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Degree of Soil Development in Some Alfisols of Subtropical India with Special Reference to the Nature and Distribution of Fe and Al*

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Abstract: Different extractants were used to determine various forms of Fe and Al in three soil profiles from different parts of West Bengal, India. The mean contents of Fe and Al extracted by different extracting reagents were found to be in descending order as follows $Al_{dith} > Al_{oxa} > Al_{pyr}$ and $Fe_{dith} > Fe_{oxa} > Fe_{pyr}$. Analysis of pyrophosphate, oxalate and dithionate extractable Fe and Al showed that with increasing soil age, the crystalline Fe and Al oxides increased at the expense of the poorly crystalline form. The mean content of amorphous Fe and Al, crystalline Fe and Al and their ratio values estimated the degree of soil development and were found to be in the following descending order Matimahal > Anandapur > Mirgindih > Kasipur. Correlation between different forms of Fe and Al and selected soil properties were examined. Multiple regression equations were formulated to show the interrelationship among different soil properties and different forms of Fe and Al.

Key words: Pedogenic process, soil, forms of Fe, forms of Al

Introduction

Distribution of different forms of iron and aluminum in soil is important in order to understand Fe and Al chemistry, physicochemical properties and the soil forming process. Profile distribution of different forms of Fe and Al oxides particularly dithionite and oxalate extractable Fe and Al serve as useful indicators to identify the horizon of accumulation of secondary oxides (Bera *et al*., 2005) and depth of argillic horizon (Dolui and Chakraborty, 1998; Dolui and Chattopadhyay, 1997). The Fe and Al are released during the weathering of Fe and Al bearing parent materials. They are re-precipitated in the soils as oxides or hydroxide and oxyhydroxide of iron and aluminium. The quantity of these alternation products generally increased with soil age (Dolui and Bera, 2001). The amount and distribution of extractable Fe and Al oxides in soil profiles indicate the stage and degree of soil development (Mahaney and Fahey, 1988). However, very meager information is available on the degree of soil development and the direction of pedogenic processes in the alfisols developed under subtropical environment in India. The present study is intended to investigate the different forms of Fe and Al and the interrelationship among themselves as well as with some important soil characteristics in relation to pedogenic processes in some alfisols of West Bengal, India.

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Materials and Methods

Four soil profiles belonging to Alfisols (Anandapur, Kasipur, Matimahal and Mirgindih) in West Bengal, India were selected for the present investigation. The study was undertaken in NBSS and LUP in 2004. The profiles were classified according to Soil Survey Staff (1998). The Anandapur series belongs to fine, mixed, hyperthermic Ultic Paleustalfs, Kasipur series to fine loamy, mixed hyperthermic Typic Haplustalfs, Matimahal series to fine, mixed, hyperthermic Typic Paleustalfs and Mirgindih series to fine loamy, mixed, hyperthermic Ultic Paleustalfs. Soils of each horizon were processed (<2 mm) and used for analysis. The physicochemical properties of the soils were determined by the standard methods (Jackson, 1973) and are presented in Table 1. Fraction of Fe and Al were determined in the soil by separate extractions with (i) sodium pyrophosphate, overnight extraction at pH 10 (Agriculture Canada, 1984); (ii) acid ammonium oxalate (0.2), four hour extraction at pH 3 (Agriculture Canada, 1984); (iii) dicarbonate-citrate-bicarbonate, 20 min extraction twice (CSSC Subcommittee on Methods of Analysis, 1978). Fe and Al in the extract was determined colorimetrically using Orthophenanthroline and 'Alizarin red S' reagent, respectively by Chen and He (1985) and Parker and Goddard (1950).

