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PROFILE DISTRIBUTION OF DIFFERENT FORMS OF IRON OXIDES IN SOME EAST PAKISTAN SOILS

A. Karim

East Pakistan Agricultural University, Mymensingh

M. S. Hussain

Department of Soil Science, Dacca University, Dacca

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The distrbution of different iron oxides in soils has been studied with reference to their location in the landscape. The highland and the lowland soils showed different distributional trends of iron oxides within their profiles which indicated that different soil-forming processes were in operation.

The forms and concentrations of iron in soils are governed by various physico-chemical factors such as texture, pH and oxidation–reduction potentials. To this may be added the climatic factor in which the soils are located and the length of time for which the soil-forming processes have been in operation. The effect of the climatic factor on the iron oxide content in soils may be seen if two prominent soil groups on the surface of the earth are taken into consideration. These soils may be podzols and latosols. In the podzol soils because of the "cheluviation" process iron and aluminium move down the profile and are accumulated in the B horizons.[13] Iron occurs in the podzolic B horizons (Spodic horizons) as oxides with different degrees of hydration. In the latosols, on the other hand, the distribution pattern of iron oxides is reverse of that of the podzols. In the latosols the iron and aluminium oxides stay near the surface, and there is rapid loss of silica and bases from these soils after the decomposition of silicate minerals. A field example of this is found in the humic ferruginous latosols of Hawaii.[10] These humic ferruginous latosols were formed from olivinebasalts which had an iron oxide content of 3.4% Fe_2O_3 and 7.5% FeO. After the formation of latosols, the surface horizon was found to have an iron oxide content of 45.5%.[10] An extreme example of the laterites in the tropics is found in some Cuban soils. Bennet and Allison[2] reported 71.1% Fe_2O_3 and 1.8% SiO_2 in a Cuban soil but the parent material of this soil had 41.9% SiO_2 and 7.8% Fe_2O_3.

The above examples show that iron may move or accumulate during pedochemical weathering depending on environmental conditions and that is possibly the reason that all pedologists determine iron content in soils in any study of soils genesis. Another group of soils in which iron may move during pedogenesis are the gray hydromorphic and the gley soils. The man-made soils such as the paddy soils also come under this group.[8] In these soils because of the existence of high degree of reduction condition the ferric iron is transformed to ferrous iron such as:

$$Fe^{+++} + e^- \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftarrows}} Fe^{++}$$

In this reaction there is a gain of electron when ferric goes to ferrous form of iron. Since ferrous iron is more soluble and is a stronger base than the ferric iron, as a result of this transformation the pH of the soil system increases with an increase in concentration of the ferrous ion. Moreover, the ferrous ion does not easily form any complex with organic chelates and this iron is chemically more active and does not easily precipitate out of the active soil solution. As a result the system becomes more stable. But these ferrous ions are liable to be leached out from the soil profile with draining water. Because of this fact the free iron oxide content in the gley soils is lower than the free iron oxide content of the adjoining highland soils.[4]

Iron may occur both as ferrous and ferric in rocks, minerals and soils. Some clay minerals which are synthesised in soils have also high concentrations of iron in them. Examples of these minerals may be nontronite and greenalite. But the iron that is present inside the crystals may be affected during the oxidation–reduction reactions in the soils even if the crystals are not broken by chemical weathering. Regarding the weathering of minerals containing ferrous iron Barshad[1] observed that when Fe^{++} ion is present in a crystal of a primary silicate mineral, the mineral breaks comparatively easily than those which have ferric iron in them. As the crystals break, the Fe^{++} iron comes in contact with dissolved oxygen and becomes oxidised to ferric. The ferric iron hydroxylises readily. In the pH range of most soils, the Fe^{+++} will precipitate as $Fe(OH)_3$ and will, therefore, rarely participate in clay mineral formation but will remain as free Fe_2O_3 in soils.

