Pakistan J. Sci. Ind. Res., Vol. 14, Nos. 4–5, August–October 1971

A STUDY OF THE PROFILE DISTRIBUTION ON MANGANESE IN SOME SOILS OF EAST PAKISTAN AND ITS PEDOGENIC SIGNIFICANCE

A. Karim

East Pakistan Agricultural University, Mymensingh

M.S. Hussain

Department of Soil Science, Dacca University, Dacca 2

(Received October 21, 1970; revised December 19, 1970)

This communication deals with the translocation and concentration of manganese in the soil profiles from a 'hilo' topographic area in East Pakistan. A higher proprotion of manganese was present in the free oxide form in the soils of uplands compared to that in the lowland soils. Of all forms of manganese only soluble manganese was found to be influenced by vegetative cycle. Pedogenic significance of the vertical and horizontal distribution pattern of manganese in these soils has been discussed.

Manganese occurs to the extent of 1250 p.p.m. in igneous rocks which constitute around 95% of the earth's crust.[1,2] In sedimentary rocks, however, the amount of manganese varies from 1000 p.p.m. in shale to less than 200 p.p.m. in sandstone.[3] But in soils manganese is mostly known as an element important for plant growth and soil fertility. As a result, a vast literature exists regarding its uptake by plants and its availability in soils.[4,5] Little work has been reported about the behaviour of manganese during pedogenic reorganisation of soil parent materials. Pedological importance of manganese and its movement in soil was first emphasized by Fujimoto and Sherman[6] in some tropical soils. Recently few more works have been reported.[7,8,9]

It is known that a portion of manganese present in soils occurs in certain ferromagnesian minerals and other complex silicates. Manganese is reported to occur also in secondary layer silicates in which this element usually occupies a place in the octahedral layer by isomorphous replacement. Some of these minerals are so insoluble that they may not be readily decomposed even by concentrated acids and, therefore, are not considered to be 'available' manganese in soils.

The two forms of manganese in soils which are thought to be important as the source of this element for plants are replaceable manganese, and manganese dioxide that may readily be reduced to divalent manganese on flooding a soil.[5] Bohn[10] reported that the concentration of Mn^{2+} increased in soil suspension which differed widely from those calculated by previous models of manganese behaviour. He derived an equation of $pH-\frac{1}{2}\,pMn$ for expressing the equilibrium solubility of MnO_2 in soil suspension.

Many authors worked on the chemical behaviour of manganese on flooding a soil. Conner[11] found a significant increase in the amount of replaceable manganese after flooding a soil. Schollenberger[12] also reported that submerged soils in which strongly reducing condition prevails are characterised by increased amount of divalent manganese content. Piper[13] and Adams[14] tried to correlate the amount of Mn^{2+} in soils with their redox potentials.

The precipitation of manganese from soil solutions has been an important source for the occurence of manganese concretions in soils, manganese present in concretions are mostly oxidised and chemically inert. Leeper[15] classified the manganese in soils into three distinct forms which exists in an equilibrium with each other. His classification may be presented as follows:

$$\text{Manganous manganese} \rightleftharpoons \text{Colloidal hydrated } MnO_2 \rightleftharpoons \text{Inert } MnO_2$$
(Soluble) (Slightly soluble) (Insoluble)

Dion and Mann[16] studied the manganese cycle in soils on the basis of oxidation—reduction equilibrium between the divalent and tetravalent manganese oxides and reported the existance of a trivalent manganese in soils which undergoes dismutation to give rise to divalent and tetravalent manganese.

In this paper the distribution of manganese in some well-drained and imperfectly drained soils of East Pakistan has been discussed with reference to their pedogenic significance.