Table 1: Physico-chemical properties of the soils

Depth (cm)	pH (1:2.5) H_2O	pH (1:2.5) KCl	Specific conductance (1:5) (dS m^{-1})	Organic carbon (g kg^{-1})	Particle size distribution (g kg^{-1}) Sand	Silt	Clay	Texture	CEC cmol (p+) kg^{-1}
Pedon A: Anandapur Series: Fine, mixed, hyperthermic Ultic Paleustalfs									
Ap 0-10	5.25	4.24	0.14	5.39	263	493	244	l	4.9
BA 10-26	5.42	4.40	0.10	2.36	220	528	252	sil	5.2
Bt1 26-51	5.71	4.72	0.06	1.01	315	232	453	c	9.4
Bt2 51-89	6.20	5.12	0.04	0.60	294	241	465	c	10.2
Bt3 89-120	5.94	4.92	0.04	0.60	283	262	455	c	9.8
Mean	5.70	4.68	0.08	1.99	275	351	374	cl	7.9
Pedon B: Kasipur Series: Fine loamy, mixed, hyperthermic Typic Haplustalfs									
Ap 0-14	5.83	4.84	0.04	2.16	728	152	120	sl	4.7
Bt1 14-51	6.32	5.28	0.04	1.08	541	243	216	scl	6.7
Bt2 51-87	6.36	5.33	0.02	0.46	477	227	296	scl	8.4
Bt3 87-141	6.51	5.50	0.01	0.41	471	221	308	scl	8.4
Bt L_1 141-150	6.74	5.72	0.01	0.30	481	232	287	scl	8.2
Mean	6.35	5.33	0.02	0.88	540	215	245	scl	7.3
Pedon C: Matimahal Series: Fine, mixed, hyperthermic Typic Paleustalfs									
Ap 0-11	5.70	4.68	0.04	2.30	286	492	231	l	4.8
BA 11-26	6.00	5.92	0.03	1.60	329	284	387	cl	7.5
Bt1 26-52	6.42	5.44	0.03	1.10	267	291	442	c	8.8
Bt2 52-88	6.64	5.66	0.01	0.80	255	292	453	c	9.4
Bt3 88-120	6.51	5.47	0.01	0.60	243	294	463	c	9.4
Mean	6.25	5.43	0.02	1.28	276	331	395	cl	8.0
Pedon D: Mrigindih Series: Fine loamy, mixed, hyperthermic Ultic Paleustalfs									
Ap 0-9	4.88	3.78	0.18	1.40	536	305	159	sl	8.2
BA 9-26	5.26	4.20	0.08	1.20	501	332	161	sl	8.3
Bt1 26-59	5.42	4.39	0.10	0.80	530	181	289	scl	10.1
Bt2 59-86	6.40	5.22	0.06	0.30	468	194	338	scl	14.6
Bt3 86-144+	6.00	5.04	0.06	0.20	456	238	306	scl	13.2
Mean	5.59	4.53	0.10	0.78	498	250	251	scl	10.9

Result and Discussion

The data on the amount of Fe and Al extracted by different extractant, some ratios, their relationship with soil properties and among themselves are presented in Table 2-4. Pyrophosphate extractant dissolved the fraction of iron (Loveland and Digby, 1984) and Al (Driscoll *et al*., 1985) bound with organic matter. The fraction of iron (0.05-0.14 g kg^{-1}, mean 0.09 g kg^{-1}) decreased with depth. The fraction of Al followed the same trend varying from 0.06-0.17 g kg^{-1} with mean of 0.11 g kg^{-1}. Comparison of amount of Fe and Al extracted by pyrophosphate in different soil series indicated that the largest Fe and Al was obtained from Matimahal series followed by Anandapur, Mirgindih and Kasipur series. Comparatively more Al was extracted, which may be due to the fact that the present materials are rich in Al or because pyrophosphate is not very specific for organic complexed Al, dissolving inorganic Al compounds as well (Dolui and Mazumdar, 2003).

Acid ammonium oxalate extractable Fe and Al-Oxalate extractant has been used to dissolve amorphous Fe and Al hydroxides and oxyhydroxides from soil (McKeague *et al*., 1971). Al compounds associated with organic matter are also extracted as amorphous alumino-silicates including allophane and imogolite (Kodama and Ross, 1991). Oxalate dissolved both 'amorphous' and organically bound forms of Fe and Al, but not the crystalline forms (Parfitt and childs, 1988). This form of Fe (0.15-0.72 g kg^{-1}, mean 0.50 g kg^{-1}) was more in illuvial horizon of all the soil series indicating translocation of Fe. The fraction of Al (0.18-0.88 g kg^{-1}, mean 0.61 g kg^{-1}) followed the same trend

