

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

PART I. EFFECT OF NH_4^+ , K^+ , Cu^{2+} , Ca^{2+} and Fe^{2+}

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The retention and fixation of Mn^{++} applied to soils is greatly affected by the antagonistic effect of cations such as NH_4^+ , K^+ , Cu^{2+} , Ca^{2+} and Fe^{2+} . The presence of Fe^{2+} ions in the system increases the availability due to the redox processes taking place in the soil.

INTRODUCTION

Boken (1956a) has shown that a dressing of ferrous sulphate could act as manganese dressing on several soils. She has further suggested (Boken 1956b) that hydroquinone and ferrous sulphate can extract the reducible form of manganese equally well and found exchangeable Mn to increase considerably by the addition of ferrous sulphate to the extracting agent. Page (1962) observed that an increase of 21 per cent in the yield of dry matter and an increase of about 200 per cent in manganese uptake per pot took place when pyrolusite was added with ferrous sulphate in comparison to pyrolusite alone.

Heintze and Mann (1947, 1949) were the first to report that some manganese of soils forms a complex with organic matter. They observed that ammonium acetate containing inorganic salts extracted more manganese than did ammonium acetate alone. Passioura and Leeper (1963) have reported that both quinol and copper sulphate extract the same amount of manganese from organic soils hence copper has got solubilizing effect on higher oxides of manganese.

Gilbert (1934) demonstrated that a pH range of 6.8-7.6 was related to manganese deficiency which could be overcome by the application of ammonium sulphate. But Burtrom (1940) found that in the presence of available nitrogen the availability of Mn is reduced. Heintze (1946) is also of the view that, in the presence of nitrifiable nitrogen, the availability of Mn is reduced.

Kitchener (1957) suggested a lyotropic series for anion-exchange resin and found that the series holds good for soils also.



According to Page (1964), this evidence should not be taken to mean that divalent Mn^{2+} always assumes this relationship towards Ca^{2+} . This may be changed according to anionic field strength of exchangers as has been demonstrated by Eiseman (1962). Heintze and Mann (1949) showed that Ca^{2+} was more effective in preventing the uptake of Mn by plants.

The present paper deals with the effect of cations on the retention and transformation of manganese added to soils.

EXPERIMENTAL PROCEDURE

Three soil samples (black, red and alkali) collected from Ballia, Mirzapur and Saraon tehsils of Ballia, Mirzapur and Allahabad districts of Uttar Pradesh have been used. These soils were air-dried in the shade, powdered by rubbing the soil with a wooden hammer and sieved through a 100 mesh sieve and were used for the study of retention and transformation of applied manganese.

For retention studies 5 g of soil samples were taken in 100 ml conical flasks and 50 ml of $MnSO_4$ solution containing 1100 ppm Mn was added. The soil with solution was shaken for 1 hr and, after keeping it for 18 hr, was filtered through a Whatman filter paper No. 42, fitted on a Buchner funnel using suction. The residue on the filter paper was washed free of Mn^{2+} ions by small lots of distilled water thrice in each case. The amount of Mn^{2+} ions in the filtrates was determined colorimetrically following the method outlined in Jackson's book (1962).

The filtrate thus obtained was dried over a hot plate and then the organic matter was destroyed by the treatment of HNO_3 . The residue then remaining in the beaker was diluted. To this 5 ml of phosphoric acid (Mn-free) was added and the colour of $KMnO_4$ was developed using potassium periodate. The intensity of the colour was measured using green filter (515 $m\mu$) in a photoelectric colorimeter.

The amount of Mn^{2+} retained by the soil was obtained by subtracting the amount of Mn^{2+} in the filtrates from the amount of manganese added originally. This amount has been represented by R form or R value.

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 again shaken for 1 hr and kept for 18 hr as before and the solution was separated by filtration the next day. The soil on the filter paper was washed thrice with N ammonium acetate to remove any Mn^{2+} adhering on the surface. The manganese in the filtrate was determined as before. This represented the amount of manganese retained in the exchangeable form which will be henceforth denoted by E form or E value.

The soil remaining on the filter paper after the removal of exchangeable manganese was treated with 50 ml of N ammonium acetate containing 0.2 per cent hydroquinone. The contents were shaken, kept and filtered as before.

The manganese obtained in the filtrate gives the value of manganese retained in the reducible form, to be denoted henceforth by r value or r form of Mn. The total of $E+r$ form has been represented as A value, which denotes available form of manganese. The difference between the R and A , i.e. ($R-A$), has been taken to be 'fixed form' of manganese, henceforth denoted by ' F form' of Mn.

