Indian Journal of Agricultural Sciences **80** (4): 316–20, April 2010

Impact of continuous fertilizer use on fractions of manganese in soil and their contribution to availability and its uptake by maize (*Zea mays*)–wheat (*Triticum aestivum*) cropping system*

SANJIB KUMAR BEHERA[1] and DHYAN SINGH[2]

Indian Agricultural Research Institute, New Delhi 110 012

Received: 6 July 2009; Accepted: 28 January 2010

Key words: Fractions of manganese, Inceptisol, Long-term experiment, Mn availability, Mn uptake, Maize–wheat cropping system

Micronutrient deficiencies in crop plants are widespread in all over the world because of increased micronutrient demands from intensive cropping practices and adaptation of high-yielding cultivars having higher micronutrient demand. Moreover, enhanced production of crops on marginal soils that contain low levels of essential nutrients, increased use of high analysis fertilizers with low amounts of micronutrient contamination, decreased use of animal manures, composts, and crop residues, use of soils that are inherently low in micronutrient reserves and involvement of natural and anthropogenic factors that limit adequate plant availability add to the cause (Fageria *et al.* 2002). In India, intensive cropping with nutrient exhaustive high-yielding varieties coupled with the use of high analysis fertilizers for enhancing foodgrain production have catalyzed the rapid depletion of available micronutrients in soil in general (Singh 2009) and available manganese (Mn) in some areas in particular (Nayyar *et al.* 1990). Long-term experiments (LTE) offer a better platform to visualize the status of micronutrients in soil under intensive cropping and their contribution to sustained production. Uptake of manganese by crop plants is determined by soil properties, plant factors, and their interactions at the soil-root interface. Knowledge of the reactions at the interface is basic to the prediction of soil Mn availability and to an understanding of soil-plant-Mn relationships. One aspect of the processes is the quantitative estimation of those fractions of native soil Mn that interact with plant roots and contribute to availability in soil and plant uptake. Although many studies show that various fractions of Mn exist in soil, few quantitative data exist that reveal its availability, amounts in each fraction in Inceptisol which might have altered as a result of continuous fertilizer use and intensive cropping and their contribution for plant uptake. Keeping the above facts in view, the present investigation was carried out to assess the native Mn fractions in Inceptisol under continuous cropping and their contribution to availability and crop uptake.

An on-going long-term experiments commenced in 1971 on a Typic Haplustept soil of Indian Agricultural Research Institute farm, New Delhi (28°N latitude, 77°E longitude, and 250 m above mean sea level), India was used for this study. The climate of New Delhi is semi-arid, sub-tropical with dry hot summer and cold winter. The average annual rainfall is 650 mm of which nearly 80% is received through south-west monsoon during July to September. The average monthly minimum and maximum temperature are 18.3 and 30.4°C, respectively with May the hottest month and January the coolest. The soil was sandy clay loam (29% clay, 54% sand, 17% silt) of alluvial origin, non-calcareous, very deep (> 2 m), well drained, flat (about 1% slope) and belongs to hyperthermic family. At the onset of the LTE in 1971, the surface soil (0–15 cm depth) was mainly alkaline (*p*H (H_2O) 8.3) and non-saline (EC 0.45 dS/m) and contained 0.45% organic C, 16 kg/ha Olsen P, 155 kg/ha NH_4OAc extractable K and 20 mg/kg of DTPA extractable Mn.

The long-term experiment is being carried out on an undisturbed lay out since 1971, with 10 treatments comprising different nutrient management options imposed in a randomized block design with 4 replications to an maize (*Zea mays* L)–wheat (*Triticum aestivum* L emend. Fiori & Paol.) cropping system (earlier pearl millet–wheat–forage cowpea cropping system till 1982). However, for this investigation 4 treatments, as detailed below, had been chosen:

C: Unfertilized (unmanured control)

NPK : Recommended N, P and K through fertilizer to both the crops

---

*Short note

Based on a part of Ph D thesis of the first author submitted to IARI, New Delhi during 2006

[1] Scientist (email: sanjib_bls@rediffmail.com) Indian Institute of Soil Science, Nabibagh, Berasia Road, Bhopal 462 038

[2] Principal Scientist (email: dhyansingh_01@yahoo.com)

NPK + farmyard manure: Recommended N, P and K through fertilizer to both the crops, and 15 tonnes farmyard manure ha/year to maize only and NPK + Zn: Recommended N, P and K through fertilizer to both the crops, and 10 kg zinc sulfate/ha to wheat only.

