Agropedology 2006, 16 (2), 77-85

Pedogenic distribution of iron and manganese in some Vertisols of Rajasthan

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Abstract: Different forms of iron and manganese and their depth-wise distribution was studied in four Benchmark soil series namely Sanawata (Typic Haplusterts), Bhupalsagar (Calcic Haplusterts), Taswaria (Petrocalcic Haplusterts) and Bhatewar (Sodic Haplusterts) of eastern Rajasthan uplands. The Bhatewar series recorded higher values for total, residual and crystalline fractions of Mn. Similarly Taswaria series had higher values for amorphous, organically bound and complexed Mn fractions, whereas the exchangeable fraction was high in Sanawata series. The Bhupalsagar series contained high values of total, residual and crystalline Fe fractions. The Taswaria series had higher values for complexed and amorphous fractions of Fe. Bhatewar soils had high values of organically bound and exchangeable Fe fractions. The different fractions of Mn and Fe were positively correlated amongst themselves and with the soil properties. Soil properties (silt, clay, organic carbon and $CaCO_3$) along with different fractions of Fe and Mn accounted for 70 and 79, 83 and 82, 95 and 91, 96 and 82 and 85 and 64 per cent variation in exchangeable, complexed, organically bound, amorphous and crystalline forms, respectively. The lower values of exchangeable, complexed, organically bound and amorphous forms of iron and manganese could be attributed to the calcareousness of the soils.

Additional keywords **:** *Micronutrient cations, forms of iron, manganese, Vertisols*

Introduction

The availability of micronutrients is influenced by their distribution within the soil profile and other site characteristic (Singh *et al.* 1989). Micronutrients occur in different forms associated with inorganic and organic components of soil. They are held in the mineral matter and the finer fractions of soil (Miller 1986; Follet and Lindsay 1970). An understanding of the distribution of micronutrients in different fractions is imperative to appreciate their retention in soils and release to plants (Shuman 1979). The relative contribution of the different forms towards the plant available pool varies proportionately and defines the inherent nutrient supplying capacity of soils. Although several investigations have been conducted to evaluate the availability (DTPA - extractable) of iron and manganese in Vertisols (Murthy *et al.* 1997; Jagdish-Prasad and Gajbhiye 1999; Yeresheemi *et al.* 1998; Mali *et al.* 2002; Sharma *et al.* 2006), scanty information is available on the quantitative assessment of forms of iron and manganese in Vertisols of Rajasthan. In view of the above, the present work was undertaken to study the four Benchmark Vertisols in Eastern Rajasthan for their total micronutrient content and the distribution in different fractions of Fe and Mn.

Materials and Methods

Four Benchmark soils namely Sanawata, Bhupalsagar, Taswaria and Bhatewar series (Shyampura *et al.* 2002) developed on dolomitic granite-gneiss with diverse pedogenic manifestation were selected for study. The area lies between $24^0 36'$ to $25^0 37'$ N latitude and $73^0 31'$ to $74^0 04'$E longitude covering the areas of Udaipur, Bhilwara and Chittorgarh districts. The area receives 775 mm of annual precipitation and has a mean annual temperature of 25.6^{0}C. Different fractions of Fe and Mn were determined following the procedure described by Edward Raja and Iyengar (1986). Slight modification for the complexed fraction was introduced by using DTPA-extractant instead of $Cu(OAc)_2$. Fe and Mn fractions were estimated by atomic absorption spectrophotometer. The step-wise regression equations were obtained for all the soil properties and the different fractions of Fe and Mn individually and in combination.

Results and Discussion

Relevant soil properties are reported in table 1. The exchangeable, complexed, organically bound, amorphous, crystalline, residual and total Fe and Mn were evaluated (Table 2 and 3). The most significant pedo-transfer functions for all the forms of Fe and Mn are presented in table 4.