In order to find out the effect of NH_4^+ , K^+ , Fe^{2+} , Cu^{2+} and Ca^{2+} ions on the retention and transformation of added manganese by soils, five doses of the above cations in the form of $(\text{NH}_4)_2\text{SO}_4$, KH_2PO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, FeSO_4 and CuSO_4 and 50 ml manganese sulphate solution containing 1100 ppm Mn were added to 5 g of soils. The retention of Mn^{2+} ions and their transformation in the presence of these cations were determined as before.

RESULTS AND DISCUSSION

Soil is a heterogenous system where many species of ions (cations and anions) are found both in the exchange-complex and outside it in the solution. They, thus, influence the retention and transformation of manganese in soils depending upon their concentration. If the cations are added to a soil, they are bound to exhibit their effect on retention and fixation of manganese applied to soil in a soluble form. From the results given in Table I, it is observed that maximum Mn^{2+} is retained by alkali soil followed by black soil and least by the red soil.

TABLE I
Retention of manganese by the soils used
(Concentration of Mn^{2+} added, 1100 ppm)

Soils	R (ppm)	Forms in which manganese is retained (ppm*)				A/R
		E	r	A	F	
Black ..	983	578	175	753	230	0.77
Red ..	705	484	76	556	149	0.80
Alkali ..	1088	364	442	806	282	0.74

* Native manganese of soils has been deducted.

The introduction of these cations in increasing doses leads to a decrease in the retention of Mn^{2+} by the soil from manganese sulphate solution. In alkali soil Cu^{2+} , Fe^{2+} and NH_4^+ ions do not seem to affect the retention of manganese (Table II, Figs. 1-4).

The cations, when added to a soil, can affect the retention of Mn in two ways:

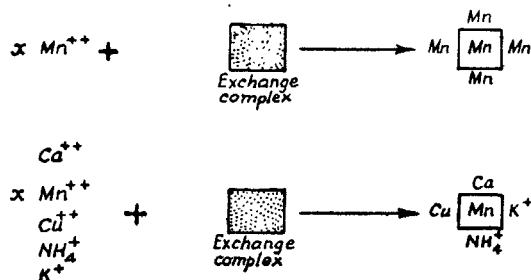
(1) *Cations may compete with Mn^{2+}* —In the presence of competing cations such as NH_4^+ , K^+ , Fe^{2+} , Cu^{2+} and Ca^{2+} , the chances for the entry of Mn^{2+}

TABLE II
Effect of copper sulphate on the retention of applied manganese
 (Concentration of Mn^{2+} added, 1100 ppm)

Cu^{2+} added (ppm)	<i>R</i> (ppm)	Forms in which manganese is retained (ppm*)				<i>A/R</i>
		<i>E</i>	<i>r</i>	<i>A</i>	<i>F</i>	
BLACK SOIL						
Control	983	578	175	753	230	0.770
200	963	614	136	750	213	0.780
400	951	622	122	744	207	0.782
600	936	614	118	732	204	0.782
800	916	614	99	713	203	0.780
1000	900	618	78	696	204	0.767
RED SOIL						
Control	705	484	76	556	149	0.800
200	586	448	36	484	102	0.820
400	524	402	30	432	92	0.824
600	452	358	22	380	72	0.840
800	425	325	17	342	83	0.805
1000	398	298	14	312	86	0.789
ALKALI SOIL						
Control	1088	364	442	806	282	0.740
200	1088	356	450	806	282	0.741
400	1089	356	452	808	281	0.741
600	1088	356	452	808	280	0.742
800	1087	364	442	806	281	0.741
1000	1087	356	450	806	281	0.741

* Native manganese of soils has been deducted.

into the exchange-complex decrease. Hence decrease in *E* values is observed, because less Mn^{2+} will enter into the exchange positions and even lesser positions will be actually occupied at the surface of soil colloids. Thus a decreased retention will take place.