The recommended fertilizer rate for maize and wheat was 120 kg N, 26 kg P and 33 kg K/ha, which remained unchanged over the years of experimentation. Fertilizer N, P, K and Zn were applied through urea, diammonium phosphate, muriate of potash and zinc sulphate, respectively. Entire amount of P, K and Zn and half of the recommended N were applied as basal dressing, whereas remaining half of the N was top-dressed at tillering in wheat and at knee-high stage in maize. 'Ganga Safed 2' Maize was sown in 75 cm apart rows during last week of June and subsequent. 'HD 2329' Wheat in 20 cm apart rows during second week of November. The crops were harvested manually at the maturity, and the above ground biomass was removed from the field.

Soil samples were collected with a screw type auger from 0–15, 15–30, 30–45 and 45–60 cm depths before sowing of the maize (2003) and after harvest of wheat (2003–04). The sub-samples collected from randomly chosen points in each plot (21 m × 8 m size) were mixed thoroughly to obtain a representative soil sample. The samples were air-dried, ground in wooden mortar and pestle and passed through a 2 mm sieve. The soil samples were analyzed for different fractions of manganese following the fractionation scheme developed by Ma and Uren (1995). The extractions were conducted in 50 ml polypropylene centrifuge tubes. Between each successive extraction, the supernatant was obtained by centrifuging for 15 min. (3 000 rpm) and filtering. The total concentration of the metal was determined after digesting the soil with H_2SO_4-$HClO_4$-HNO_3-HF mixture. The concentration of Mn in the supernatant was measured using GBC 904 AA atomic absorption spectrophotometer. DTPA extractable Mn was also determined by the method outlined by Lindsay and Norvell (1978).

Data on soil Mn content was subjected to 'F' test using the procedures for randomized block design (Gomez and Gomez 1984). Determination of correlation co-efficients and path co-efficient analysis were done with the help of SPSS and SPAR 1 softwares, respectively.

The values of DTPA extractable Mn, under different treatments, in 4 soil layers are given in Table 1. There was no significant difference among the different treatments with respect to available Mn content, except in 30–45 cm depth at premaize as well as post- wheat stages. In all the treatments available Mn content decreased with increase in soil-depth. This is in line with the findings of Kher (1993) in an Alfisol under maize–wheat system.

The data regarding fractions of Mn in soil samples collected from different soil layers, after 31 years of continuous cropping are given in Table 2. The overall mean values of water soluble and sorbed manganese varied from 0.65 to 0.80 and 2.52 to 3.45 mg/kg, respectively under various treatments. The highest amount of sorbed manganese (SORB-Mn) was recorded under NPK + farmyard manure in the surface and immediate sub-soil which may be partially ascribed to increased surface area and adsorption sites provided by presence of higher amount of organic matter. However, the mean values of SORB-Mn declined in 30–45 and 45–60 cm depths as compared to the upper 2 layers (0–15 and 15–30 cm) probably on account of less and less organic matter at lower depths. Contents of easily reducible manganese across the treatments and sampling stages were 48.9, 11.7, 11.0 and 9.9 mg/kg in 0–15, 15–30, 30–45 and 45–60 cm soil depths, respectively, and that of carbonate bound Mn were 22.6, 19.7, 7.52 and 9.50 mg/kg of soil.

The overall mean values of OM- and FeOx-Mn varied from 13.3 to 15.6 and 18.6 to 23.2 mg/kg, respectively, under different treatments. Mn bound to Fe and Al oxides was present in higher quantity in surface soil than that in sub-surface layers. All the fractions of Mn kept on changing in the cropping year, viz pre-maize stage to post-wheat stage. It is in line with the observations recorded by Michael and Badiger (1981) in Vertisols of India and by Agbenin (2003) in Alfisol of Savanna. It may be ascribed to the sensitiveness of manganese fractions to continuous cultivation and management practices. Mobilization and conversion of one form to another continue in a cropping year due to redox reactions in soil.

