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MIGRATION OF IONS IN SOILS

II. MOVEMENT OF Mn^{54} FROM SURFACE APPLICATION OF MANGANESE SULPHATE IN SOIL COLUMNS

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SUMMARY

When surface-applied $MnSO_4$ labelled with Mn^{54} was leached with rain water equivalent to 300 mm precipitation, Mn moved to a depth of 18 cm in soil A and throughout the whole of soil B, although a higher concentration of Mn was retained by the upper 3 cm of soil. A similar pattern but with relatively higher concentrations at depths below 3 cm resulted on leaching with water equivalent to 1200 mm of precipitation. With alternate leaching and drying, the depth of penetration of Mn increased to 24 cm in soil A, and relatively greater amounts of Mn moved to depths below 15 cm in soil B. The presence of Zn cation had no appreciable effect on the distribution of Mn in soil columns. Exchangeable Mn displayed distribution patterns similar to total Mn. The percentage of the CEC occupied by Mn in the upper 3 cm averaged 24 and 5% in soils A and B when Mn was applied alone. This decreased to 11% in soil A and remained unchanged in soil B when Mn was applied in combination with Zn. Exchangeable Ca and Mg were lowest in the upper 3 cm, and then increased to a depth of 6 to 9 cm, becoming nearly uniform lower down in both soils. Mn movement in soil not only depends on CEC and clay content, but also involves other factors such as water-flow-rate, pH, migration of clay fractions and oxidation reduction conditions.

INTRODUCTION

The movement of manganese in fine textured soils is rather limited. Working with ion exchange units, Tepe and Leidenfrost [14] found that manganese is relatively immobile in soils. Singh and Pathak [13] reported that in drier climates, total and available manganese was higher in surface soils and tended to leach downward with increasing precipitation. On the other hand, in calcareous soils with high clay content, surface applied $MnSO_4$ leached to a depth of 5 to 10 cm but the depth of penetration increased to 35 cm when applied as Mn–EDTA [10].

However, information on the downward movement of manganese in different soils under different precipitation levels is scanty. The present experiment was therefore designed to study the downward movement of surface applied $MnSO_4$ labelled with Mn^{54} as influenced by precipitation, Zn cation and oxidation-reduction conditions of the soil environment.

EXPERIMENTAL PROCEDURE

The preparation of soil columns, leaching procedure, counting and analytical methods, and physicochemical properties of the soils have been previously described [12]. The rate of $MnSO_4$ application and level of activity were also the same as used previously.

RESULTS AND DISCUSSION

Though a higher concentration of total Mn was retained by the upper 3 cm of soil, the movement of Mn from surface-applied labelled $MnSO_4$ was observed to a depth of 18 cm in soil A, and to the bottom of soil B, on leaching with artificial rain water equivalent to 300 mm of precipitation. A similar pattern of Mn distribution was obtained on leaching with water equivalent to 1200 mm of precipitation, though relatively higher concentrations of Mn^{54} occurred at depths below 3 cm (Table 1). This may have resulted from increased solubility of manganese under relatively more pronounced reducing conditions. The decrease to total Mn at consecutively lower depths was higher in soil A than in soil B since, below 9 cm total Mn dropped to a very low value in soil A. This effect was consistent in almost all treatments.

When rain water equivalent to 1200 mm of precipitation was applied in four-portions in an alternate leaching and drying sequence, the distribution pattern of Mn differed slightly to that when water was applied continuously. In soil A, the depth of penetration increased from 15 cm to 24 cm and in soil B proportionately greater amounts of total Mn moved below 15 cm. These results indicate that Mn availability in soil columns was slightly affected by alternating oxidation and reduction conditions. The effect of redox-potential on Mn availability has been reported by other workers [4 5 15]. They con-

