Influence of calcium on distribution of different forms of iron in Vertisols

RESHMI SARKAR[2], B. BASAVARAJ[1] AND SANDIPTA KAR[2]

[1] *Department of Soil Science and Agricultural Chemistry, University of Agricultural Sciences, Dharwad, 580 005, India*

[2] *Department of Agricultural and Food Engineering, Indian Institute of Technology, Kharagpur, 721302, India*

Abstract : Depth-wise distribution of free $CaCO_3$, water soluble Ca, exchangeable Ca, Fe oxides, water soluble Fe, DTPA-Fe and bicarbonate ions in different profiles from Dharwad, Hebballi and Hebsur of North Karnataka was studied. Free $CaCO_3$, exchangeable Ca and water soluble Ca were found in maximum concentration at 60-100 cm depth in all the three profiles, which consequently increased the concentration of bicarbonate ion in subsurface soils than in surface soils. DTPA-Fe and water soluble Fe was concentrated in the surface layers and was in reduced concentration at deeper soil layers, whereas, both the Fe oxides were accumulated in the subsurface layers. Correlation study indicated a positive significant correlation of water soluble Ca and exchangeable Ca with $CaCO_3$. A positive significant correlation was found between oxalate extractable iron and CBD extractable iron oxide. The forms of Ca, free $CaCO_3$ and bicarbonate ion did not show any negative effect on presence of the Fe oxides. However, DTPA-Fe and water soluble Fe showed negative correlation with bicarbonate ion.

Additional Key Words : *Water soluble Ca and Fe, calcareous soil, free $CaCO_3$, DTPA-Fe, bicarbonate ion, distribution of Fe-oxides.*

Introduction

Iron is not readily available to plants mainly due to high soil pH, calcareousness, low organic matter content and erosion (Hansen *et al.* 2003). Vertisols of southern India are high in soil pH and calcareous, which results in iron deficiency in these soils. High calcium carbonate in Vertisols leads to high concentration of bicarbonate ions in soil and this interferes with iron uptake by plants (White and Robson 1989). Different soil processes viz. calcification, translocation and hydrolysis of lime, coating, precipitation and crystallization of iron oxides and hydroxylation and chelation of iron are mainly responsible for movement, solubility and availability of calcium and iron in calcareous soil. Through the present study an attempt has been made to assess the depth-wise distribution of different forms of iron, calcium and bicarbonate ion in calcareous soils of North Karnataka and their relationships among themselves.

Materials and Methods

Soil samples were collected at 4 depths viz. 0-15, 15-30, 30-60 and 60-100 cm from profiles of Dharwad and Hebballi (Typic Calciusterts) and Hebsur (Typic Pellusterts) in North Karnataka.

The soil samples were air-dried, ground and passed through 2 mm sieve and used for analysis. Soil pH and electrical conductivity were determined in 1: 2.5 (soil : water) suspension using pH meter and conductivity meter respectively (Jackson 1967). Organic carbon was estimated by Wakley and Black wet oxidation method (Jackson 1967). The ammonium acetate pH 7.0 method was used to determine the CEC of soils (Chapman 1965). Free calcium carbonate was determined by acid dilution method (Piper 1966). Exchangeable Calcium was extracted with KCl-TEA buffer solution and estimated by Versenate method (Jackson 1967). Water soluble calcium was extracted with double distilled

water in 1 : 1 (soil : water) suspension and determined by Versenate method (Black 1965). Carbonate and bicarbonate was estimated by titration of soil extract (1 : 2.5, soil : water) as per method described by Jackson (1967). Oxalate extractable iron oxide was extracted by oxalate reagent (Miller *et. al.* 1986) and citrate bicarbonate dithionite (CBD) method was followed to extract free iron oxide (Mehra and Jackson 1960). Soil and double distilled water in a ratio of 1 : 40 were shaken for 16 hours to extract water soluble Fe (Miller *et. al.* 1986). The method developed by Lindsay and Norvell (1978) was followed to determine the DTPA extractable iron. Both the Fe oxides, water soluble Fe and DTPA-Fe were estimated by atomic absorption spectrophotometer. MSTAT-C software was used for correlation analysis.