Total and residual Mn contents ranged from 491 to 543 and 417 to 465 mg/kg, respectively, under various treatments over sampling stages and depths of sampling. Residual

Table 1 Influence of continuous cropping on the DTPA-extractable Mn (mg/kg) in soil during 32nd cropping cycle

Treatment	Pre-maize 2003					Post-wheat 2003-04		
	0–15 cm	15–30 cm	30–45 cm	45–60 cm	0–15 cm	15–30 cm	30–45 cm	45–60 cm
C	18.51	17.34	15.18	13.70	18.58	17.59	14.36	11.21
NPK	17.74	16.43	14.80	12.53	18.59	17.60	13.10	11.66
NPK+FYM	17.73	16.38	15.10	12.89	18.97	17.89	15.30	13.14
NPK+Zn	18.78	17.27	15.85	12.75	19.85	18.71	16.51	14.01
CD (*P*=0.05)	NS	NS	1.28	NS	NS	NS	2.39	NS

CD, Critical difference; NS, not significant

Table 2 Depth-wise distribution of different forms of manganese in soil under varying fertilizer treatments

Treatment	Water-soluble manganese (mg/kg)												Overall mean
	0–15 cm			15–30 cm			30–45 cm			45–60 cm			
	PM	PW	Mean	PM	PW	Mean	PM	PW	Mean	PM	PW	Mean	
C	0.85	0.89	0.87	1.25	0.65	0.95	0.72	0.46	0.59	0.19	0.21	0.20	0.65
NPK	1.10	1.18	1.14	1.39	0.61	1.00	0.78	0.59	0.68	0.32	0.46	0.39	0.80
NPK+FYM	0.89	1.14	1.01	1.50	0.49	0.99	0.82	0.30	0.56	0.18	0.14	0.16	0.68
NPK+Zn	0.98	1.19	1.08	1.43	0.45	0.94	0.80	0.80	0.80	0.25	0.39	0.32	0.78
Mean	0.95	1.10	1.02	1.39	0.55	0.97	0.78	0.54	0.66	0.23	0.30	0.27	
CD (P=0.05)	Sampling stage (SS): 0.04			Fertilizer treatment (FT): 0.07			Sampling depth (SD): 0.06			FT×SD: 0.15			SS×FT×SD: 0.21
	Sorbed manganese (mg/kg)												
C	2.74	4.03	3.38	3.30	2.45	2.87	1.48	2.77	2.12	1.34	2.11	1.72	2.52
NPK	2.66	3.93	3.29	3.68	1.94	2.81	1.59	2.76	2.17	1.62	2.27	1.94	2.55
NPK+FYM	2.31	5.85	4.08	5.50	4.95	5.22	1.95	2.43	2.19	1.72	2.92	2.32	3.45
NPK+Zn	2.35	4.72	3.53	4.25	2.38	3.31	1.85	2.67	2.26	1.60	2.22	1.91	2.75
Mean	2.51	4.63	3.57	4.18	2.93	3.55	1.71	2.66	2.18	1.57	2.38	1.97	
CD (P=0.05)	Sampling stage (SS): 0.14			Fertilizer treatment (FT): 0.25			Sampling depth (SD): 0.20			FT×SD: 0.50			SS×FT×SD: 0.70
	Easily reducible manganese (mg/kg)												
C	53.3	45.7	49.5	12.2	11.1	11.6	10.4	11.1	10.8	10.1	9.6	9.8	20.4
NPK	52.6	45.2	48.9	13.0	10.7	11.8	11.1	10.2	10.7	10.9	8.6	9.7	20.3
NPK+FYM	53.8	46.1	49.9	13.3	10.8	12.1	11.9	11.6	11.7	11.3	9.7	10.5	21.1
NPK+Zn	51.5	43.8	47.6	13.0	9.6	11.3	10.9	10.3	10.6	11.0	8.7	9.8	19.8
Mean	52.8	45.2	48.9	12.9	10.6	11.7	11.1	10.8	11.0	10.8	9.2	9.9	
CD (P=0.05)	Sampling stage (SS): 0.24			Fertilizer treatment (FT): 0.42			Sampling depth (SD): 0.34			FT×SD: 0.84			SS×FT×SD: 1.19