Table 2: Extractable Fe and Al oxides of the soils

	Pyrophosphate extractable (g kg^{-1})		Oxalate extractable (g kg^{-1})		Dithionate extractable (g kg^{-1})	
Depth (cm)	Fe_p	Al_p	Fe_o	Al_o	Fe_d	Al_d
Pedon A (Anandapur Series)						
0-10	0.14	0.17	0.28	0.33	0.82	1.02
10-26	0.12	0.15	0.32	0.38	0.90	1.12
26-51	0.12	0.15	0.64	0.78	1.66	2.05
51-89	0.09	0.11	0.72	0.88	1.84	2.27
89-120	0.08	0.10	0.68	0.83	1.76	2.18
Mean	0.11	0.14	0.53	0.64	1.40	1.73
Pedon B (Kasipur Series)						
0-14	0.08	0.10	0.15	0.18	0.56	0.70
14-51	0.09	0.11	0.36	0.44	0.82	1.02
51-87	0.06	0.08	0.53	0.65	1.42	1.76
87-141	0.06	0.07	0.53	0.65	1.46	1.80
141-150	0.05	0.06	0.51	0.63	1.38	1.71
Mean	0.07	0.08	0.42	0.51	1.13	1.40
Pedon C (Matimahal Series)						
0-11	0.13	0.16	0.28	0.34	0.72	0.90
11-26	0.14	0.17	0.46	0.56	1.24	1.54
26-52	0.12	0.15	0.59	0.72	1.64	2.03
52-88	0.10	0.12	0.65	0.80	1.66	2.05
88-120	0.09	0.11	0.68	0.84	1.76	2.18
Mean	0.12	0.14	0.53	0.65	1.40	1.74
Pedon D (Mrigindih Series)						
0-9	0.09	0.11	0.37	0.45	0.92	1.14
9-26	0.08	0.10	0.38	0.46	0.94	1.17
26-59	0.08	0.10	0.57	0.71	1.36	1.68
59-86	0.06	0.07	0.62	0.76	1.54	1.90
86-144+	0.05	0.06	0.63	0.77	1.58	1.95
Mean	0.07	0.09	0.51	0.63	1.27	1.57

Table 3: Different forms of Fe and Al of the soils

	Amorphous (g kg^{-1})		Crystalline (g kg^{-1})		Degree of activation		Co-migration of clay	
Depth (cm)	Fe_2O_3 (Fe_o-Fe_p)	Al_2O_3 (Al_o-Al_p)	Fe_2O_3 (Fe_d-Fe_o)	Al_2O_3 (Al_d-Al_o)	Of Fe (Fe_0 / Fe_d)	Of Al (Al_o / Al_d)	Clay/Fe_{dith}	Clay/Al_{dith}
Pedon A (Anandapur series)								
0-10	0.14	0.16	0.54	0.69	0.34	0.33	297.56	239.45
10-26	0.20	0.24	0.58	0.73	0.36	0.34	280.00	225.60
26-51	0.52	0.63	1.02	1.27	0.39	0.38	272.89	220.76
51-89	0.63	0.76	1.12	1.40	0.39	0.39	252.72	204.67
89-120	0.60	0.73	1.08	1.34	0.39	0.38	258.52	209.20
Mean	0.42	0.51	0.87	1.09	0.38	0.37	267.77	216.44
Pedon B (Kasipur series)								
0-14	0.07	0.08	0.41	0.52	0.27	0.26	214.29	171.67
14-51	0.27	0.33	0.46	0.58	0.44	0.43	263.41	212.18
51-87	0.47	0.58	0.89	1.11	0.37	0.37	208.45	168.47
87-141	0.47	0.58	0.93	1.15	0.36	0.36	210.96	170.83
141-150	0.46	0.57	0.87	1.09	0.37	0.37	207.97	167.44
Mean	0.35	0.42	0.71	0.89	0.37	0.36	217.55	175.51
Pedon C (Matimahal series)								
0-11	0.15	0.18	0.44	0.56	0.39	0.38	320.83	257.81
11-26	0.32	0.39	0.78	0.98	0.37	0.36	312.10	252.12
26-52	0.47	0.57	1.05	1.31	0.36	0.36	269.51	218.06
52-88	0.55	0.67	1.01	1.25	0.39	0.39	272.89	220.87
88-120	0.59	0.73	1.08	1.34	0.39	0.38	263.07	212.87
Mean	0.42	0.51	0.87	1.09	0.38	0.37	281.48	227.54
Pedon D (Mrigindih series)								
0-9	0.28	0.34	0.55	0.69	0.40	0.39	172.83	139.23
9-26	0.30	0.36	0.56	0.71	0.40	0.40	171.28	137.96
26-59	0.49	0.61	0.79	0.97	0.42	0.42	212.50	171.72
59-86	0.56	0.69	0.92	1.14	0.40	0.40	219.48	178.08
86-144+	0.58	0.71	0.95	1.18	0.40	0.40	193.67	156.68
Mean	0.44	0.54	0.75	0.94	0.41	0.40	197.63	159.76