Materials and Methods

Six soils profiles were collected from an area of undulating topography in the district of Sylhet in East Pakistan on natural horizon basis. The hills and hillocks of Sylhet are the outliers of the main ranges that surround this district from the north and south.[17] The parent materials of these soils were ferroginous sandstone and were of mixed origin. The deposition of these sediments and their subsequent upheaval into hills and valleys took place during the late Tertiary Period.[18] The area wherefrom the present soil samples were collected was situated at a distance of around 8 miles north of Sylhet town. The natural environmental conditions alongwith the morphological features of these soils have been reported in a previous communication.[19] Three soil profiles were collected from highland areas having free drainage conditions. Other three profiles were collected from the nearby lowland areas where the drainage was impeded.

Water-soluble manganese was determined on an aliquot of the water extract at a soil water ratio of 1:5. Total manganese in soils and clays was determined from the sodium carbonate fusion extract prepared according to the method of Piper.[20] In all cases manganese was determined colorimetrically according to the method of Jackson.[21] Total iron in soils was determined volumetrically by the $KMnO_4$ oxidation method from an aliquot of the fusion extract. pH of the soils was determined with a Pye pH meter at a soil: water ratio of 1:2.5. Percent clay in the soils was determined by the Pipette method as described by Piper.[20] Free iron oxides in soils were determined according to the nascent hydrogen method of Karim.[22] Free manganese in soils was determined by the sodium dithionite reduction method of Daniel *et al.*[23]

Results and Discussion

Water-soluble Manganese in Soils.—In the upland soils water-soluble manganese is concentrated near the surface (Table 1). This may be due to the cycling of manganese by the natural vegetation cover in this area. All the soils from the upland area were undisturbed and had on them a natural forest vegetation cover at the time of their sampling.

In the valley soils, however, the distribution of water-soluble manganese was irregular in nature. The distribution of Mn^{2+} in these soils has been influenced by vegetation cover alongwith some other factors such as the texture of different horizons and the fluctuating ground water table. Karim *et al.*[24] studied the exchangeable Mn^{2+} content in some East Pakistan soils and reported a surface concentration of this type of manganese in both the highland and lowland soils. It should be noted that the above authors studied exchangeable Mn^{2+} in soil samples up to an arbitrary depth from the surface and did not collect samples on natural genetic horizon basis.

The high concentration of soluble manganese near the surface might also be due to the low pH of these soils.[13] When soluble manganese was plotted against pH, a high concentration was observed around pH 5.4 (Fig. 1). The water-soluble manganese content decreased when the pH values were either above or below 5.4. Water soluble Mn^{2+} was negatively correlated with total iron oxide in soils (Fig. 2). This may be due to the fact that iron probably has inhibited the availability of manganese in these soils.

The mean water-soluble manganese content in the hill soils is lower than that in the valley soils. This shows that under reducing conditions manganese is more soluble than under oxidizing condition. In the lowland soils reducing environment prevails during the rainy season and oxidizing condition in the dry season, while in the high land soils oxidizing condition prevails for most of the year.

Free Manganese in Soils.—Free manganes oxides show an irregular distribution pattern in both the upland and the lowland soils. It ranges from as low as 5 to as high as 100 mg% (Table 1). The highest free manganese is encountered in the C horizon of the Lackatoorah profile. The colour of this soil was blackish which was probably due to the free manganese coating on other soil particles. In general the free manganese content in the upland and the lowland soils was more or less same when Lackatoorah profile was left out.

It appears that the ratio of Free Mn/Total Mn is higher in the upland soils than that of the lowland soils. The mean ratio is 0.7 in the upland and 0.3 in the lowland soils (Table 1). This means that comparatively higher proportion of Mn

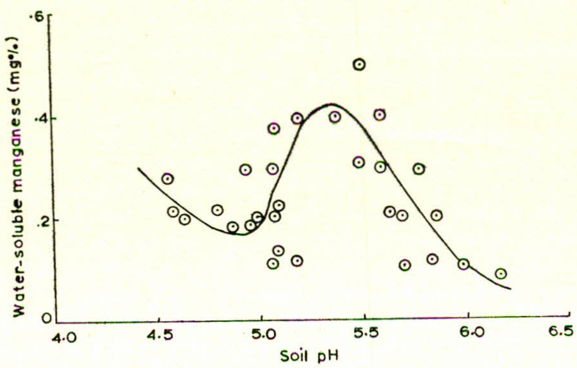

Fig. 1.—Relationship between water-soluble manganese and pH of soils.