	Carbonate-bound manganese (mg/kg)												
C	25.4	16.6	20.9	20.6	17.5	19.1	7.53	6.70	7.11	8.95	9.12	9.03	14.1
NPK	33.9	18.7	26.3	22.4	17.4	19.9	8.54	8.25	8.39	9.57	10.36	9.96	16.1
NPK+FYM	26.2	17.7	21.9	22.6	12.8	17.7	7.75	5.47	6.61	9.65	9.71	9.68	14.0
NPK+Zn	37.3	17.4	21.3	23.5	20.8	22.2	8.21	7.74	7.97	9.23	9.43	9.33	16.7
Mean	30.7	17.6	22.6	22.3	17.1	19.7	8.00	7.04	7.52	9.35	9.65	9.50	
CD (0.05)	Sampling stage (SS): 0.57			Fertilizer treatment (FT): 0.66			Sampling depth (SD): 0.81			FT×SD: 1.99			SS×FT×SD: 2.82
	Organic matter-bound manganese (mg/kg)												
C	14.2	8.34	11.3	14.2	11.7	12.9	12.1	8.30	10.2	20.4	17.5	18.9	13.3
NPK	19.8	9.84	14.8	15.4	17.1	16.2	12.6	11.9	12.2	20.9	17.9	19.4	15.6
NPK+FYM	22.0	10.7	16.4	16.2	9.40	12.8	13.2	7.98	10.6	23.1	14.0	18.6	14.6
NPK+Zn	19.5	10.5	15.0	15.9	13.2	14.6	12.7	11.8	12.3	22.0	17.6	19.8	15.4
Mean	18.9	9.84	14.4	15.4	12.8	14.1	12.6	10.0	11.3	21.6	16.7	19.2	
CD (P=0.05)	Sampling stage (SS): 0.40			Fertilizer treatment (FT): 0.70			Sampling depth (SD): 0.57			FT×SD: 1.39			SS×FT×SD: 1.97
	Iron oxide-bound manganese (mg/kg)												
C	24.0	18.2	21.1	18.0	17.1	17.6	20.1	15.5	17.8	18.0	24.5	21.2	19.4
NPK	31.8	19.2	25.5	19.0	15.1	17.1	21.4	21.9	21.6	20.1	26.2	23.2	21.8
NPK+FYM	27.3	18.1	20.5	18.5	14.1	16.3	20.5	15.7	18.1	19.8	19.4	19.6	18.6
NPK+Zn	31.1	21.5	26.8	19.2	20.6	19.9	21.8	24.5	23.2	19.5	26.3	22.1	23.2
Mean	28.5	19.2	23.5	18.7	16.7	17.7	20.9	19.4	20.2	19.3	24.1	21.5	
CD (P=0.05)	Sampling stage (SS): 0.60			Fertilizer treatment (FT): 1.03			Sampling depth (SD): 0.85			FT×SD: 2.07			SS×FT×SD: 2.93
	Residual manganese (mg/kg)												
C	393	365	379	438	409	423	456	451	453	383	469	426	420
NPK	443	412	427	487	456	471	534	469	501	399	522	460	465
NPK+FYM	380	367	373	477	404	440	483	410	446	398	425	411	417
NPK+Zn	431	405	418	481	438	459	485	467	476	405	495	450	451
Mean	412	387	399	471	427	448	489	449	469	396	478	437	
CD (P=0.05)	Sampling stage (SS): 8.0			Fertilizer treatment (FT): 14.0			Sampling depth (SD): 11.0			FT×SD: NS			SS×FT×SD: NS
	Total manganese (mg/kg)												
C	514	459	486	508	470	489	509	496	502	442	532	487	491
NPK	585	510	547	562	519	541	590	525	558	462	588	525	543
NPK+FYM	513	467	490	555	457	506	539	453	496	464	481	473	491
NPK+Zn	574	504	539	558	505	532	541	525	533	468	560	514	529
Mean	546	485	515	546	488	517	545	500	522	459	540	500	
CD (P=0.05)	Sampling stage (SS): 16.0			Fertilizer treatment (FT) :28.0			Sampling depth (SD): NS			FT×SD: NS			SS×FT×SD: NS

