

EFFECT OF CATIONS ON THE ADSORPTION AND RELEASE OF Mn^{2+} BY SOILS

PART II. Mn RETENTION BY HOMOIONIC SOILS

by S. G. MISRA and P. C. MISHRA, *Agricultural Chemistry Section,
Department of Chemistry, University of Allahabad, Allahabad*

(Communicated by S. P. Raychaudhuri, F.N.I.)

(Received 16 December 1967)

Unsaturation of soils leads to a decreased retention of manganese in comparison to the soils saturated singly with Ca^{2+} , Mg^{2+} and K^+ ions. Exchangeable manganese tends to attain highest value in the case of soils saturated with K^+ ions. A complete absence of reducible form of manganese is observed in the unsaturated soils (H-soils) prepared from alkali soil. Ca and Mg saturated soils behave almost alike.

INTRODUCTION

Cations present in soils have been found to play an important role in the retention and transformation of manganese applied to soils. It has been found (Heintze and Mann 1949) that Ca^{2+} is more effective than NH_4^+ in replacing Mn^{2+} hence the use of $Ca(NO_3)_2$ rather than ammonium acetate for the extraction of exchangeable form of manganese has been suggested.

Page (1962) observed pH to be functionally related with the complex formation with organic matter hence it affects much the retention and transformation of manganese applied to soil. Rich (1956) related pH with solubility and oxidation state of Mn compounds in soils and supports the view of Eriksson (1953)—'It may be safe to conclude that in freely drained soils most probably $pMn^{2+} - 2pH = O$ ', where pMn^{2+} is the negative logarithm of Mn^{2+} activity.

The present paper deals with the retention and transformation of manganese applied to homoionic soils prepared from the original black, red and alkali soils. This represents a case where exchange complex is saturated with respect to Ca^{2+} , Mg^{2+} , K^+ and H^+ ions.

EXPERIMENTAL PROCEDURE

Three surface samples of black, red and alkali soils have been used in the present study. These soil samples were collected from a Karail soil region of Ballia, Vindhyan hills of Mirzapur and an alkali soil patch of Allahabad districts of Uttar Pradesh. These soils were processed as described in Part I of this series (Misra and Mishra 1969).

Preparation of homoionic soils—H-, Ca-, Mg- and K-soils were prepared from the original soil samples. The H-soil was prepared by treating the samples with 0.1 N HCl. The soil : solution ratio was kept 1 : 10. The contents were shaken for one hour and then kept overnight. The liquid was separated from the soil by filtration the next day. The soil was washed thrice with 0.1 N HCl and then with water and lastly with alcohol. The soil was dried and powdered. This soil represents mainly H-soil of the original soils used which is unsaturated with respect to bases. Ca-, Mg- and K-soils* were prepared in the same way by treating the original soil samples with 1 N solutions of CaCl₂, MgCl₂ and KCl, respectively. These samples were utilized for the study of retention and release of manganese applied to soils. The pH of the original and derivative soils are reported in Table I.

TABLE I
pH of the soils used

Soils	Black	Red	Alkali
Original ..	8.0	6.4	9.7
H-soil ..	4.2	4.1	4.5
Ca-soil ..	7.5	7.1	8.8
Mg-soil ..	7.55	6.7	9.2
K-soil ..	8.7	7.5	9.9

Retention of Mn—In order to study the comparative retention of manganese by homoionic soils (derivative soils) 5 gm soil samples were taken in 100 ml pyrex conical flasks and 50 ml of MnSO₄ solution containing 110 and 1,100 ppm Mn was added. The soil with these solutions was shaken for one hour and the contents were kept in contact overnight. Next day, the solutions were filtered through Buchner funnels fitted with Whatman filter papers No. 42 using suction. The residues on the filter papers were washed free of Mn²⁺ ions by small lots of distilled water thrice in each case. The whole of the filtrates were utilized for the determination of manganese using colorimetric periodate method (Jackson 1962).

The filtrate thus obtained was transferred in a beaker and the contents were dried over a hot plate. Organic matter, if any, was destroyed by a treatment of nitric acid. The residue in the beaker was diluted by distilled water and 5 ml of phosphoric acid (Mn-free) was added. The KMnO₄ colour was developed using potassium periodate. The intensity of colour was measured using a green filter (515 m μ) in a Klett-Summerson photoelectric colorimeter.