Table 1. Physical and chemical properties of soils

Depth (cm)	Horizon	Sand	Silt	Clay	pH	Org.C	$CaCO_3$	CEC	Exch. Na	ESP
		%				%		cmol(p+)kg^{-1}		
					Sanawata -Typic Haplusterts					
0-22	Ap	29.3	24.5	48.2	7.8	0.78	0.9	39.6	0.30	0.7
22-58	Bw	25.7	26.1	48.2	8.0	0.50	2.3	43.2	0.30	2.0
58-86	Bss1	27.3	26.3	46.4	8.2	0.28	2.7	40.9	1.14	2.8
86-104	Bss2	30.3	26.8	42.9	8.2	0.35	2.4	42.8	0.93	2.2
104-135	Bss3	31.9	27.0	41.1	8.3	0.35	3.4	42.5	0.94	2.2
					Bhupalsagar - Calcic Haplusterts					
0-24	Ap	22.7	22.9	54.4	8.5	0.83	3.7	40.6	5.2	13.0
24-50	Bss1	18.5	22.7	58.8	8.5	0.20	4.2	52.2	9.3	17.9
50-70	Bss2	19.2	25.6	55.2	8.8	0.26	11.2	51.5	10.2	19.1
70-100	2Ck	45.9	16.6	37.7	9.0	0.11	27.0	22.4	6.7	29.4
100-115	C	69.9	14.3	15.8	9.1	0.07	6.1	13.9	5.2	37.0
					Taswaria - Petrocalcic Haplusterts					
0-19	Ap	41.4	16.1	42.5	7.7	0.57	1.0	32.6	0.28	0.9
19-34	Bss1	34.5	20.9	44.6	7.7	0.44	1.0	38.6	0.38	1.0
34-56	Bss2	33.8	14.6	51.6	8.3	0.38	1.0	47.5	0.16	1.0
56-75	Ck1	36.9	17.3	45.9	8.6	0.42	26.6	52.8	0.46	0.9
75-100	Ck2	59.9	14.8	54.3	8.7	0.27	58.9	38.9	0.56	1.4
100-125	Ck3	52.3	14.3	33.4	8.8	0.21	66.1	28.6	0.49	1.7
					Bhatewar - Sodic Haplusterts					
0-21	Ap	33.4	23.8	42.8	8.8	0.78	2.3	37.2	5.9	15.9
21-45	Bw	28.5	24.6	46.9	8.7	0.45	2.6	48.8	8.6	21.1
45-68	Bss1	22.6	26.2	51.2	9.2	0.48	2.4	44.9	10.7	24.1
68-85	Bss2	18.1	27.3	54.6	9.3	0.49	2.8	48.2	11.9	35.1
85-100	BC	21.5	25.3	53.2	8.9	0.36	6.7	48.6	7.9	36.8
100-130	Ck	54.6	17.6	27.8	8.6	0.25	27.0	25.2	10.6	42.1

Table 2. Iron fractions in soils

Horizon	Exch.	Complex DTPA	Organic bound	Amorphous	Crystalline	Residual	Total
	mg kg^{-1}						
			Sanawata - Typic Haplusterts				
Ap	0.59	12.36	635.6	987.4	254.2	22034.9	23925
Bw	0.57	12.24	634.0	1012.7	252.1	21428.4	23340
Bss1	0.50	11.66	850.4	1038.0	195.8	22975.6	25072
Bss2	0.52	10.57	776.4	1034.0	172.9	23930.6	25925
Bss3	0.52	11.01	802.1	1132.7	170.1	22963.6	25080
			Bhupalsagar - Calcic Haplusterts				
Ap	0.28	30.5	982.8	1076.0	670.0	26925.4	29685
Bss1	0.14	9.46	1076.0	1110.0	170.3	26029.1	28395
Bss2	0.14	11.00	1069.0	1203.0	264.3	25537.5	28085
2Ck	0.11	5.58	672.1	1632.0	17.6	20757.6	23085
C	0.07	4.47	458.0	1092.1	30.4	29394.9	30980
			Taswaria - Petrocalcic Haplusterts				
Ap	0.68	14.08	464.5	974.7	131.1	24034.9	25620
Bss1	0.69	15.93	358.5	1002.1	136.5	25471.3	26985
Bss2	0.42	14.57	309.6	1014.7	176.1	26494.6	28010
Ck1	0.34	11.63	342.2	1588.7	85.2	21007.0	23035
Ck2	0.27	6.50	220.0	1721.0	38.6	18988.6	20975
			Bhatewar - Sodic Haplusterts				
Ap	0.76	10.15	721.6	1113.98	206.3	18442.2	20495
Bw	0.76	10.81	974.0	1101.32	249.5	24063.6	26400
Bss1	0.67	11.47	1215.0	1164.61	132.4	23935.9	26460
Bss2	0.64	10.87	1224.0	1177.27	86.7	23850.5	26350
BC	0.46	10.54	1089.0	1226.63	64.8	24193.6	26585
Ck	0.47	10.48	779.4	1688.66	150.0	23141.0	25770