PM, Pre-maize; PW, post-wheat; NS, not significant

Table 3 Interrelations among manganese fractions in pre-maize and post-wheat surface soil

	WS-Mn	SORB-Mn	ERMn	CA-Mn	OM-Mn	FeOx-Mn	RES-Mn
Pre-maize							
WS-Mn	1.00	0.01	–0.44	0.64	0.24	0.58	0.72
SORB-Mn		1.00	0.31	–0.37	–0.70	–0.49	0.29
ERMn			1.00	–0.94**	–1.00	–0.72	–0.65
CA-Mn				1.00	0.36	0.88*	0.74
OM-Mn					1.00	0.64	0.06
FeOx-Mn						1.00	0.58
RES-Mn							1.00
Post-wheat							
WS-Mn	1.00	0.49	0.04	–0.11	0.53	0.18	0.66
SORB-Mn		1.00	0.40	–0.31	0.41	–0.27	–0.31
ERMn			1.00	–0.24	–0.49	–0.96**	–0.47
CA-Mn				1.00	–0.06	0.05	0.15
OM-Mn					1.00	0.60	0.35
FeOx-Mn						1.00	0.60
RES-Mn							1.00

fractions of Mn consisted of dominant portion of total Mn present in soil. Metals held within silicate mineral structures often termed 'residual' constitute a substantial portion of the total metals in this form (Miller *et al.* 1986, Randhawa and Singh 1997). However, Zhu and Alva (1993) reported the existence of major portion of Mn as precipitate form in some sandy soils of Florida under intensive citrus production, whereas it was predominantly present as organically bound form in the Spodosols and as organically bound, oxide and amorphous fractions in the Alfisols and Entisols (Zhang *et al.* 1997).

Data in Table 3 revealed significant and positive correlation between CA-Mn and FeOx-Mn (r = 0.88*), in pre-maize soil, whereas ERMn was negatively correlated with CA-Mn (r = –0.94**). ERMn was negatively correlated with FeOx-Mn (r = –0.96**) also in the post-wheat soil. Correlations among the different fractions of Mn in soil have also been reported by other workers (Randhawa and Singh 1997). Simple correlation co-efficient values (table not given) indicated that overall effect of each fraction of Mn on DTPA-extractable Mn in pre-maize as well as post-wheat soil was not significant. However, path co-efficient analysis revealed that WS-Mn ($P = 0.57$), CA-Mn ($P = 1.70$) and OM-Mn ($P = 0.17$) contributed directly towards DTPA-extractable Mn at pre-maize stage, while OM-Mn ($P = 0.61$), FeOx-Mn ($P = 1.49$), RES-Mn ($P = 1.26$) contributed indirectly through CA-Mn. But at post-wheat stage DTPA- Mn was directly influenced by WS-Mn ($P = 0.27$), SORB-Mn ($P = 0.75$), ERMn-Mn ($P = 0.71$) and FeOx-Mn ($P = 0.99$). This suggests that DTPA extracts manganese directly from water soluble, carbonate-bound and organic matter-bound fractions in pre-maize soil and from WS-Mn, SORB-Mn, ERMn-Mn and FeOx-Mn in post-wheat soil although indirect contribution of other fractions was visible. Water-soluble form contributed directly at both the stages of sampling. Soil solution and easily exchangeable form together constitute readily soluble Mn and although it is important source of Mn to plants, its content in soils is known to vary by orders of magnitude within short time spans. Easily reducible and sesquioxide bound manganese also contribute towards Mn availability to plants (Uren 1981).