The portion of iron in soils that reacts promptly with the oxidation–reduction reactions are the free iron oxides. A large proportion of total iron in soils is frequently in the form of free oxides. These free iron oxides usually exist as discrete particles, as coatings on soil peds and as a cementing agent between two mineral particles as in concretions. The quantitative determination of free iron oxides in soils is of interest because of their role in the podzolisation, laterisation, gleization and other processes of soil formation. To the agornomists the free iron oxides are important because they have the capacity of fixing very high amount of phosphate in soils. And this affects the availability of phosphorus to plants.

In the present study the distribution of different forms of iron oxides in some soils formed in an area of undulating topography has been studied with reference to their drainage conditions. The iron oxides of a group of soils from free drainage condition has been compared with the iron oxides of a group of soils from restricted drainage condition.

Materials and Methods

Twenty-nine soil samples representing six soil profiles were collected on natural horizon basis. The soils were collected from an area of undulating topography where there are hills and valleys side by side. The area lies around seven miles north of Sylhet town. Three profiles were selected from the flat tops of hills where the drainage is free and are designated as the highland soils in this study. Another three profiles were collected from the bottom of broad valleys where both the internal and external drainage was restricted,[7] and these were designated as lowland soils in this study. As a result of the difference in the drainage conditions the upland soils were reddish in colour throughout the profile, while the valley soils were greyish in colour near the surface and bluish grey at the subsurface.

Methods of Analyses

Soils were treated with hydrogen peroxide to remove organic matter and were then washed by centrifugation. The samples were then dispersed with an electric stirrer and using sodium hydroxide as the dispersing solution. The clay ($<2\mu$) fraction was then separated from this soil suspension by repeated decantation after suitable time interval. The separated clays were flocculated with calcium chloride and washed several times with the above reagent to make them Ca-saturated clays. The clays were then washed three times with 95% alcohol to remove excess calcium. The clay samples were then dried and powdered. Total iron was then determined from these clay fractions by sodium carbonate fusion method as described by Piper.[9]

Free iron oxides in the soils and clays ($<2\mu$ fraction) were determined by the nascent hydrogen reduction method of Karim.[6] Percent concentration of free Fe_2O_3 in clays were calculated in the followg way:

$$\%\ \text{Concentration of free } Fe_2O_3 = \frac{\text{Free } Fe_2O_3 \text{ in clay}}{\text{Total } Ee_2O_3 \text{ in clay}} \times 100$$

Results and Discussion

The results of different forms of iron oxides in the soils under the investigation have been presented in Table 1. The distribution pattern of free iron oxides down the profiles in the upland soils exhibits an accumulation in the B horizons which probably is an indication of the presence of podzolic process of soil formation. But in the valley soils there is no regular downward movement of free iron oxides and their accumulation seems to depend on the fluctuation of the groundwater table. The free iron oxides in the valley soils are present mostly in the form of mottles. This is indicated by the fact that the free iron oxides are high in those horizons where the mottles are abundant.

The free iron oxide contents in the upland soils are higher than those of the lowland soils. This is exemplified by the mean iron oxide contents of those two groups of soils. In the upland soils the mean free iron oxide content is 2.7% while in the lowland soils the mean free iron oxide content is 1.7%. This lower free iron oxide content in the poorly drained soils may be an indication of the fact that under gleization process there is loss of free iron oxides from the soil profiles. Hussain[3] in a study of some grey hydromorphic soils reported similar results. In the upland soils, on the other hand, the iron oxides have moved down and precipitated, but they were not lost from the soil profiles.

Two lowland soils have typical gley (G) horizon in them. In these gley horizons there is low content of free iron oxides (Table 1). Because of extreme reducing condition in the lower horizons of the valley soils iron goes in its lowest valency state (Fe^{++}). The ferrous iron thus formed remains in soil solution and move up and down with the fluctuation of the groundwater table. When condition in any horizon is suitable for oxidation, because of downward transfusion of oxygen through the soil, the mottling occurs. The formation of these mottles seems to depend on the texture and structure of the soils. The presence of mottles in a horizon indicates that oxidation–reduction conditions alternate there at different seasons, which in turn is caused by the fluctuation of the groundwater table.