Exchangeable Fe and Mn

The mean values for exchangeable Fe (Ex-Fe) fraction ranged from 0.15 to 0.63 mg kg^{-1} in different pedons. The Ex-Fe fraction had higher value in Sodic Haplusterts followed by Typic Haplusterts and least in Calcic Haplusterts. The per cent contribution of this fraction towards the total Fe pool ranged between 0.001 to 0.002, the least being in the Calcic Haplusterts. Ex-Fe is weakly correlated with silt, clay $CaCO_3$ content and organic carbon. Within the different fractions, it did not show significant correlation. Thus values suggest poor adsorption capacity for this fraction by finer fractions in the soil (Sharma *et al.* 2000). The analysis of pedo-transfer functions (Table 4) showed that silt, clay and organic carbon contributed 48 per cent. The silt, clay and organic carbon together with complexed, organically bound, amorphous and crystalline forms caused 70 per cent variation in exchangeable Fe content.

The mean values for exchangeable Mn (Ex-Mn) fraction ranged from 0.22 to 4.80 mg kg^{-1} and contributed 0.05 to 1.42 per cent to the total Mn pool. The Typic

Table 3. Manganese fractions in soils

Horizon	Exch.	Complex DTPA	Organic bound	Amorphous	Crystalline	Residual	Total
	mg/kg^{-1}						
			Sanawata - Typic Haplusterts				
Ap	3.83	21.09	27.28	56.60	64.84	303.86	477.5
Bw	4.12	19.87	26.24	55.13	69.90	222.24	397.5
Bss1	4.26	16.13	17.80	51.52	41.64	196.65	327.0
Bss2	5.93	12.34	15.00	49.20	52.92	189.11	324.5
Bss3	5.87	11.96	14.95	48.76	51.97	138.99	272.5
			Bhupalsagar - Calcic Haplusterts				
Ap	1.84	26.43	37.40	45.68	40.80	608.85	761.0
Bss1	0.05	25.60	38.00	44.26	22.90	376.69	507.5
Bss2	0.04	24.15	24.10	46.24	58.30	292.67	445.5
2Ck	0.03	14.15	8.60	41.45	32.40	447.37	544.0
C	0.03	13.50	7.20	13.76	23.80	475.71	534.0
			Taswaria - Petrocalcic Haplusterts				
Ap	0.22	29.92	87.20	67.36	65.88	239.92	490.5
Bss1	0.28	32.25	92.70	75.00	66.12	248.65	515.0
Bss2	0.32	29.08	78.90	78.16	75.68	251.86	514.0
Ck1	0.08	17.72	50.80	75.08	34.24	233.08	411.0
Ck2	0.20	5.29	11.30	22.00	7.44	182.77	229.0
			Bhatewar - Sodic Haplusterts				
Ap	0.83	21.27	43.80	38.16	120.5	335.94	560.5
Bw	0.74	20.56	29.90	29.32	114.9	482.08	677.5
Bss1	0.75	19.26	24.50	11.74	127.6	463.65	647.5
Bss2	0.85	16.20	13.90	9.40	84.9	516.25	641.5
BC	0.72	11.21	7.00	15.58	37.6	483.89	556.0
Ck	0.78	8.99	5.40	13.16	35.4	399.27	463.0

Haplusterts had higher values and Petrocalcic Haplusterts had the least values. It was significantly correlated with silt and had inconspicuous correlation with other soil properties and different forms also. This fraction had lower values than that reported by other worker (Joshi *et al.* 1981). The reason is low organic matter in the Typic Haplusterts, thus lacking sufficient electrostatic forces needed for chelating this fraction (Randhawa and Singh 1997). The dominant contributor for this fraction is the combined pool along with soil properties, followed by different forms and soil properties alone being 79, 53 and 43 per cent, respectively (Table 4).