TABLE 1

Effect of precipitation on the movement of total Mn * in soil columns

Soil	Depth	Precipitation (mm)					
		300		1200		1200 **	
	cm	pH	* Total Mn * me/100 g	pH	* Total Mn * me/100 g	pH	* Total Mn* me/100 g
A	3	7.00	6.00	6.91	4.95	6.82	4.53
	6	7.15	1.20	7.06	2.73	6.92	0.97
	9	7.13	0.35	7.06	0.61	7.04	0.25
	12	7.13	0.09	7.09	0.13	7.04	0.16
	15	7.15	0.09	7.09	0.03	7.11	0.07
	18	7.12	0.05	7.09	—	7.12	0.01
	21	7.12	—	7.15	—	7.14	0.05
	24	7.15	—	7.12	—	7.12	0.05
	27	7.15	—	7.12	—	7.14	—
	30	7.15	—	7.12	—	7.16	—
B	3	6.21	4.85	6.39	1.41	6.28	0.87
	6	6.27	1.19	6.43	0.92	6.30	0.51
	9	6.25	0.50	6.50	1.39	6.24	0.93
	12	6.32	0.29	6.48	1.50	6.28	0.40
	15	6.34	0.22	6.55	1.24	6.24	0.46
	18	6.32	0.13	6.55	0.35	6.30	0.66
	21	6.26	0.10	6.55	0.32	6.17	0.99
	24	6.25	0.10	6.64	0.13	6.42	0.73
	27	6.26	0.02	6.64	0.06	6.45	0.32
	30	6.25	—	6.69	0.01	6.40	0.22

* Total Mn * determined from activity counts.

** In four 300-mm portions in an alternate leaching and drying sequence.

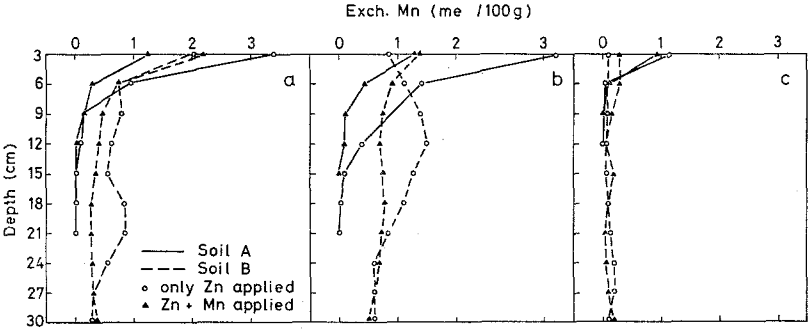

Fig. 1. Exchangeable manganese in soil columns leached with water equivalent to 300 mm (**a**), 1200 mm (**b**), and 1200 mm of precipitation in four 300 mm-portions in an alternate leaching and drying sequence (**c**).

TABLE 2

Effect of zinc on the movement of total Mn * (me/100 g) under different precipitations

Depth cm	Precipitation (mm)					
	Soil A			Soil B		
	300	1200	1200 **	300	1200	1200 **
3	2.10	2.00	1.78	2.96	1.82	2.68
6	0.29	0.72	0.54	0.59	0.55	1.27
9	0.24	0.17	0.19	0.26	0.32	0.47
12	0.04	0.01	0.25	0.19	0.26	0.05
15	—	—	0.18	0.10	0.20	
18	—	—	0.14	0.03	0.11	
21	—	—	0.06	0.01	0.03	
24	—	—	—	0.01		
27	—	—	—			
30	—	—	—			

* Total Mn * determined from activity counts.

** In four 300-mm portions in an alternate leaching and drying sequence.

cluded that the condition of alternating oxidation and reduction has a marked influence on the distribution of Mn in soil profile.

A solution containing 10 me of Mn plus 10 me Zn labelled with the respective isotopes, was applied to soil columns in order to study the influence of Zn on Mn distribution. Soil columns were leached with the same amounts of water used earlier. The distribution patterns of total Mn were similar to that of Mn added alone, however, the depth of penetration decreased in both soils (Table 2). These results suggest that depth of penetration of Mn from surface application depends upon the amount applied. Similar results were obtained with Zn by Barrows *et al.*[1].

Exchangeable Mn displayed a distribution pattern similar to that of total Mn in all the treatments. (Fig. 1). The percentage of the CEC occupied by Mn in the upper 3 cm was nearly the same at the 300 mm and 1200 mm precipitation levels, but decreased as the result of alternate leaching and drying, especially in soil B. The decrease in exchangeable Mn in the latter treatment may simply reflect greater mobility of Mn down the profile. The percentage of the CEC occupied by Mn in the upper 3 cm averaged 24 and 5 per cent in soils A and B when Mn was applied alone. This decreased to 11 per cent in soil A when Mn was applied in combination with Zn, though it remained unchanged in soil B. These results seem to indicate that in soil B, more exchange sites specific for Mn were occupied by native Mn, and thus a greater fraction of applied Mn remained in soil solution. This may possibly be one of the reasons for higher mobility of Mn in soil B compared with soil A. In contrast to exchangeable Mn, exchangeable Ca and Mg were lowest in the upper 3 cm, increased to a depth of 6 to 9 cm and thereafter became nearly uniform in both the soils. (Fig. 2 and 3). Alternate leaching and drying treatment of soil B produced a fairly uniform distribution of exchangeable Mn, Ca, and Mg throughout the soil columns.