* By such a treatment, all positions cannot be taken up by Ca, Mg or K hence practically we have Ca, Mg or K predominant soils rather than Ca-, Mg-, K-soils. The H-soils may be practically H-Al soils or Al-Ca soils.

The amount of Mn^{2+} retained by the homoionic soils used was obtained by subtracting the amount of Mn^{2+} present in the filtrates from the amounts of Mn^{2+} added to soils. This has been termed as R value or R form of Mn.

The washed soil, over the filter paper was again transferred into the same conical flask with the help of 50 ml of N ammonium acetate. The contents were shaken, kept overnight and filtered through a Buchner funnel fitted with Whatman filter paper No. 42 under suction. Manganese in the filtrate was determined as described above. This represented the amount of manganese retained in the exchangeable form, henceforth denoted by E form or E value.

The soil after the removal of exchangeable manganese was treated with 0.2 per cent hydroquinone in ammonium acetate. The contents were shaken, kept, filtered and manganese in the filtrate was determined as before. The manganese thus obtained represented the reducible form of Mn to be denoted henceforth by r form or r value of Mn.

The total of E and r has been represented by 'A value' which denotes 'available form' of Mn. The difference between R and A , i.e. ($R-A$), has been taken to be fixed form of manganese, henceforth denoted by 'F form' of Mn.

RESULTS AND DISCUSSION

The study on the role of competing cations will be incomplete if the effect of saturating the soils with monovalent and divalent cations such as H^+ , K^+ , Ca^{2+} and Mg^{2+} is not considered. These homoionic soils as used in this paper represent a state in which one cation saturates the exchange complex. Under natural conditions the soils are saturated with a number of cations and thus we have a mixed species of cations. Hence, while comparing the retention data of homoionic soils with the retention data of original soils, it has always to be kept in mind that a special case is being considered which is a deviation from the normal. But even then some important conclusions can be arrived at:

(1) H-soils (unsaturated soils) usually show lesser R values in comparison to Ca-, Mg- and K-soils. The order being H-soil < Ca-soil < Mg-soil < K-soil < original soil (= alkali soil). This relation holds better at 1,100 ppm Mn than at 110 ppm Mn. It appears primarily an effect of pH .

(2) E values show variable pattern at low concentration of Mn (110 ppm). H-soils show minimum E values in the case of red and alkali soils at 1,100 ppm of Mn added but at 110 ppm E values for H-soils are comparatively higher. But it is curious that in the case of H-soils most of the retained Mn is in the exchangeable form (Tables II and III).

(3) r values for H-soils are minimum at 1,100 ppm of Mn added whilst it is not so at 110 ppm of Mn. However, a salient feature is the absence of r form of Mn in H-soils obtained from alkali soil at both the levels of Mn addition. It is due to reducing action under acidic condition.

TABLE II
Effect of converting soils into homoionic soils on retention of applied manganese
 (Concentration of the Mn^{2+} added, 110 ppm)

Soils	R (ppm)	Forms in which manganese is retained (ppm*)				A/R
		E	r	A	F	
BLACK SOIL						
Original soil	.. 110	36	42	78	32	0.710
H-soil	.. 110	62	35	97	13	0.882
Ca-soil	.. 110	62	19	81	29	0.736
Mg-soil	.. 110	64	27	87	23	0.790
K-soil	.. 110	70	17	87	23	0.790
RED SOIL						
Original soil	.. 110	81	19	100	10	0.900
H-soil	.. 91	65	15	80	11	0.880
Ca-soil	.. 100	76	14	90	10	0.900
Mg-soil	.. 100	78	15	93	7	0.930
K-soil	.. 110	82	12	94	16	0.855
ALKALI SOIL						
Original soil	.. 110	27	48	75	35	0.682
H-soil	.. 79	56	nil	56	23	0.710
Ca-soil	.. 102	26	48	74	28	0.720
Mg-soil	.. 103	19	51	70	33	0.680
K-soil	.. 102	28	50	78	24	0.760

* Native manganese of soils has been deducted.

(4) A values are greater and F values are smaller for H-soils at both the levels of Mn additions. It is because of low pH conditions the persistence of higher oxides of Mn is meagre.