probably due to the deposition of translocated Al-fulvate complex, protoimogolite and hydroxy polymers of aluminum (Farmer *et al*., 1980) in the horizons. So the difference between oxalate and pyrophosphate extractable Fe and Al gave a measure of amorphous inorganic Fe and Al (Dolui and Bera, 2001; Dolui and Chakraborty, 1998).

Data (Table 3) shows that amorphous Fe (Fe_{oxa}-Fe_{pyr}) of the soil ranged from 0.07-0.63 g kg^{-1} with mean of 0.41 g kg^{-1} with a wide variation among the soils. Amorphous Al (Al_{oxa}-Al_{pyr}) of the soils varied from 0.08-0.76 g kg^{-1} with an average of 0.50 g kg^{-1}. The data presented provides evidence that an approximate differentiation can be made between organically complexed Fe and Al and amorphous inorganic Fe and Al by selective extraction of soils with pyrophosphate and oxalate. The large apparent increase in the quantities of Fe_{oxa}-Fe_{pyr} and Al_{oxa}-Al_{pyr} suggested a shift towards inorganic, pedogenic phases, at the expense of organically bound phase (Jersak *et al*., 1992); although non-crystalline Fe and Al do not have a definite composition or structure and are only poorly defined, there is probably no precise differentiation between crystalline and non-crystalline material. The microprobe investigation of Norrish and Rossier (1983) indicated that amorphous or microcrystalline Fe and Al oxides were unlikely to exist as separate entities in soils.

Dithionite-citrate-bicarbonate (DCB) extractable Fe and Al- Two dissolution reagents in particular are common (i) acid ammonium oxalate (pH 3) for extraction of non crystalline Fe and Al and (ii) dithionite- citrate-bicarbonate (DCB) for extraction of non-crystalline plus crystalline Fe and Al. In the DCB procedure (Mehra and Jacson, 1960), dithionite is a powerful reductant. Bicarbonate buffers

Table 4: Correlation between forms of Fe and Al and different soil properties

Parameters	Fe_p	Al_p	Fe_o	Al_o	Fe_d	Al_d
Fe_p						
Al_p	0.986**					
Fe_o	-0.258	-0.252				
Al_o	-0.270	-0.264	0.998**			
Fe_d	-0.226	-0.220	0.984**	0.983**		
Al_d	-0.226	-0.220	0.984**	0.982**	0.997**	
PH_W	-0.339	-0.329	0.469*	0.472*	0.522**	0.522**
PH_{KCl}	-0.144	-0.137	0.405*	0.407*	0.467*	0.467*
Organic C	0.687**	0.685**	-0.653	-0.661**	-0.612**	-0.612**
Clay	0.208	0.216	0.846**	0.840**	0.885**	0.884**
CEC	-0.534**	-0.534**	0.784**	0.789**	0.720**	0.718**

* Significant at 5% level, ** Significant at 1% level

the system (pH 7-9) and sodium citrate is added to prevent the reprecipitation of dissolved Fe and Al (Borggaard, 1988). The procedure dissolves both non-crystalline and crystalline Fe and Al oxides, extracts may also include small amount of water soluble, exchangeable and organically bound Fe and Al and limited amount of Fe and Al bearing silicates (Borggaard, 1988). The difference between the values obtained by the two methods represent the amount of Fe and Al present in definite crystalline form (Dolui *et al*., 1988; Dolui and Chakraborty, 1998). The Fe_{dith} of the soils showed a variation of 0.56-1.84 g kg^{-1} with an average of 1.30 g kg^{-1}. The Al_{dith} of the soils showed a variation of 0.70-2.27 g kg^{-1} with an average of 1.61 g kg^{-1}.