Total iron oxide content in the upland soils ranges from 3.2 to 9.9% while in the valley soils the total iron oxides range from 2.1 to 7.7%. Total iron oxides which include both free and combined iron show a downward movement in the upland soils. In the valley soils the total iron oxide is high in those horizons where the free iron oxide contents are also high. The percent concentration of free iron oxides is higher for the hill soils than that for the valley soils. The mean percent concentration of free iron oxides is 47 for the highland soils as compared to 31 for the lowland soils. This shows that a higher proportion of total iron is in the free oxide form in the upland soils than that of the valley soils. In a given locality, therefore, the content of free iron oxides may be used as a criteria for classifying the soils.

The free iron oxides in the clay fractions of the upland soils range from 4.0 to 13.2%. On the other hand, the range of free iron oxides in the clay fractions of the valley soils varies from 0.9 to 5.2%. The mean free iron oxide content in the colloid fractions of the upland soils is 7.7% while in the lowland soils the mean value is 3.0%. This shows that the free Fe_2O_3 in the colloidal fractions

TABLE 1.—DISTRIBUTION OF IRON OXIDES IN SOME EAST PAKISTAN SOILS.

Soil types	Horizons	Total Fe_2O_3 in soil	Free FeO_3 in soil	% Conc of free Fe_2O_3 in soil	Total Fe_2O_3 in clay	Free Fe_2O_3 in clay	% Conc of free Fe_2O_3 in clay	Location of the soils
Salia SL	A1a	4.3	1.5	35	12.1	8.0	66	
	A1b	4.6	2.6	56	14.2	5.5	39	
	A_2)?)	3.6	1.9	53	13.6	7.6	56	
	B	6.2	3.3	53	13.2	8.4	36	
	C	4.2	2.3	55	18.2	8.1	44	
Mughlipara FSL	A11	5.3	1.7	32	12.5	4.9	39	Upland soils
	B21	7.6	3.4	45	14.4	5.6	39	
	B_{22}	9.9	3.6	36	15.7	5.6	36	
	BC	6.7	2.8	42	8.6	4.0	46	
	C	5.3	3.5	66	17.5	9.3	53	
Lackatoorah LS	A1a	4.4	1.7	40	14.9	7.9	53	
	A1b	5.2	2.9	56	17.7	6.9	39	
	B1	6.6	2.6	40	18.6	9.8	53	
	B_2	9.1	3.4	37	28.8	12.1	51	
	BC	5.3	3.4	64	29.1	13.2	45	
	Mean	5.8	2.7	47	16.6	7.7	46	
Nacksapara sCL	A1a	4.6	0.8	17	8.9	3.0	34	
	A1b	4.4	0.7	16	8.5	1.8	21	
	B1g	7.6	2.5	33	12.1	4.0	33	
	B ?g	7.5	3.0	40	16.2	4.7	29	
	BCG	4.4	0.6	14	8.1	0.9	11	
Salehpur sL	A1a	4.5	0.7	16	8.3	1.2	15	Lowland soils
	B1g	7.7	3.2	41	12.1	4.3	36	
	B2g	5.3	2.4	45	21.9	5.2	24	
	B3g	4.3	1.9	44	10.3	2.7	26	
	BCG	4.1	0.6	15	7.4	1.3	17	
Khakurpara sC	A11g	6.4	2.2	34	8.9	3.6	40	
	A12g	2.1	0.7	33	7.9	1.9	24	
	B1g	4.5	2.0	44	13.1	3.8	29	
	B2g	3.5	1.5	43	10.7	3.3	31	
	Mean	5.7	1.7	31	11.3	3.0	26	

of the upland soils are much higher than those of the lowland soils. This was expected because iron tends to oxidise and accumulate under the free drainage conditions of the upland soils than under the restricted drainage condition as is encountered in the valley soils. Again, the free iron oxides in both the upland and lowland soils are lower than the free iron oxide contents of their respective clay fractions. This is evident from the mean free iron oxide contents of the valley and upland soils. The mean free iron oxide content of all the soils is only 2.2%, while in their clay fractions the mean free iron oxide content is 5.4%. The reason for this higher concentration of free iron oxides in the clay fraction is that the particle size of these free oxides is lower than 2μ, and easily can come in the clay fraction at the time of their seperation from sands and silts.