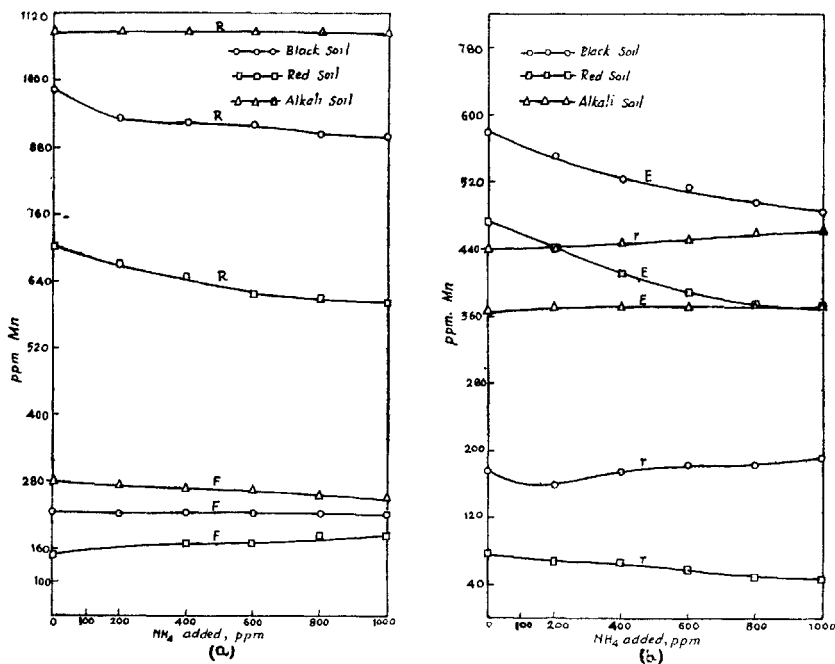


FIG. 1. (a) Effect of NH_4^+ [added as $(\text{NH}_4)_2\text{SO}_4$] on the retention and fixation of added manganese. (b) Effect of NH_4^+ [added as $(\text{NH}_4)_2\text{SO}_4$] on the distribution of retained manganese into exchangeable and reducible forms.

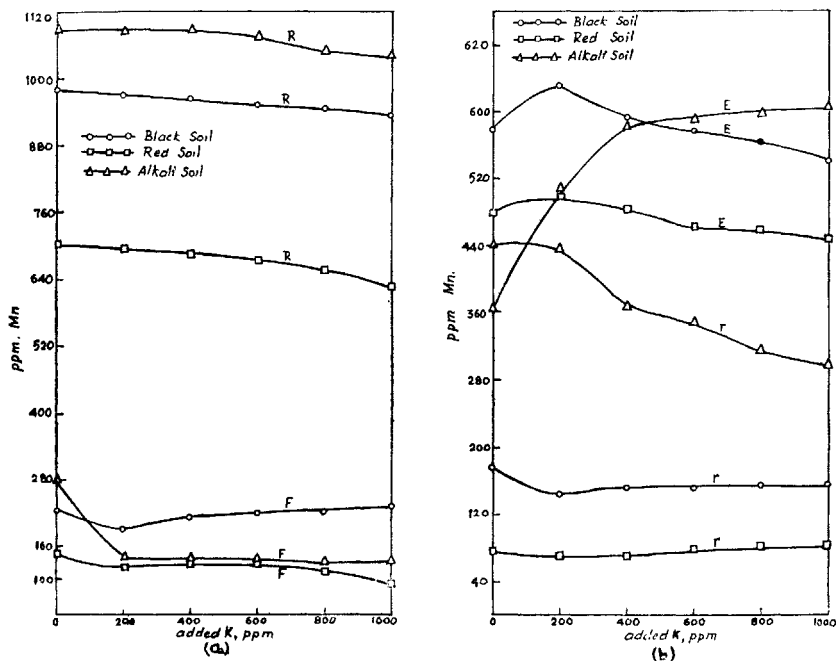


FIG. 2. (a) Effect of K^+ (added as KH_2PO_4) on the retention and fixation of added manganese. (b) Effect of K^+ (added as KH_2PO_4) on the distribution of retained manganese into exchangeable and reducible forms.

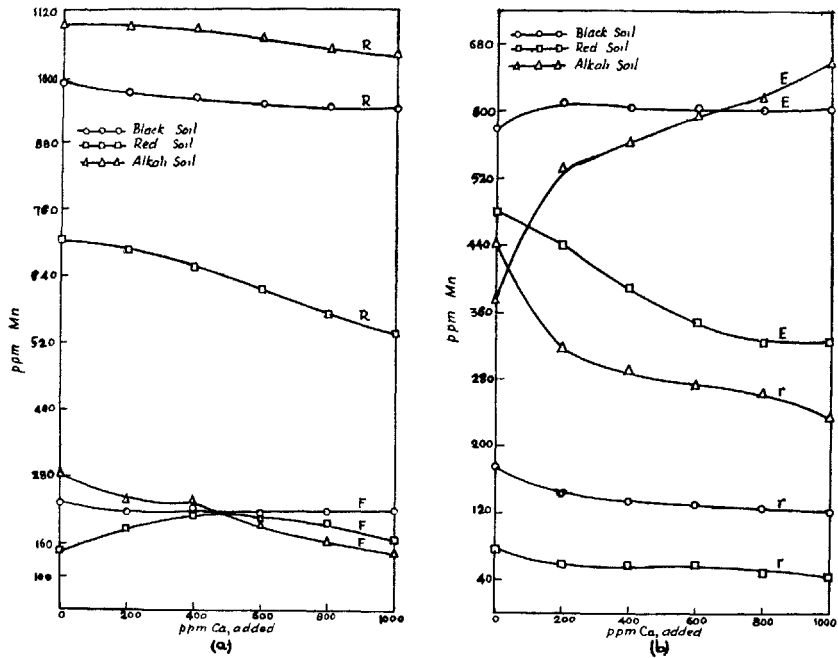


FIG. 3. (a) Effect of Ca^{2+} (added as monocalcium phosphate) on the retention and fixation of added manganese. (b) Effect of Ca^{2+} (added as monocalcium phosphate) on the distribution of retained manganese into exchangeable and reducible forms.