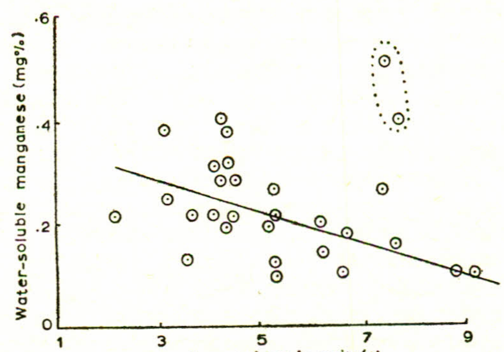

Fig. 2.—Relationship between water-soluble manganese and total iron oxide in soil.

occurs in the free oxide from in the upland soils than that in the lowland soils. Therefore, the proportion of silicate-manganese is higher in the lowland soils than that in the upland soils. The amount of combined manganese is high in the Lackatoorah soils which means that most of the manganese occurs in silicate minerals.

Free iron oxide in the upland soils is higher than that in the lowland soils. In the upland soils the mean free iron oxide content is 2.7% while in the lowland soils it is 1.7% (Table 2). The reason for the low free iron in the lowland soils may be the reducing condition during the rainy season when iron is reduced and probably is lost from the soils alongwith the drainage water.[8]

Total Manganese in Soils.—Total manganese content in the soils ranges from 14 to 412 mg% (Table 1). Rankama and Sahama[25] reported that total manganese content in the sedimentary rocks does not usually exceed 100 mg% unless they contain manganese bearing minerals. The Lackatoorah profile contains the highest amount of total manganese amongst the present soils. Since in the lower horizons of the Lackatoorah

TABLE 1.—DISTRIBUTION OF DIFFERENT FORMS OF MANGANESE IN SOILS AND CLAYS.

Soil Type	Horizon	Depth (in)	Water-soluble Mn in soil (mg%)	Free Mn in soil (mg%)	Total Mn in soil (mg%)	Free Mn Total Mn ratio	Total Mn in clay (mg%)	Physio-graphy
Salia sandy loam	Ala	1–5	0.4	20	25	0.8	53	
	Alb	5–15	0.4	21	28	0.8	40	
	A2	15–24	0.2	17	19	0.9	54	
	B	24–47	0.1	20	25	0.8	79	
	—	47–70	0.2	27	39	0.7	156	
Mughlipara fine sandy loam	Ala	1–6	0.3	25	32	0.8	35	Upland soils
	Alb	6–16	0.2	26	36	0.7	44	
	—	16–34	0.1	15	16	0.9	31	
	B1	34–58	0.2	14	16	0.9	17	
	BC	58–75	0.1	15	17	0.9	88	
Lackatoorah loamy sand	Ala	1–6	0.3	70	100	0.7	201	
	Alb	6–19	0.2	70	94	0.7	174	
	A2	19–43	0.1	42	56	0.8	525	
	—	43–55	0.1	45	204	0.4	1300	
	C	55	0.1	100	412	0.2	3250	
	Mean	—	0.2	37	61	0.7	403	
Nacksapara silty clay loam	Ala	1–4	0.3	10	27	0.4	39	
	Alb	4–9	0.4	10	28	0.4	42	
	A2	9–27	0.3	27	94	0.3	118	
	B1	27–61	0.5	32	117	0.3	134	
	B2	61–80	0.2	9	43	0.2	61	
Salehpur silty loam	Ala	1–4	0.3	9	23	0.4	49	
	Alb*q*	4–14	0.4	26	86	0.3	106	
	A2	14–21	0.2	18	46	0.4	71	Lowland soils
	B1	21–30	0.3	29	111	0.2	140	
	B2	30–58	0.2	8	26	0.3	31	
Khakurpara silty clay	A1	1–6	0.2	9	22	0.4	27	
	A2	6–14	0.2	5	16	0.3	25	
	B1	14–38	0.2	11	24	0.5	42	
	B2	38–68	0.1	8	19	0.4	36	
	Mean	—	0.3	15	49	0.3	66	

TABLE 2.—CHEMICAL PROPERTIES OF SOILS FROM SYLHET.