From Table I it is evident that the percent concentration of free iron oxides in the colloid fractions of the soils under study range from 11 to 66. This variation is large indeed. In the valley soils alone the percent concentration of free iron oxides in the colloid fractions are quite low (mean 26). But in the colloid fraction of the upland soils the mean is 46%. In the case of the colloid fraction of the upland soils the percent concentration of free iron oxides rises with depth following a fall. The argument may be put forward at this place that the higher concentration may be only consequential to higher clay content in the respective horizon which would mean that the iron oxides had no movement of their own, but the percentage of free Fe_2O_3 in the clay fractions disapproved this contention. The vertical distribution pattern of free iron oxides in the colloidal fractions of the upland soils indicates the presence of podzolic proces of soil formation in them.[15]

The restricted internal drainage condition in the valley soils prepares the ground for the formation of mottles in the fluctuating oxidation–reduction zones of the profiles. Due to the presence of the reducing conditions in these valley soils for a large part of the year there is the possibility of the entry of iron in the lattices of clay minerals, which are synthesised on soils. This is because when ferric iron is transformed to the ferrous state, it becomes chemically more reactive. And due to this increase in activity, the ferrous iron may take part in crystal lattice formation of clays. Therefore, the clay minerals synthesised in the valley soils may be more iron bearing than those formed in the upland soils.[11] In the present investigation this is exemplified by the fact that the average free iron concentration in the colloid fraction of the upland soils is 46% as compared to 26% for that of the lowland soils. This means that a higher proportion of iron in the upland soil colloids remains as free oxides, while in the colloidal fraction of the lowland soils a comparatively higher proportion of iron is present in the combined form and occurs in the lattices of clay minerals.

In consideration of the above discussion regarding the distribution of different forms of iron oxides it has been indicated that in the soils of the upland areas podzolic features are present. It is suggested therefore, that podzolisation is possibly the major process of soil formation there. In the valley soils, on the other hand, where the drainage condition is restricted the distribution of free iron oxides is controlled by local hydrology. And gleization seems to be the major process of soil formation in these lowland soils. This is testified by the presence of gley (G) and mottled (g) horizons in the profiles of the lowland soils. Typical gley horizons (G) are present in the subsurface zones of Nackspara Silty Clay Loam and Salephur Silty Loam. Mottled horizons (g) which are regarded as poor expression of gleization process of soil formation are present in all the soils of the lowland area.

Summary

Twentynine soil samples representing six soil profiles were collected, on horizon basis, from a rolling-topography area in the Sylhet district in East Pakistan. Three profiles were collected from the upland areas and another three profiles from the bottom of broad valleys. In the upland soils drainage was free and the groundwater table was far below the reach of soil profiles. In the valley soils the groundwater table was very close to the surface of the soils even in the month of January, and is flooded in the rainy season.

Average free iron oxide content in the upland soils was higher than that of the lowland soils. In the upland soils there was a distinct sign of the movement and subsequent deposition of free iron oxides with depth. This was regarded as a feature formed by podzolisation process. In the valley soils the distribution of free iron oxides was irregular. Among the valley soils the free iron oxide contents were higher in the mottled horizons than that of the unmottled ones. Distribution of the mottles seems to have had been guided by the fluctuations of the groundwater table i.e. local hydrology. Some of the profiles among the lowland soils developed gley (G) horizon in them. This showed that gleization might be the major process of soil formation in them.

Free iron oxides associated with the clay fractions of the upland soils were much higher

than those of the valley soils. The high concentration of combined iron in the clay fractions of the lowland soils indicated that there were possibly some iron-rich minerals in them. The lowland soils might be seperated from the upland soils on the basis of their free iron oxide contents. It was concluded that the distribution of different forms of iron oxides might give some clues regarding the processes of soil formation which were in operation in these soils.

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