Results and Discussion

The important physical and chemical properties of soils have been presented in Table 1. The concentration of free $CaCO_3$ and bicarbonate ion increased with depth in Hebballi pedon but no definite trend was found in other pedons (Table 2). The higher concentration of free $CaCO_3$ in 60-100 cm layer might be due to deposition of $CaCO_3$ through the process of downward movement and it was also associated with higher concentration of bicarbonate ion in presence of more moisture. Rao *et al.* (1993) also found a positive correlation (r = 0.96) between soil water and

concentration of HCO_3^- ions. No definite trend in distribution of WS-Ca (water soluble Ca) was found in these pedons, whereas, Ex-Ca (exchangeable Ca) increased with depth in these pedons. The presence of more Ex-Ca in subsurface layers might be attributed to higher clay content (r = 0.74**). Similar findings were also reported by Mengel and Kirkby (1996). The concentration of Ex-Ca, WS-Ca and free $CaCO_3$ were high in 60-90 cm layer of these pedons.

The depth-wise distribution of DTPA-Fe indicated that DTPA-Fe decreased with depth of soil at Hebballi, whereas it did not follow any definite trend in other profiles. The higher concentration of DTPA-Fe in surface layer than subsurface ones was mainly due to higher content of organic matter in the surface layer (Katyal and Sharma 1991).

The concentration of WS-Fe (water soluble Fe) was relatively low in subsurface layers than the surface ones (Table 2) which might be due to the presence of more clay and less organic matters in the subsurface layer. Yerriswamy *et al.* (1995) also found highly significant negative correlation between WS-Fe and clay and positive correlation with organic matter.

The concentration of oxalate extractable Fe oxide (Fe_o) increased with depth in these pedons (Table 2). Park and Burt (1999) also reported positive correlation between Fe_o and depth of soils. There was no definite trend of distribution for CBD-extractable Fe oxide (Fe_c) at Hebballi and Hebsur pedons, but

Table 1. Physical and chemical properties of soils

	Depth (cm)	pH	E.C. (dSm⁻¹)	O.C. (%)	Clay content (%)	sCEC (cmol kg⁻¹)
Dharwad	0-15	6.70	0.43	0.6	29.6	37.2
	15-30	7.19	0.54	0.51	34.2	39.6
	30-60	7.69	0.62	0.48	35.8	41.1
	60-100	7.33	0.55	0.36	38.7	44.5
Hebballi	0-15	7.72	0.56	0.6	65.0	39.5
	15-30	7.87	0.50	0.57	69.1	40.1
	30-60	7.83	0.68	0.51	71.1	41.5
	60-100	7.01	0.72	0.45	75.2	44.7
Hebsur	0-15	8.96	0.68	0.6	62.8	43.5
	15-30	8.96	0.65	0.54	66.1	44.2
	30-60	8.84	0.66	0.48	68.2	48.4
	60-100	8.78	0.66	0.39	70.0	51.8

Table 2. Distribution of free CaCO₃, bicarbonate ions and exchangeable-, water soluble- and oxide forms of calcium and iron

	Depth (cm)	Free $CaCO_3$ (%)	Bicarbonate in solution (mg kg⁻¹)	Exchangeable Ca (cmol kg⁻¹)	Water Soluble Ca (mg kg⁻¹)	DTPA-Fe (mg kg⁻¹)	Water Soluble Fe (mg kg⁻¹)	Fe_o Oxide* (mg kg⁻¹)	Fe_c Oxide** (mg kg⁻¹)
Dharwad	0-15	4	152.5	24.6	226.7	5.2	0.76	1095.8	175.6
	15-30	2	305	27	266.7	2.67	0.68	1157.8	177
	30-60	2	305	27.6	260	1.75	0.68	1188.2	179.4
	60-100	9	305	28.4	400	2.12	0.44	1434	210.6
Hebballi	0-15	2	457.5	39	70	1.64	0.48	789.8	191.8
	15-30	3	610	39	40	1.06	0.44	907	153.6
	30-60	3.5	610	39.2	60	1.03	0.46	914.8	209.2
	60-100	5.5	762.5	45.8	150	0.3	0.46	1072.8	319
Hebsur	0-15	16.5	305	28.2	90	2.35	0.36	479.6	99.7
	15-30	13.5	762	26.6	50	0.45	0.22	344.2	76.1
	30-60	13	762	30.6	40	0.49	0.26	678.4	98.3
	60-100	17.5	610	42.6	120	1.02	0.24	1222	122.7