Soil type	Horizon	Depth (in)	Free Fe_2O_3 in soils(%)	Total Fe_2O_3 in soil (%)	Clay (%)	pH	Physiography
Silica sandy loam	Ala	1–5	1.5	4.3	12	5.4	
	Alb	5–15	2.6	4.6	5	5.2	
	A2	15–24	1.9	3.7	4	5.0	
	B	24–47	3.3	6.2	10	5.1	
	—	47–70	2.3	3.2	7	5.1	
Mughlipura fine sandy loam	Ala	1–6	1.7	5.3	21	4.9	
	Alb	6–16	3.4	7.6	29	5.1	
	—	16–34	3.6	8.9	18	5.1	Upland soil
	B1	34–58	2.8	6.7	60	4.6	
	Bc	58–75	3.5	5.3	11	5.7	
Lackatoorah loamy sand	Ala	1–6	1.7	4.4	13	5.8	
	Alb	6–19	2.9	5.2	11	5.6	
	A2	19–43	2.6	6.6	7	5.8	
	—	43–55	3.4	9.1	4	6.0	
	C	66+	3.4	5.3	6	6.2	
	Mean	—	2.7	5.8	15	—	
Nacksapara silty clay loam	Ala	1–4	0.8	4.6	33	5.1	
	Alb	4–9	0.7	3.4	34	5.6	
	A2	9–27	2.5	7.6	30	5.5	
	B1	27–61	3.0	7.5	31	5.5	
	B2	61–80	0.6	4.4	36	4.8	
Salehpur silty loam	Ala	1–4	0.7	4.5	16	4.6	
	Alb	4–14	3.2	7.7	31	5.2	
	A2	14–21	2.4	5.3	11	5.9	Lowland soil
	B1	21–30	1.9	4.3	23	5.6	
	B2	30–58	0.6	4.1	24	5.7	
Khakurpara silty clay	Al	1–6	2.2	6.2	42	4.6	
	A2	6–14	0.7	2.1	12	4.9	
	B1	14–38	2.0	4.5	26	5.0	
	B2	38–68	1.5	3.5	19	5.4	
	Mean	—	1.7	5.5	26	—	

profile, the amount of total manganese far exceeds the 100 mg% mark, it may be logical to conclude that these horizons contain certain manganese bearing minerals. The soluble manganese in this profile, however, was very low compared to the total amount present.

In all the soils mobilization of manganese has taken place. But the forces behind the mobilization in the upland and lowland soils appear to be different. In the upland soils total manganese content is reasonably higher near the surface and gradually rises with depth following a fall. This feature indicates that the redistribution of manganese in the upland soils has probably been caused by the pedogenic processes. The vertical distribution pattern of manganese in the lowland soils is more or less erratic. In these soils concentration of manganese seems to be controlled not so much by the usual eluviation–illuviation processes but by the fluctuating ground water table and the texture of the soils materials.

The mean manganese contents in the upland and the lowland soils are 61 and 49 mg% respectively. This may indicate that the lowland soils have lower manganese content than the uplands oils. But when the Lackatoorah profile is left out there is no significant difference in manganese content between the highland and the lowland soils.