Complexed Fe and Mn

The mean values for DTPA-extractable Fe ranged from 10.70 to 12.54 mg kg^{-1} and contributed 0.04 to 0.05 per cent towards the total Fe content in the soil. The Petrocalcic and Calcic Hapusterts had higher values for this fraction and the least was observed in Sodic Haplusterts. This might be attributed to the higher pH of Sodic Haplusterts leading

Table 4. Pedo-transfer functions for different forms of iron and manganese

Forms	Regression equation	r2
	Iron	
Exchangeable	0.066+0.017A-0.005B+0.619C	0.48
	0.758+0.021F+0.001G-0.004H+0.001I	0.23
	-0.015+0.025A-0.005B+0.80C+0.017F+0.0001 G-0.0001H-0.001I	0.70
Complexed	4.145-0.18A+0.109B+15.805C	0.49
	5.688+3.033E-0.002G+0.0003H+0.033I	0.78
	6.417-0.227A+0.072B+5.275C+0.028I	0.81
	9.12-0.40A+0.09B+0.55C+5.04E+0.001G-0.001H+0.03I	0.83
Organically bound	-348.56+47.25A+3.50B-238.0C	0.55
	838.0+171.62E-31.13F-0.066H+1.567I	0.15
	-682.8+56.02A+0.47B-246.0C-211.3E+8.4F+0.2H+0.23I	0.62
	-248.3+38.38A+0.54B-60.62C+45.95D-188.42E+14.22F-0.10H-0.17I	0.95
Amorphous	1051.93+15.297M	0.82
	1079.36-0.97L+15.83M	0.83
	3164.33-16.77A-23.17B-22.79L+24.30M	0.96
	1506.7-417.4E+2.28F-0.03G-0.70I	0.30
	3090-24.3A-22.2B+79.4C-21.8L+24.2M+102.0E+0.53F+0.16G-0.24I	0.99
Crystalline	-82.23+1.70A+1.37B+381.16C	0.41
	-96.48+23.11F	0.75
	-21.31-89.9E+22.1F+0.08G-0.07H	0.79
	-104.4+8.05A-1.98B+225.0C-242.7E+19.1F+0.02G-0.02H	0.85
	Manganese	
Exchangeable	-2.165+0.289A-0.067B+1.099C	0.43
	-0.462-0.069F+0.074G+0.097H+0.025I	0.53
	-2.678+0.313A-0.067B+2.74C-0.129F-0.014G+0.065H-0.009I	0.79
Complexed	12.69-0.414A+0.201B+14.617C	0.27
	8.393-0.476E+0.165G+0.071H+0.05I	0.76
	11.413+0.236G	0.72
	2.389+0.295A+0.038B+1.265C+0.246G	0.78
	-1.751+0.677A-0.063B+4.634C-1.475E+0.179G+0.089H-0.006I	0.82
Organically bound	41.95-2.89A+0.663B+54.37C	0.36
	-23.50-3.90E+1.25F+0.70H+0.133I	0.86
	-1.43-1.52A+0.093B+6.40C-1.39E+1.50F+0.54H+0.18I	0.88
	-0.425-1.46A+0.55B+13.23C+2.167F+0.357H	0.86
	0.39-0.25A+0.011B-0.71C-2.44D-4.31E+1.195F+0.21H+0.158I	0.91
Amorphous	41.67-1.49A+0.48B+26.52C	0.15
	67.7-2.68A+0.78B+9.89C-0.72M	0.28
	16.47+4.98E+0.52F+0.68G-0.22I	0.85
	25.77-1.88A+0.49B-22.52C+7.7E+0.89F+0.51G	0.81
	21.37-1.10A+0.33B-14.65C+6.67E+0.798F+0.56G-0.12I	0.82
Crystalline	-5.87+2.54A-0.48B+75.48C	0.39
	34.69+8.32E+2.41F+0.83G-1.43H	0.43
	-24.60+5.30A-1.01B+52.0C-4.21E-0.26F+0.85G-0.55H	0.64

A=silt per cent, B= clay per cent, C=organic carbon per cent, D=exch. Na, E=exchangeable, F=complexed, G=organically, H=amorphous, I=crystalline, L=sand and M= $CaCO_3$

to the formation of insoluble hydroxides due to oxidation of divalent cations to higher valent forms which are relatively less soluble. These values were significantly correlated with clay (r=0.37) and organic carbon (r=0.67). Similar relationship with clay and organic carbon was also reported (Yelvikar *et al.* 1996; Sharma *et al.* 2006). Among the different forms, it is correlated significantly with crystalline form (r=0.86) but other forms did not show any strong correlation. Silt, clay and organic carbon along with exchangeable, organically bound, amorphous and crystalline forms could explain 83 per cent variation towards complexed Fe, whereas, these soil factors contributed 49 per cent. Different forms in the pool contributed 78 per cent towards complexed Fe indicating their dynamic participation.