The comigration of Fe and Al with clay is evident by the ratio of clay/Fe_{dith} and clay/Al_{dith} in different soil profiles, which increased with the increase of depth with a few exceptions in all the soil series. Within the profile where horizon formation is well expressed and established, the ratio increased with depth (Dolui and Bera, 2001). This suggested that Fe and Al oxide movement is partially independent of clay movement. The co-migration of clay with Fe and Al in other soils have been reported by Dolui and Bera (2001) Dolui and Mazumdar, (2003).

The DCB extract Fe and Al values were higher than the acid ammonium oxalate extracted Fe and Al values in all the soils studied indicating that a considerable fraction was present in crystalline form. Crystalline Fe (Fe_{dith}-Fe_{oxa}) in the soils ranged from 0.41-1.12 g kg^{-1} with an average of 0.80 g kg^{-1} while crystalline Al (Al_{dith}-Al_{oxa}) in the soils varied from 0.52-1.40 g kg^{-1} with an average of 1.00 g kg^{-1}. High temperature and prolonged dry season (4-5 months annually) may be responsible for high amount of crystalline Fe and Al fraction in these soils.

The ratio of Fe_{oxa}/Fe_{dith} and Al_{oxa}/Al_{dith} in the solums of all the soils was low being less than one. This supports the fact that free Fe and Al oxides in most of these soils were at an advanced stage of crystallinity or ageing (Mahaney *et al*., 1991) and supports the formation of alfisols which is formed due to prolonged weathering. With the increasing soil age, the crystalline Fe and Al oxides increased at the expense of the poorly crystalline forms. This trend was reflected in the ratio of Fe_{oxa}/Fe_{dith} and Al_{oxa}/Al_{dith}, which decreases with increasing soil age (Mahaney and Fahey, 1988). According to Mahaney *et al*. (1991), soils with high ratios were younger soils; where as low ratios indicated older soils. The mean Fe and Al ratio of all the series were low, varying from 0.27 to 0.42 (mean 0.38) and 0.26 to 0.42 with mean of 0.38, respectively, which suggested that soils could be older, or weathering could have progressed relatively well to advanced stage, which is also the characteristics feature of alfisols.

Interrelationship among different forms-Acid ammonium extractable Fe was positively and significantly correlated (0.984**) with DCB extractable Fe. Similar trend was observed in case of Al (0.982**) also. Similar type of relationship was reported by Dolui *et al*. (1987), Dolui and Bera (2001).

The close positive correlation suggested that Fe_{pyr} and Fe_{oxa} (also Al_{pyr} and Al_{oxa}) were function of the same pedological factors and more importantly that both extractants removed essentially the same form of Fe and Al (Table 4).

Relationship with soil properties-pH of the soils was found to have significant effect on the availability of the different forms of Fe and Al. Pyrophosphate extractable Fe and Al showed significant positive correlation with organic carbon, whereas significant negative correlation was observed between acid ammonium oxalate extracted Fe and Al with organic carbon. The significant correlation of clay with Fe_{dith} provides an indication that this fraction might have been present within the crystal lattice or sorbed on the surface and the interlayer of clay and iron oxides (Hawkers and Web, 1962). The cation exchange capacity gives a measure of the total negative charges of the colloid and in soil it may be correlated to the availability of Fe and Al from the charge sites.

Fractionation of soil Fe and Al by sequential extraction is useful in determining various forms of Fe and Al in soils. Present investigation supports the findings of other workers (Walia and Rao, 1999; Sidhu *et al*., 2000; Nayak *et al*., 2002; Bhowmick *et al*., 2004) who worked upon the pedogenesis of alfisols of India. The findings also support the fact that the amount and distribution of extractable Fe and Al oxides in soil profiles serve as indicators of the stage and degree of soil development specially in subtropical climatic environment. However further comparative study is required, taking different type of soils originating from different parent materials and developed under different micro-climatic conditions to establish these relationships in Indian soils.

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