samples were digested in a di acid mixture of HNO_3 and $HClO_4$ (3:1) for the analysis of total Fe and Mn (Page *et al.,* 1982). The determination of Fe and Mn was performed on the different extracts collected from sequential extraction and extracts of rice and wheat grain samples were determined atomic absorption spectrophometer (Varian AAS-FS Model).

Statistical analysis:

Micronutrient cation concentrations were subjected to randomized complete block design analysis of variance. Least significant difference was used to compare the treatments effects at $P<0.05$. The statistical analysis was done with the help of method described by Panse and Sukhamte (1985).

RESULTS AND DISCUSSION

The results of the present study alongwith relevant discussion have been presented as under:

Water soluble and exchangeable (WSEX) fractions:

The WSEX-Fe contents of soil increased appreciably over its initial value of 9.40 mg kg^{-1} in all the treatments over control (Fig. 1). The maximum WSEX- Fe content (41.6 mg kg^{-1}) was reported where 50 per cent of recommended N was applied through GM and it was 26.4 per cent higher over T_2 treatment (32.9 mg kg^{-1}) where only chemical fertilizers were applied to rice and wheat crops. Similarly, T_3 and T_6 treatments associated with FYM reported almost the same trend of WSEX-Fe. The WSEX- Fe under different treatments ranged from 32.9-41.6 mg kg^{-1} after harvest of wheat in 27th crop rotation. The WSEX-Mn in different treatments tended to increase than its initial value of 9.06 mg kg^{-1} except in control where it decreased to 6.86 mg kg^{-1}. Further, among the different organic sources, application of FYM in T_3 and T_6 registered 19.05 mg kg^{-1} and 20.73 mg kg^{-1} WSEX-Mn, respectively, which is higher over control (Fig. 1). The maximum concentration of WSEX-Mn was reported by T_5 treatment with application of GM. The increase in WSEX-Mn may be attributed to the reduction of higher valent forms of Mn (Mn^{4+}) to its available form (Mn^{2+}) accompanied by increase in its solubility under submerged conditions and chelating action of organic manures. The increase in Fe status of soil over its initial status may be due to the induced submerged conditions which lowered the pH of the soil during rice growing season, thereby resulting in an increase in the soluble Fe^{2+} ions in the soil.

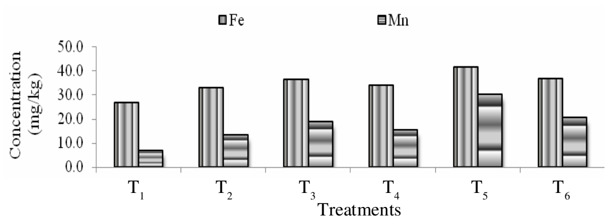

Fig. 1: Effect of manures and fertilizers on WSEX fraction (mg kg^{-1})

The WSEX-Fe contents of soil increased appreciably over its initial value of 9.6 mg kg^{-1} in all the treatments over control (Fig. 1). Hellal, (2007) reported from his green house pot experiment that addition of composted mixtures increased WSEX-Fe in soil, as a result of application of composted mixture. Behera and Singh (2009) reported the data regarding WSEX- Fe and Mn in soil before sowing of maize and after harvest of wheat during 32nd cropping cycle of maize-wheat system. Kopec and Przetaczek-Kaczmarczyk (2006) showed comparison of metals in the 3rd and in the 37th year of the experiment and it was found that these contents decreased in the 37th year in case of Mn by 57.2-74.1 per cent and whereas, in case of Fe its content was higher by 23-59 per cent.

Specifically adsorbed (SPAD) fractions:

The SPAD-Fe reported highest magnitude in T_5 (3.69 mg kg^{-1}) treatment with GM compared with FYM (T_3 and T_6) followed by WCS (T_4) treatment (Fig. 2). Nearly equal magnitude of SPAD-Fe was observed in both T_3 and T_6 treatments. In case of SPAD-Mn, again the highest amount of Mn was reported in T_5 followed by T_3 and T_6 treatments. Control treatment reported the minimum level of SPAD-Mn (8.80 mg kg^{-1}). However, treatment T_5 with GM addition reported the highest magnitude of SPAD-Mn. In general, a significant increase in SPAD-Mn was observed in all the treatments with NPK, GM, FYM and WCS. The magnitude of SPAD-Mn was low in case of chemical fertilizers alone (T_2). The treatment T_4 where 50 per cent NPK were substituted through WCS reported low level of SPAD-Mn as compared to the treatments T_3 and T_5 where 50 per cent NPK was substituted through FYM and GM, respectively. The additional 50 per cent NPK substitution through FYM (T_6) did not help in increasing SPAD-Mn over GM application (T_5). Iu *et al.* (1981) reported increase in amount of SPAD- Fe and Mn with the addition of GM. These results are also in agreement with the results obtained by Chatterjee *et al.* (1992) who reported increase in this form with addition of GM.