The mean values for complexed Mn fraction ranged from 16.08 to 22.85 mg kg^{-1} in the pedons. The Petrocalcic Haplusterts had higher value and the least being in Typic Haplusterts. This fraction contributed 2.71 to 4.93 per cent to the total Mn pool. It was significantly correlated with organic carbon (r=0.42) and clay (r=0.30) but inversely correlated with $CaCO_3$ (r=-0.52). Within different forms, this fraction was significantly correlated with all the forms (r = 0.36 to 0.82) except residual Mn (r= 0.09) indicating dynamic equilibrium among different fractions. The DTPA-extractable Mn fraction in these Vertisols is lower than the Inceptisols of Maharashtra as reported by Nipunage *et al.* (1996) and well in agreement to the values reported by Chattopadhyay *et al.* (1996).The regression analysis depicts 78, 76 and 72 per cent contribution towards this fraction by organically bound, different forms and organically bound alone, respectively.

Organically bound Fe and Mn

The mean values ranged between 338.96 to 1000.50 mg kg^{-1} and its share towards total Fe was 1.36 to 4.01 per cent. The higher values were recorded for the Sodic Haplusterts and least for Petrocalcic Haplusterts. Significant correlation was recorded with pH (r=0.46), silt (r=0.74) and clay (r=0.33) and within the forms with crystalline and total Fe fractions. Effectiveness of organic ligand complexes increases with increase in pH causing enhanced dispersion and ionization of surface ligands (Stevenson 1991). This might be the key factor for higher values in Sodic Haplusterts. The contribution by soil parameters and forms towards this fraction accounted to 95 per cent, whereas soil parameters alone explained 55 per cent variation.

The mean values for organically bound Mn (OB-Mn) fraction ranged between 20.25 to 64.18 mg kg^{-1} and contributed 3.43 to 13.68 per cent to the total Mn pool. The Petrocalcic Haplusterts contained high amount of OB-Mn and the Typic Haplusterts the least. The correlation studies showed significant correlation with clay (r=0.20) and organic carbon (r=0.37) and within the different forms, it was significantly correlated with complexed (r=0.82), amorphous (r=0.57) and crystalline (r=0.36). This corroborated the findings of Randhawa and Singh (1997). The soil parameters alone accounted for 36 per cent and soil properties in association with other forms contributed the major share (91per cent) towards organically bound manganese.

Amorphous Fe and Mn

The mean values for amorphous Fe (Am-Fe) fraction ranged between 1040.97 to 1260.24 mg kg^{-1} in the soils and it contributed optimally between 4.22 to 5.25 per cent to the total Fe content in the soils. The Petrocalcic Haplusterts had the higher Am-Fe content and the least in the Typic Haplusterts. Presence of high calcium carbonate and pH might have favoured the precipitation or oxidation of iron oxides. It was significantly correlated with sand (r=0.48), pH (r=0.44) and $CaCO_3$ (r=0.91) and inversely with different forms of Fe. Silt and clay together with sand and $CaCO_3$ contributed 96 per cent out of which sand fraction along with $CaCO_3$ contributed 83 per cent whereas $CaCO_3$ alone accounted for 82 per cent attributing the strong association of this fraction with solid phase of carbonates (Yerriswamy *et al.* 1995).

The mean amorphous Mn (Am-Mn) content ranged from 19.56 to 63.52 mg kg^{-1} with the highest value in Petrocalcic and least in Sodic Haplusterts. It contributed

3.34 to 14.91 per cent to the total Mn pool. It was moderately correlated with clay and organic carbon. Within the forms, it was significantly correlated with complexed (r=0.57) and organically bound (r=0.75) forms of Mn. Silt, clay and organic carbon contributed 15 per cent and the different fractions explained 85 per cent variation. Inclusion of $CaCO_3$ in the regression equation along with soil properties increased the predictability by 28 per cent and ascribed to the existence of this form as chemisorbed/co-precipitated with carbonates and related carbonate minerals (Warden and Reisenauer 1991).