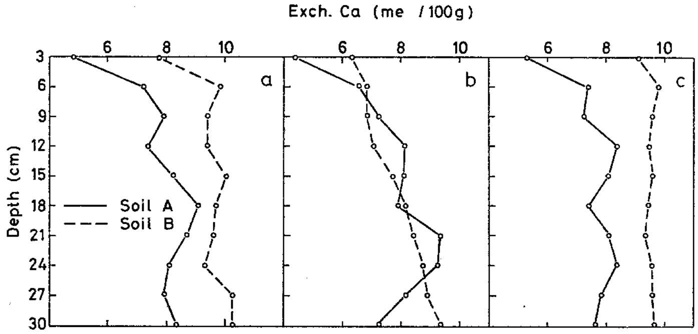

Fig. 2. Exchangeable calcium in soil columns leached with rain water equivalent to 300 mm (**a**), 1200 mm (**b**), and 1200 mm of precipitation in four 300 mm-portions in an alternate leaching and drying sequence (**c**).

Generally, the results presented in Tables 1 and 2 indicate that depth of penetration of Mn was higher in soil B than in soil A, which is contrary to the assumption that Mn mobility is limited in fine textured soils of high clay content and high CEC. The results, however, resemble those obtained previously for Zn [12]. Mn is known to be affected to a greater extent by redox potential, organic matter, and pH changes, and these effects will be discussed in further details to explain the differences observed in this paper.

(I). In soil B, leaching was relatively very slow as it took more than 6 months to leach about 10 litres of rainwater through soil columns. This extended period may affect the movement of Mn ions in two ways. (1) Through diffusion of Mn ions against the concen-

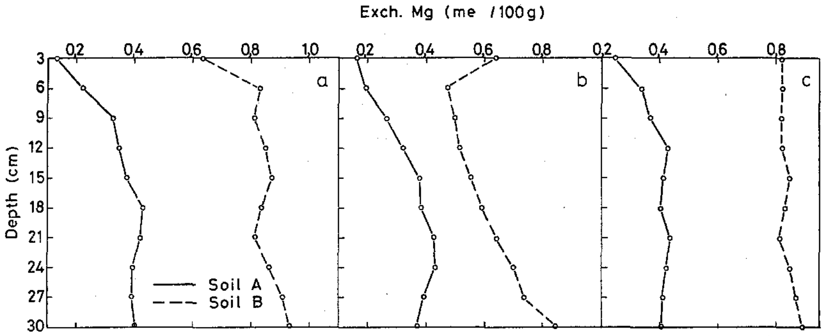

Fig. 3. Exchangeable magnesium in soil columns leached with rain water equivalent to 300 mm (**a**), 1200 mm (**b**), and 1200 mm of precipitation in four 300–mm portions in an alternate leaching and drying sequence (**c**).

tration gradient and movement with migrating clay particles as observed in case of Zn [12]. (2) Water-logging of the soil for an extended period may promote the growth of Mn reducing microorganisms, which reduce Mn oxides to soluble Mn^{++}, and consequently increase the mobility of Mn^{++} in soil columns. Schachtschabel [11] reported that Mn^{++} and exchangeable ions increase with decreasing redox-potentials associated with poor aeration under moist conditions, and with low pH values. Manganese accumulated to a greater extent under anaerobic than aerobic conditions [6 8]. MnO_2 can be reduced to Mn^{++} by certain compounds formed by microbial metabolism *e.g.*, H_2S [9].

(II). Manganese retention by clays is a function of pH. At pH 7.1 clay retained 31.5 per cent of total Mn added, whereas below pH 6.3 the retention was negligible [7]. The pH variation in the present soils were also of the same magnitude and possibly the lower pH in soil B may have promoted the movement of Mn.

(III). The relatively higher organic matter in soil B may also have influenced the movement of Mn. The application of natural organic materials to acid mineral soils was reported to increase the exchangeable and easily reducible Mn of the soil and this was due to biological reduction of Mn [2 3].

In comparison with data on zinc movement reported by the author in a previous paper [12], it can be seen that the movement of Mn under identical experimental conditions was greater than that of Zn when comparable amounts of Zn as $ZnSO_4$ were applied. This suggests that the two ions behave differently when applied under comparable soil conditions. This may be possibly due to the fact that Mn is more affected by the physical conditions of the soil than Zn, because, as Erkama [5] points out, any factor which influences the oxidation-reduction potential of the soil has a corresponding effect on the valence and activity of Mn.

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