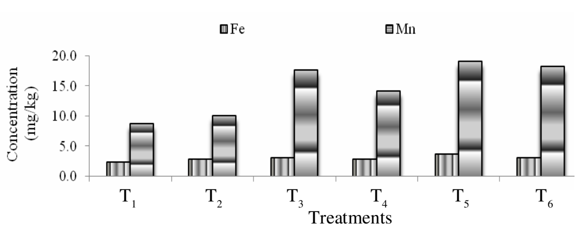

Fig. 2: Effect of manures and fertilizers on SPAD fraction (mg kg^{-1})

Mn-oxide (MnOX) bound fractions:

MnOx-Fe fraction was almost two times more in T_5 treatment as compared to T_1. Among GM, FYM and WCS, the lowest amount of MnOX-Fe was reported by WCS which was attributed to slow decomposition rate of manure in the soil (Fig. 3). MnOx-Mn showed significant increase in its fraction with fertilizer and manure. The highest amount of this fraction was reported in T_5 followed by T_6 where 50 per cent additional N was substituted through FYM (Fig. 3) whereas, GM reported 1.5 times more MnOx-Mn fraction over T_1. The fertilizer treatment T_2 was not able to induce this fraction to the level as maintained by FYM, GM and WCS. Sekhon *et al.* (2006) reported that addition of GM to rice increased potentially available fraction of Fe and Mn under rice-wheat rotation. Hellal (2007) reported that addition of composted mixtures increased MnOX–Fe and Mn in soil, as a result Fe availability is increased in calcareous soil by high acidulation effect of compost. Herencia *et al.* (2008) showed the percentage of Fe and Mn in the specific fractions with respect to the total content are Mn>Fe and addition of OM caused Zn and Fe to move from less soluble forms to more plant available fraction which was always favoured by organic amendment.

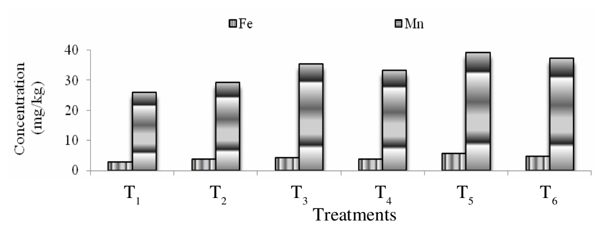

Fig. 3: Effect of manures and fertilizers combinations on MnOX fraction (mg kg^{-1})

Amorphous Fe-oxides (AFeOX) bound fractions:

The AFeOX-Fe reported nearly 2.4 times more concentration in T_5 over T_1. Different treatments released AFeOX-Fe in the solution varying from 55.17 to 127.87 mg kg^{-1} (Fig. 4). The manure addition significantly increased the AFeOX-Fe over T_1. On the other hand AFeOX-Mn showed similar pattern of increase in its fraction varying from 47.93-83.10 mg kg^{-1}. Among the three manures, GM in T_5 treatment showed higher release of AFeOX-Mn in the solution. Our results reported that AFeOX-Mn showed its higher content released in soil solution with application FYM, WCS and GM,

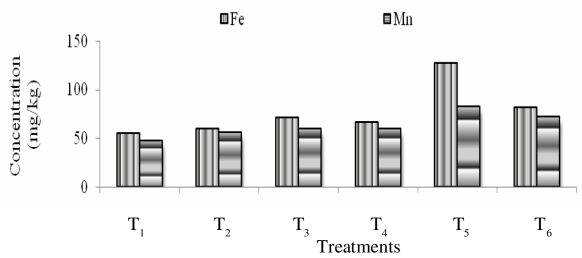

Fig. 4: Effect of manures and fertilizers combinations on AFeOX fraction (mg kg^{-1})

which further confirmed that Mn content for plant growth could be maintained from this fraction. Sekhon *et al.* (2006) reported that addition of GM to rice increased AFeOX form of Fe and Mn under rice-wheat rotation. Singh *et al.* (1988) in a study on 11 soils reported that 9 and 5 per cent of total Fe and Mn was associated with AFeOX fraction. Hellal (2007) reported that addition of composted mixtures increased AFeOX fraction but occluded Fe did not differ significantly due to application of composted mixture. Agbenin (2003) reported a similar increase in AFeOX-Fe and Mn fractions fertilized with NPK, FYM and FYM+NPK.