Unsaturation leads to the destruction of carbonates and other oxidizing agents, thereby the retention of manganese is lowered to a considerable degree. The per cent reduction in retention of manganese due to unsaturation for the three soils used is as follows:

Soils	Per cent reduction in retention	
	At 110 ppm Mn addition	At 1,100 ppm Mn addition
Black	.. nil	3.3
Red	.. 9.0	32.0
Alkali	.. 19.0	65.0

A lesser R value of H-soils in comparison to Ca-, Mg- and K-soils points to an unsaturation which leads to low pH (4.1-4.5), the K-soils have the

TABLE III

Effect of converting soils into homoionic soils on the retention of applied manganese
(Concentration of Mn^{2+} added, 1,100 ppm)

Soils	R (ppm)	Forms in which manganese is retained (ppm*)				A/R
		E	r	A	F	
BLACK SOIL						
Original soil	.. 984	576	178	754	230	0.770
H-soil	.. 952	730	70	800	152	0.832
Ca-soil	.. 1,012	665	162	827	185	0.817
Mg-soil	.. 1,018	665	165	830	188	0.818
K-soil	.. 1,083	720	145	865	218	0.800
RED SOIL						
Original soil	.. 705	476	79	555	150	0.800
H-soil	.. 478	319	38	357	121	0.747
Ca-soil	.. 696	504	68	572	124	0.820
Mg-soil	.. 709	514	66	580	129	0.818
K-soil	.. 960	748	47	795	165	0.830
ALKALI SOIL						
Original soil	.. 1,088	356	450	806	282	0.74
H-soil	.. 380	244	nil	244	136	0.642
Ca-soil	.. 704	391	158	549	191	0.741
Mg-soil	.. 807	382	203	585	222	0.720
K-soil	.. 922	622	134	756	166	0.820

* Native manganese of soils has been deducted.

highest pH of all the homoionic soils (8.7–9.5), hence the highest retention by K-soils can be related with the high pH of the soil.

Introduction of K^+ ions into the exchange-complex increases the exchangeable manganese which shows that K^+ ions are easily replaced by Mn ions from the exchange-complex than other cations.

A complete absence of the r form of the manganese in the H-soil prepared from alkali soil shows that all oxidizing conditions from alkali soils (i.e. the carbonates, thus the pH is lowered) have been removed. Whilst in black and red soils such conditions still prevail due to entrapped oxygen.

From the results obtained, it appears that the entry of Mn and the retention of Mn in general are not much favoured by bringing about such changes in soils as of completely transforming them into homoionic soils. The only exception is the H-soil, where the reducible form of Mn has little chance to be formed and that is in accordance with expectation. The pH value of H-soils vary in the range of 4.1 to 4.5 and at such a low pH the redox potential for the conversion of Mn^{++} to MnO_2 will not be favoured. However, Mn can occupy exchange positions.

Ca- and Mg-soils show a very small difference in the available and fixed form of manganese. If considered minutely, a mixed species in the exchange-complex is as good as homoionic system of soils in retaining Mn and converting it into *A* and *F* forms. The presence of exchangeable manganese in the homoionic soils saturated with divalent cations (Ca^{2+} , Mg^{2+}) is due to the similarity in the ionic radii of Mn^{2+} (0.91 Å) and Ca^{2+} (1.06 Å) (Goldschmidt 1954).

REFERENCES

- Eriksson, E. (1953). The physicochemical behaviour of nutrients in soils. *J. Soil Sci.*, 3, 238-252.
- Goldschmidt, V. M. (1954). Geochemistry edited by A. Muir. Clarendon Press, 225 and 621.
- Heintze, S. G., and Mann, P. J. G. (1949). Studies on soil manganese. Part I. Pyrophosphate as extractant of soil manganese. *J. Agric. Sci.*, 39, 80-95.
- Jackson, M. L. (1962). Soil Chemical Analysis. Asia Publishing House, pp. 187.
- Misra, S. G., and Mishra, P. C. (1969). Effect of cations on the adsorption and release of Mn^{2+} by soil. Part I. Effect of NH_4^+ , K^+ , Cu^{2+} and Fe^{2+} . *Proc. natn. Inst. Sci.*, A 35, 406.
- Page, E. R. (1962). Studies on soil and plant manganese. Part II. The availability of higher oxides to plants. *Pl. Soil*, 17, 99-108.
- Rich, C. I. (1956). Manganese content of Peanut leaves as related to soil factors. *Soil Sci.*, 82, 353-363.