* Fe_o Oxide = Oxalate extracted Fe oxide; ** Fe_C Oxide = CBD extractable Fe oxide

Table 3. Coefficients of correlation among free CaCO₃, HCO₃⁻ and different forms of Ca and Fe in different pedons

	Free $CaCO_3$ (%)	Exchangeable Ca (c.mol kg⁻¹)	Water Soluble Ca (mg kg⁻¹)	HCO_3^- in solution (mg kg⁻¹)	Oxalate extracted Fe oxide (mg kg⁻¹)	CBD extracted Fe oxide (mg kg⁻¹)	Water Soluble Fe (mg kg⁻¹)
Exchangeable Ca (c.mol kg⁻¹)	-0.05						
Water Soluble Ca (mg kg⁻¹)	-0.25	-0.42					
HCO_3^- in solution (mg kg⁻¹)	0.30	0.58**	-0.67*				
Oxalate extracted Fe oxide (mg kg⁻¹)	-0.37	0.14	0.77**	-0.41			
CBD extracted Fe oxide (mg kg⁻¹)	-0.61**	0.48	0.38	-0.05	0.58*		
Water Soluble Fe (mg kg⁻¹)	-0.79**	-0.32	0.56	-0.73**	0.51	0.47	
DTPA-Fe (mg kg⁻¹)	-0.27	-0.57	0.50	-0.89**	0.29	0.01	0.72**

it increased with depth at Dharwad. The amount of Fe_c oxide was more at 60 - 100 cm depth in all the pedons. This might be due to increase in accumulation of precipitated iron oxide in deeper soil layer, which crystallized to CBD extractable iron oxide in the later stages (Thakur *et al*. 1995). The depth-wise distribution of Fe_o and Fe_c indicated that these were present in more concentration at deeper layer (60-90 cm).

The correlation of different forms of Ca and HCO_3^- ion indicated that free $CaCO_3$ was positively correlated with WS-Ca and Ex-Ca in these pedons. However, the relationship between free $CaCO_3$ with HCO_3^- ion was stronger in Hebballi and Hebsur than in Dharwad. The combined correlation of different forms of Ca and HCO_3^- ion in these pedons indicated positive and negative relationships of HCO_3^- ion respectively with Ex-Ca and WS-Ca (Table 3). The Fe_o and Fe_c were positively correlated between themselves and also with WS-Ca, EX-Ca and Free $CaCO_3$ in these pedons. Barbara *et al*. (2000) also reported highly significant positive correlation between Fe_o and Fe_c oxide. However, combined correlation indicated positive correlation of Fe_o with WS-Ca and negative correlation of Fe_c with free $CaCO_3$. There were no significant relationships of WS-Fe with free $CaCO_3$, Ex-Ca and WS-Ca in Hebballi and Hebsur but strongly negative correlation of WS-Fe with all the forms of Ca was found in the profile of Dharwad. This might be due to the presence of WS-Fe in minute fraction mostly in the highly calcareous soils (Yerriswamy *et al*. 1995). DTPA-Fe was negatively correlated with Ex-Ca. Both WS-Fe and DTPA-Fe were present in minimum concentration at 60-90 cm depth, whereas HCO_3^- ion was in highest concentration. There was highly significant negative correlation of WS-Fe and DTPA-Fe with HCO_3^- ion in all the pedons, which clearly demonstrated the prominent effect of HCO_3^- ion in reducing the concentration of available forms of Fe in calcareous soils.

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