Crystalline Fe-oxides (CFeOX) bound fractions:

The CFeOX-Fe fraction increased in the soil many folds as compared to other fractions. In all the treatments CFeOX-Fe varied from 206.6 - 285.8 mg kg^{-1} in the soil (Fig. 5). After 27th rotation of rice-wheat system similar to other fractions the highest concentration of this fraction was reported in T_5 where GM played a significant role in its release in the soil solution. CFeOX-Mn showed its concentrations varying from 22.18 - 31.39 mg kg^{-1} with highest in T_5 where 50 per cent N was added through GM. The higher concentrations of CFeOX-Fe and Mn reported that Fe and Mn requirement can be maintained from this fraction as Fe and Mn associated with CFeOX released more concentration of Fe and Mn in the soil solution. Singh *et al.* (1988) in a study on 11 soils reported that 11 and 17 per cent of total Fe and Mn were associated with CFeOX fraction. Chao and Zhou (1983) reported similar increases in CFeOX fraction.

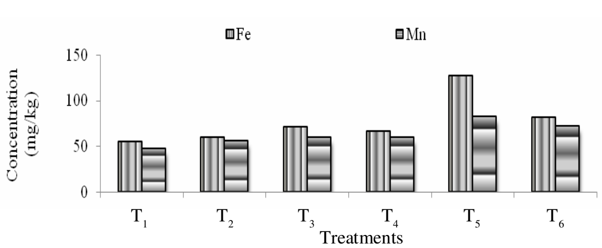

Fig. 5: Effect of manures and fertilizers combinations on AFeOX fraction (mg kg^{-1})

Organically (OM) bound fractions:

Organic bound (OM- Fe) fraction, the treatments T_3 (58.8 mg kg^{-1}) and T_6 (61.7 mg kg^{-1}) where 50 per cent N was substituted through FYM, contributed almost equally towards this fraction. In general, OM-Fe fraction varied in the soil from 49.5 - 68.64 mg kg^{-1} soil (Fig. 6). The treatment T_4 where WCS was added reported OM-Fe equivalent to T_2 where recommended fertilizers were added. Similar to OM-Fe fraction, OM-Mn showed same trend of this fraction varying from 31.0 mg kg^{-1} in control to 42.33 mg kg^{-1} in T_5 treatment. The treatments like T_1 and T_2 and T_3 and T_4 contributed equally towards this fraction. The higher concentration of OM- Fe and Mn in the soil solution indicated that the micronutrients associated with OM bound fraction may play a beneficial role in the uptake of these nutrients by the plants. The treatments like T_1 and T_2 and T_3 and T_4 contributed equally towards this fraction (Fig. 6). The higher concentration of OM- Fe and Mn in the soil solution indicated that the micro-nutrients associated with OM bound fraction may play a beneficial role in the uptake of these nutrients by the plants. Sekhon *et al.* (2006) reported that OM bound fraction of Fe and Mn increased with application of FYM in rice-wheat system.

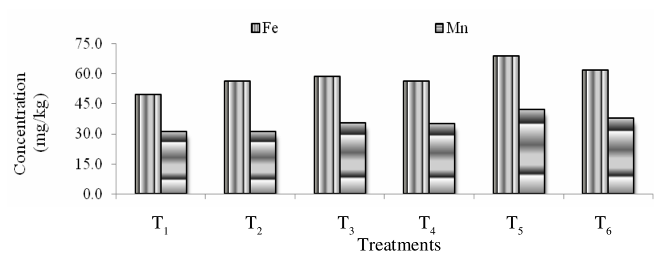

Fig. 6: Effect of manures and fertilizers combinations on OM bound fraction (mg kg^{-1})

Total micronutrient (TM) fractions:

TM-Fe reported its highest concentration in T_3 where 50 per cent N was substituted through FYM followed by T_4 where 50 per cent N was substituted through WCS (Fig. 7 and 8). The increase in TM-Fe under different treatments was not significant. TM-Mn fraction showed similar trend of Mn concentration like TM-Fe. However, highest TM-Mn was reported in T_3 followed by T_4. The T_2 and T_5 treatments were able to contribute equally towards this fraction. Agbenin and Henningsen (2004) reported distribution of TM fractions of Fe and Mn and their contribution towards availability and plant uptake of micronutrients under long-term maize-wheat cropping sequence which indicated residual micronutrients as the dominant portion of total Fe and Mn. However, Sharma *et al.* (2004) reported the decrease in total fractions with GM after the harvest of wheat which could be due to an increase

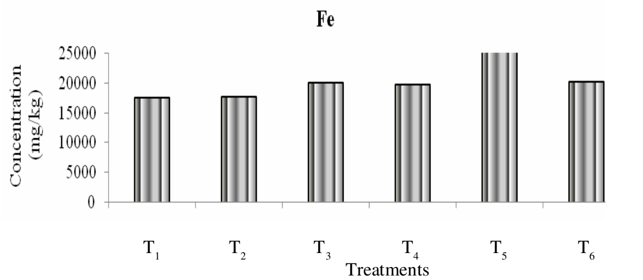

Fig. 7: Effect of different manures and fertilizers combinations on total Fe (mg kg^{-1})

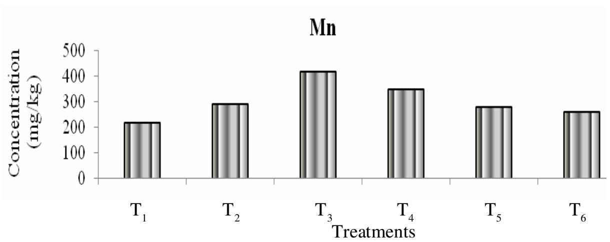

Fig. 8: Effect of different manures and fertilizers combinations on total Mn (mg kg^{-1})

in the WSEX fractions as well as held on inorganic sites. Katyal and Sharma (1991), Sharma and Bapat (2000) and Behera *et al*. (2008) reported similar results of increase in Zn, Cu, Fe and Mn cations concentration in various wheat plant parts with Zn fertilization.

Uptake of Fe and Mn by rice and wheat grains:

The perusal of data indicated that Fe uptake in rice (grain + straw) ranged from 533.0-1319.1 g ha^{-1} (Table 2). The Fe uptake in grain and straw varied from 209.6-472.0 g ha^{-1} and 323.4-847.1 g ha^{-1}, respectively. The maximum Fe uptake was registered by T_6 (1319.1 g ha^{-1}), where 50 per cent of recommended dose of N as additional dose of N through FYM was applied, which was significantly higher over other treatments. Increased Fe uptake with FYM may be ascribed to increased availability of Fe because of their favorable impact on oxidation-reduction regime and higher chelation. The data revealed that Mn uptake in rice (grain + straw) ranged from 730.6-1679.3 g ha^{-1}. The Mn uptake in grain and straw varied from 322.3-737.8 g ha^{-1} and 408.3-941.5 g ha^{-1}, respectively. The maximum Mn uptake was registered by T_6 (1679.3 g ha^{-1}), where 50 per cent of recommended dose of N as additional dose of N through FYM was applied, which was 129.8 and 9.3 per cent higher, respectively, over control (T_1) and 100 per cent of the recommended NPK dose through fertilizers (T_5). The beneficial effect of GM over FYM and WCS in improving the Fe and Mn uptake may be due to its higher availability from the unavailable forms through higher chelating capacity of green manure. Further, the perusal of data indicated that Fe uptake in rice (grain + straw) ranged from 533.0-1319.1 g ha^{-1}

Relationship between micronutrients fractions and their uptake by rice grains:

The correlation coefficients between various micronutrients fractions were worked out and the results are presented in Table 3. All the fractions of Fe were positively and significantly correlated with each other except total Fe where these fractions were significantly but negatively correlated with other fractions (Table 3). Similar observations were reported by Agbenin and Henningsen, (2004). Saha *et al.* (1999) observed that WSEX and OM bound fractions of Fe were jointly affected by application of lime and FYM. Sekhon *et al.* (2006) reported that the Fe fractions in the soil were resulted from organic matter addition under a rice-wheat cropping system. Zhang *et al.* (1997) reported interchangeability of Fe fractionation in sandy soils under citrus production. Shuman (1988) observed that fractions Fe and their distribution were strongly affected by addition of organic matter. Behera *et al.* (2009) also reported changes in fractions of Fe in soil under long term continuous cropping for more than three decades.