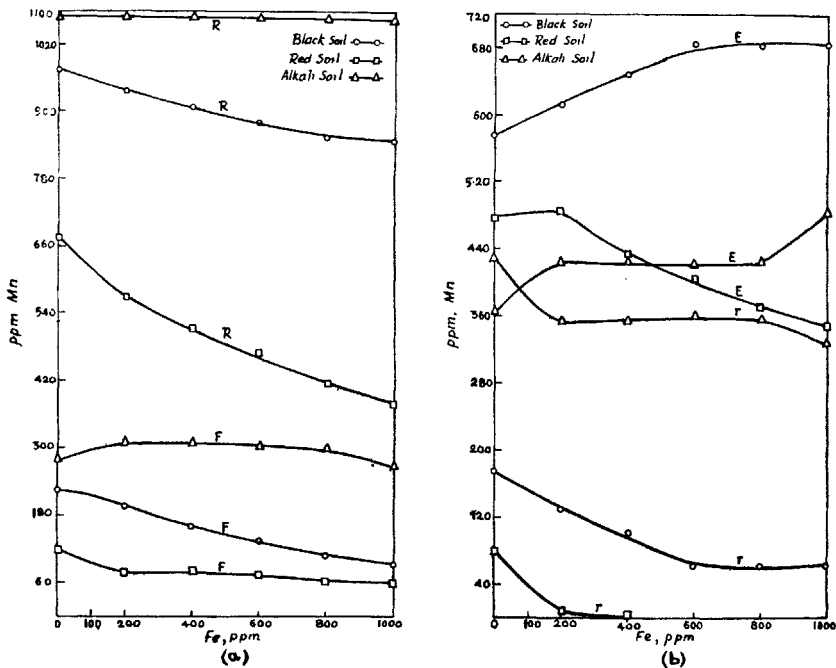
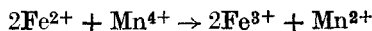


FIG. 4. (a) Effect of Fe^{2+} (added as ferrous sulphate) on the retention and fixation of added manganese. (b) Effect of Fe^{2+} (added as ferrous sulphate) on the distribution of retained manganese into exchangeable and reducible forms.

(2) The cations can give rise to decreased retention by competition but the most important explanation for a decreased retention will be that added Fe^{2+} in soils can be oxidized at the cost of MnO_2 reduction and a decreased value of the reducible form of Mn (r value) is obtained.



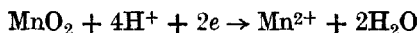
In the presence of ferrous sulphate, the higher oxides, thus reduced, will increase Mn^{2+} in soil solution in equilibrium, thereby the manganese released will either enter into exchange positions or if more competing ions are present it may come in the leachate as water soluble Mn.

Cations, which have no oxidized states, can effect the retention only by competing with Mn^{2+} to enter into the exchange-complex. These cations will not be effective in reducing higher oxides hence there are no chances of higher oxides being reduced (an exception being Cu^{2+}).

Copper has variable valency and it has been found to decrease the formation of higher oxides. Passioura and Leeper (1963) are of the opinion that copper sulphate has solubilizing effect on higher oxides of Mn, the reason being unknown. Thus Cu^{2+} will bring some manganese in a soluble state thereby increasing water soluble or exchangeable Mn. In this respect it is similar to Fe^{2+} .

Introduction of NH_4^+ , as it is used for the exchangeable manganese determination, causes reduction in E form of Mn. The effect of nitrogen on the availability of manganese as studied by Burtrom (1940) is that the availability of manganese in the presence of available nitrogen is reduced. Heintze (1946) supports Burtrom's views and has found that marsh spot could be induced in peas grown on a soil rich in available manganese by injecting simple inorganic or organic nitrogen compounds.

The production of acidity in the soil system results in a dissolution of higher oxides by reduction.



The low $p\text{H}$ values brought about by H^+ in soil system are bound to affect the redox potential of the system, hence conversion of Mn^{2+} to MnO_2 will be suppressed.

The effect of either K^+ or Ca^{2+} are not very marked hence they have been excluded from the explanation.

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