Total Manganese in the Clays.—This form of manganese is also found to suffer eluviation and illuviation and follows more or less the same distributional trend as that of the total manganese in the soils. The amount of total manganese in the clays varies within wide limits and ranges from 16 to 3250 mg% (Table 1). Clays of the Lackatoorah profile contains highest amount of manganese in comparison to that of the other soils. Such a huge amount of manganese in the clay fraction of this profile suggests the presence of some manganese-bearing clay-sized minerals. The high concentration of manganese in the lower horizons of the Lackatoorah profiles may suggest that the pedogenic weathering near the surface has removed most of the manganese bearing minerals. In the lower horizons the manganese bearing minerals seem to be unaffected by the pedochemical weathering.

The mean manganese content in the upland and the lowland clays are 403 and 66 mg% respectively. When Lackatoorah profile is left out there is no significant difference between the total manganese content in the upland and lowland clays.

Soil Reactions.—All the soils under the present investigation are acidic in reaction. The pH of these soils ranges between 4.6 and 6.2 (Table 2). From this low pH value it appears that these soils are well-leached and therefore, base-poor. The low pH and high leaching condition in these soils are expected from a consideration of the environmental conditions of these soils. The annual rainfall in this area is around 200 in. This high rainfall and the light texture of the soils have facilitated the removal of exchangeable bases from the soils and consequently in decreasing the pH of them.

Percent Clays in the Soils.—The mean clay content in the upland soils is lower than that in the valley soils (Table 2). This may be due to the fact that the clays in the upland soils has been transported away by surface runoff along the slopes and was deposited on the basin floor. As a result the valley soils became richer in clay content while the soils of the upland areas have been relatively improvised of clays.

References

1. V.M. Goldschmidt, J. Chem. Soc., 655 (1937).
2. N. Sheikh, M.Y. Qureshi and R. Rahman, Pakistan J. Sci. Res., **19,** 61(1967).
3. R.L. Mitchell, *A Chemistry of the Soils*, (Reinhold, New York, 1964).
4. J.K. Hammes and K.C. Berger, Soil Sci., **90,** 239 (1960).
5. G.D. Sherman and P.M. Harmer, Soil Sci. Soc. Am. Proc., **7,** 398(1943).
6. C.K. Fujimoto and C.D. Sherman, Soil Sci., **66,** 131(1948).
7. L.N. Mandal, Soil Sci., **91,** 121(1961).
8. M.S. Hussain, M.A. Mujib and S. Rahman, Pakistan J. Soil Sci., **5,** 37(1969).
9. S.Z. Heintz, J. Soil Sci., **8,** 287(1957).
10. H.L. Bohn, Soil Sci. Soc. Am. Proc., **34,** 195(1970).
11. S.D. Conner, J. Am. Soc. Agron., **24,** 726 (1932).
12. C. J. Schollenberger, Soil Sci., **25,** 357 (1938).
13. C.S. Piper, J. Sci. Agri. Soc., **21,** 762(1931).
14. F. Adams, *Methods of Soil Analysis*, **9,** 1011 (1965), Part II.
15. G.W. Leeper, Soil Sci., **63,** 79(1947).
16. H.G. Dion and P. J.G. Mann, J. Agri., Sci., **36,** 239(1946).
17. F.K. Khan, *An Introduction to Economic Geography* (New Age Publication, Dacca, 1959).
18. M.S. Krisnan, *Geology of India and Burma* (Higginbothams, Madras, 1968).
19. A. Karim and M.S. Hussain, Sci. Ind., **1,** 157 (1963).
20. C.S. Piper, *Soil and Plant Analysis* (Inter science, New York, 1950).
21. M.L. Jackson, *Soil Chemical Analysis*,(Prentice Hall, New Jersey, 1961).
22. A. Karim, Pakistan J. For., **3,**48(1953).
23. R.B. Daniel, J.F. Brasfield and P.F. Riecken, Soil Sci. Soc. Am. Proc., **26,**75(1962).
24. A. Q.M.B. Karim, M. Hussain and S. Choudhury, Soil Sci., **90,** 129(1960).
25. K. Rankama and T.G. Sahama, *Geochemistry* (University of Chicago Press, 1949).