Crystalline Fe and Mn

The mean values for crystalline Fe (Cry-Fe) ranged between 113.5 to 230.5 mg kg^{-1} and contributed 0.44 to 0.85 per cent to the total values. The highest value was in Calcic Haplusterts and least in Petrocalcic Haplusterts. The correlation studies showed significant values for silt (r=0.34), clay (r=0.31), organic carbon (r=0.63), complexed (r=0.86) and organically bound (r=0.28) and inversely correlated with other forms. The soil parameters and different forms accounted for 85 per cent; the different forms alone explained 79 per cent contribution and the participation of complexed fraction was of 75 per cent.

The mean values for crystalline Mn ranged between 35.64 to 86.82 mg kg^{-1} and it contributed 6.67 to 15.86 per cent to the total Mn pool. The highest values were for Sodic and least for Calcic Haplusterts. The correlation studies showed significant correlation with silt (r=0.43), organic carbon (r=0.53), complexed (r=0.36), organically bound (r=0.28) and total Mn (r=0.47) The major (64 per cent) contribution was by the combined effect of soil properties and different Mn fractions.

Residual Fe and Mn

The residual Fe contributed maximum to the total Fe pool which is a storage bean for successive release of iron depending upon the behaviour of the soil solution. The mean ranged between 2266 to 25728 mg kg^{-1} and contributed 90.59 to 92.90 per cent towards total Fe in these pedons. The maximum residual Fe fraction was stored into the Calcic Haplusterts and least in the Typic Haplusterts. This was moderately correlated with exchangeable, complexed and crystalline forms whereas more significantly with total Fe content (r=0.67). The residual Fe was inversely correlated with amorphous Fe (r=-0.36) which indicated that the bulk of Fe was held within silicate mineral lattice.

The residual Mn values was in the mean range of 21017 to 446.85 mg kg^{-1} and contributed 56.54 to 78.25 per cent to the total Mn content. The higher values of this fraction was obtained in Sodic followed by Calcic and the least in Typic Haplusterts, again being favoured by the pH of the soil solution which also showed significant values (r=0.62). Among the fractions, it was significantly correlated with total (r=0.88) but inversely with exchangeable (r= -0.46), organically bound (r= -0.27) and amorphous fractions (r=-0.59).

Total Fe and Mn

The total Fe values had mean range of 24668.4 to 28046.0 mg kg^{-1}. The higher values were registered by the Calcic Haplusterts and least in the Typic Haplusterts. It showed strong significant correlation with residual fraction (r=0.67) and weak correlation with exchangeable, organically bound, complexed and crystalline fractions. It did not refer to any significant correlation with the soil properties.

The total Mn content had mean range values of 359.8 to 591.0 mg kg^{-1}. The higher values were observed in the Sodic and least in the Typic Haplusterts. It had significant correlation with organic carbon (r=0.38) and pH (r=0.37) and weakly correlated with silt and clay. Amongst the different Mn fractions, it showed significant and strong correlation with complexed (r=0.48), crystalline (r=0.47) and residual Mn fractions (r=0.88). Though the values of total Fe and Mn were lower than the Vertisols developed on basaltic parent material as observed by Sharma *et al.* (2006)

It may be summarized that these fractions are of importance in assessing the micronutrient supplying capacity of Vertisols which alter the variation (15-86 per cent) of these nutrients among the available pools. The available pool of micronutrients is higher in the Typic Haplusterts followed by Petrocalcic, Calcic and Sodic Haplusterts because of the slightly alkaline pH range and relatively high organic carbon content in the Typic Haplusterts. This may be the result of higher exchangeability in this soil as compared to the Calcic and Petrocalcic having higher pH and the masking/overriding effect of sodium in Sodic Haplusterts. As observed from the regression studies of the pedo-transfer functions, the results of soil properties together with different forms collectively contribute more significantly to the various pools of Fe and Mn in these soils and justify that the Fe and Mn content in the soil pedon is a collective phenomenon rather than being considered in isolation.

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Received : April, 2006; Accepted : December, 2006