The data regarding yield and uptake of Mn by maize and wheat crops have already been reported (Behera and Singh 2009). Overall correlations of different fractions of Mn in the pre-maize soil with Mn uptake were insignificant. However, there was direct contribution of CA-Mn ($P = 0.42$) and OM-Mn ($P = 0.99$) towards Mn uptake by maize as obtained from path co-efficient analysis. It was also clear that WS-Mn ($P = 0.38$), CA-Mn ($P = 1.25$), and OM-Mn ($P = 1.27$) contributed directly towards Mn uptake by wheat. This indicated that uptake of Mn by both the crops will be more in a soil having higher amount of Mn associated with carbonates and organic matter. The indirect contribution of other fractions, towards crop uptake of Mn, was also evident from path co-efficient values. Hence, most of the fractions of Mn in soil contributed directly or indirectly towards DTPA extractable Mn as well as Mn uptake by the crops.

SUMMARY

From the investigation it is concluded that DTPA-extractable Mn content in soil did not differ significantly under different treatments. Distribution of various fractions of Mn in soil profile was highly erratic. Residual form was dominant portion of total Mn in all the 4 layers of soil. These fractions kept on changing during the 1-year cropping period. DTPA extractable Mn, both in pre-maize and post-wheat soil, was directly influenced by water-soluble fraction, though contribution of other fractions was also visualized. Uptake of Mn by the component crops was directly influenced by the fractions bound to carbonates and organic matter.

ACKNOWLEDGEMENTS

The first author thanks the Indian Agricultural Research Institute, New Delhi and Council of Scientific and Industrial Research, New Delhi, for providing research facilities and financial assistance, respectively for carrying out the work. The authors also thank the staffs associated with the long-term experiment of the Institute.

REFERENCES

Agbenin J O. 2003. The distribution and transformation of iron and manganese in soil fractions in Savanna Alfisol under continuous cultivation. *Nutrient Cycling in Agroecosystem* **66** (3): 259–70.

Behera S K and Singh D. 2009. Effect of 31 years of continuous cropping and fertilizer use on soil properties and uptake of micronutrients by maize (*Zea mays*)-wheat (*Triticum aestivum*) system. *Indian Journal of Agricultural Sciences* **79** (4): 264–7.

Fageria N K, Baligar V C and Clark R B. 2002. Micronutrients in crop production. *Advances in Agronomy* **77**: 185–250.

Gomez K A and Gomez A A. 1984. *Statistical Procedure for Agricultural Research*, pp 680. Wiley Interstice publication, Singapore.

Kher D. 1993. Effect of continuous liming and cropping on DTPA extractable micronutrients in an Alfisol. *Journal of Indian Society of Soil Science* **41**: 336–77.

Lindsay W L and Norvell W A. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Science Society of America Journal* **42**: 421–48.

Ma Y B and Uren N C. 1995. Application of new fractionation scheme for heavy metals in soils. *Communication in Soil Science and Plant Analysis* **26**: 3291–33.

Miller W P, Martens D C and Zelazny L W 1986. Effect of sequence on extraction of trace metals from soils. *Soil Science Society of America Journal* **50**: 589–601.

Nayyar V K, Takkar P N, Bansal R L, Singh S P, Kaur N P and Sadana U S. 1990. Status of micronutrients in Soils of Punjab. *Research Bulletin,* pp 146. Department of soils, Punjab Agricultural University, Ludhiana.

Randhawa, H S and Singh S P. 1997. Distribution of manganese fractions in alluvium derived soils in different agro climatic zones of Punjab. *Journal of Indian Society of Soil Science* **45**(1): 53–7.

Singh M V. 2009. Effect of trace element deficiencies in soil on human and animal health. *Bulletin of the Indian Society of Soil Science* **27**: 75–101.

Uren N C. 1981. Chemical reduction of an insoluble higher oxide of manganese by plant roots. *Journal of Plant Nutrition* **4**: 65–71.

Zhang M, Alva A K, Li Y C and Calvert D V. 1997. Fractionation of iron, manganese, aluminium and phosphorus in selected sandy soils under citrus production. *Soil Science Society of America Journal* **61**: 794–801.

Zhu B and Alva A K. 1993. Distribution of trace metals in some sandy soils under citrus production. *Soil Science Society of America Journal* **57**: 350–5.