In all Mn fractions WSEX-Mn reported its strong correlation with SPAD (0.997), MnOX (0.972), AFeOX (0.842) and OM (0.889) bound fractions (Table 4). Interestingly all the TM-Mn fractions except CFeOX-Mn (-0.255) showed positive

Table 1 : Effect of chemical fertilizer and organic manures on the uptake of Fe and Mn by rice

Treatments	Fertilizer use (% of recommended NPK)		Fe uptake (g ha^{-1})			Mn uptake (g ha^{-1})		
	Rice	Wheat	Grain	Straw	Total	Grain	Straw	Total
T_1	Control	Control	209.6	323.4	533	322.3	408.3	730.6
T_2	100	100	413.3	783.6	1196.9	641.6	869.8	1511.4
T_3	50+50%N(FYM)	100	420.6	798.8	1219.4	649.7	886.3	1536.0
T_4	50+50% N(WCS)	100	405.3	775.6	1180.9	548.0	817.88	1365.8
T_5	50+50% N(GM)	100	463.8	839.3	1303.1	654.2	897.4	1551.6
T_6	100+50%N(FYM)	100	472.0	847.1	1319.1	737.8	941.5	1679.3
LSD (P=0.05)			2.49	2.39	3.45	3.76	3.48	5.12

Table 2 : Coefficient of correlation of Fe with different chemical fractions

Fractions	WS+EX- Fe	SPAD- Fe	MnOX- Fe	AFeOX- Fe	CFeOX- Fe	OM - Fe
SPAD - Fe	0.885					
MnOX - Fe	0.905	0.996				
AFeOX- Fe	0.798	0.929	0.934			
CFeOX- Fe	0.778	0.924	0.900	0.800		
OM - Fe	0.880	0.996	0.997	0.927	0.892	
Total- Fe	-0.206	-0.294	-0.353	-0.468	-0.012	-0.361

Table 3 : Coefficient of correlation of Mn with different chemical fractions

Fractions	WSEX- Mn	SPAD- Mn	MnOX- Mn	AFeOX- Mn	CFeOX- Mn	OM - Mn
SPAD - Mn	0.997					
MnOX - Mn	0.972	0.980				
AFeOX- Mn	0.842	0.850	0.924			
CFeOX- Mn	0.350	0.317	0.423	0.661		
OM - Mn	0.889	0.899	0.939	0.969	0.531	
Total- Mn	0.407	0.391	0.327	0.005	-0.255	0.079

and significant correlation with other Mn fractions. Dhaliwal (2008), Dhaliwal and Manchanda (2008) and, Dhaliwal and Walia (2008) reported that with addition of GM in rice-wheat system, WSEX, SPAD and SPAD-Mn fractions increased whereas, MnOX and AMFeOx –Mn decreased. Pal (1974), Behera *et al.* (2008), Behera and Dyan Singh (2009) and Behra *et al.* (2009) in a long term study on maize-wheat system, reported uptake of Fe and Mn by continuous cropping and fertilizer application.

Conclusion:

Farm yard manure, WCS and GM helped in the many folds release of Fe and Mn and their different fractions in the soil under rice-wheat system. The Fe fractions in SPAD and MnOX decreased whereas, their corresponding Mn content increased with manures and fertilizers application. Very high contents of Fe and Mn were reported in AFeOX, CFeOX and OM bound fractions and these fractions were continuously exchanging Fe and Mn in the soil solution as their content is replenished. In overall, the WSEX, SPAD and OM bound fractions of Fe and Mn reported higher concentration indicating their contribution towards higher plant uptake. The uptake of micronutrients (Zn, Cu, Fe and Mn) increased significantly with the application of fertilizers and manures over their uptake under control plot. Among the different organic sources of N applied to rice, FYM and GM recorded significantly higher uptake of micronutrients than the uptake of these nutrients by rice where 100 per cent of the recommended NPK dose was applied through fertilizers. Amongst organic manures tried, FYM and GM proved significantly superior to WCS.

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