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THE 'EASILY REDUCIBLE' MANGANESE OF SOILS

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(With Seven Text-figures)

The chemical investigation of manganese-deficient soils for diagnostic purposes has been largely confined to estimations of exchangeable and 'easily reducible' manganese. Exchangeable manganese is usually regarded as the immediate source of this element to plants, while 'easily reducible' manganese is sometimes considered (Leeper, 1935, 1939) to be the active part of the manganese oxides of the soil which functions as an important source of divalent manganese after reduction. Leeper classified the manganese oxides of soils into three groups: (1) active, oxidizing hydroquinone at pH 7·0; (2) moderately active, oxidizing hydroquinone at pH 2·0; and (3) inert, which does not oxidize hydroquinone under either of these conditions. The active group, suggested as important in supplying manganese to the plant, is estimated by extracting with ammonium acetate and hydroquinone at pH 7·0. Leeper (1935, 1939) regards the higher manganese oxides of soils as forms of MnO_2, or Mn_2O_3. Naftel (1934) brought forward evidence favouring Mn_2O_3. Leeper considered that these oxides varied in reducibility in much the same way as the activity of colloids alters with ageing, and considered it possible that the 'active' forms of soil manganese are the freshly precipitated colloidal fractions.

Leeper's fractionation, apparently suggested by investigations on the error due to manganese oxides in measuring pH by the quinhydrone electrode, is based on data showing that certain Australian soils with manganese deficiency have small amounts of 'easily reducible' manganese. Sherman & Harmer (1942) have studied the method in the United States and are apparently satisfied that there is a relation between the amount of hydroquinone-reducible manganese in soils and the appearance of manganese-deficiency symptoms in crops. Heintze (1938, 1946) has shown, however, that soils not giving symptoms of manganese deficiency may have values for exchangeable and easily reducible manganese even lower than those for deficient soils.

The isolation of relatively large amounts of three-valent manganese from soils (Dion & Mann, 1946) suggested the possibility of linking the 'easily reducible' manganese in soils with the type of manganese oxide present. The present work was undertaken with the object of studying the reducibility of four-valent and three-valent manganese oxides at a range of pH values under different reducing conditions. It was considered that such a study might help to explain the nature of the factors controlling the values obtained for 'easily reducible' manganese in different soils.

EXPERIMENTAL

This investigation has two phases: the investigation of factors controlling the reducibility of the manganese of the soil, and the investigation of differences in the reducibility of higher manganese oxides.

The reducibility of soil manganese

For this study two soils were selected which, when extracted with ammonium acetate and hydroquinone at pH 7·0, yielded appreciably different proportions of their total manganese content. The soils were a clay loam from Rothamsted, derived from clay-with-flints, which had a total manganese content of 1480 p.p.m., a pH of 7·9 and a content of three-valent manganese of 450 p.p.m., and a marsh soil from Romney Marsh, Kent, which had a total manganese content of 300 p.p.m., a pH of 7·6, and a content of three-valent manganese of 95 p.p.m. The latter was from a field known to be manganese-deficient.

In addition to studying a range of pH values for the extractions other factors were investigated. Heintze (1946) had already used hydroquinone in calcium nitrate solution as an extracting solution, and a comparison by this method with those obtained by using hydroquinone in ammonium acetate indicated a real difference in the amount of manganese extracted. Further, Leeper (1935) had commented on the inconvenience of using hydroquinone, since it is difficult to remove before the manganese determination. Mann & Quastel (1946) had used hydroxylamine as the reducing agent in a gasometric estimation of manganese dioxide. We therefore investigated on two soils the amounts of manganese extracted at different pH values between 4·0 and 8·0 by shaking with either N $Ca(NO_3)_2$ or

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N NH₄Ac solution, in combination with either hydroquinone or hydroxylamine as reducing agents.

Method. Mixtures of 5·0 g. samples of finely ground soil and 100 ml. of the salt solution were adjusted to give a range in final pH values from 4·0 to 8·0 and then 0·2 g. of the reducing agent was added. The flasks were shaken for an hour and the pH measured with the glass electrode. The suspensions were filtered clear, and manganese estimations carried out on an aliquot of the filtrate, using the periodate method of Willard & Greathouse (1917), in the presence of nitric and phosphoric acids.

The curves showing the results obtained with the two soils are given in Figs. 1 and 2. Certain aspects of the curves are similar in both cases, and should be generally applicable, viz. the amount of manganese

tions, therefore, calcium nitrate solutions are less suitable than ammonium acetate solutions.

One noticeable difference exists between the sets of curves for the two soils. A much larger part of the reducible manganese of the mineral soil from Rothamsted is extracted at pH 7·0 than is the case with the marsh soil. The results are tabulated in Table 1.

Table 1. *Manganese extracted at pH 7·0*
(expressed as percentage of that extracted at pH 4·0)

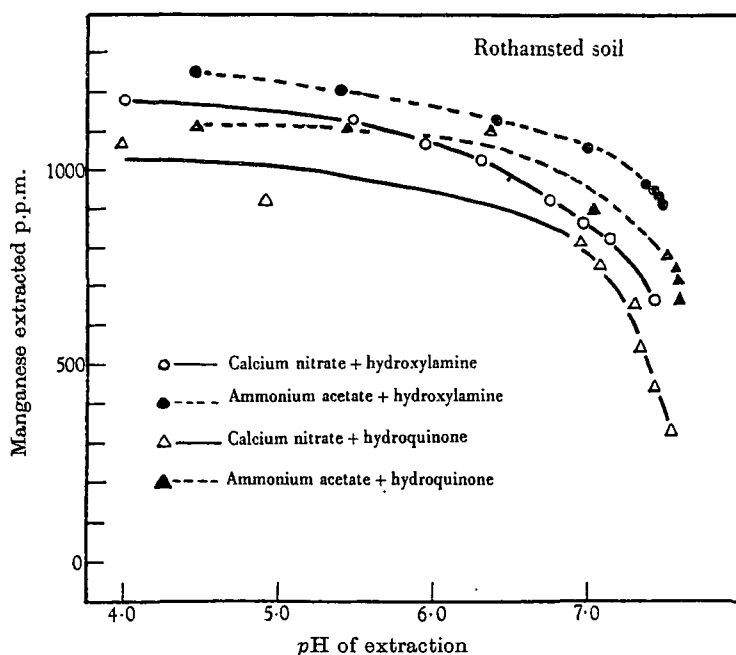| Reducing system	Marsh soil	Clay loam
Ca(NO₃)₂, hydroxylamine	53	75
Ca(NO₃)₂, hydroquinone	36	73
NH₄Ac, hydroxylamine	61	84
NH₄Ac, hydroquinone	60	76

Fig. 1.

extracted is controlled by the pH of the system, the nature of the salt solution and the nature of the reducing agent, as well as by the actual amount and forms of manganese present. Hydroxylamine extracts more manganese than hydroquinone, and ammonium acetate more than calcium nitrate, all other things being equal. Less manganese is extracted as the acidity is decreased, the curves beginning to fall off more rapidly above pH 5·5, and in general being quite steep at pH 7·0 and above.

Because of the large effect of pH in determining the amount of manganese extracted in any system, it is obvious that a well-buffered system is essential for any measurements of this type. For these determina-

The reducibility of higher manganese oxides

It seemed possible that the difference in the reducibility of the higher manganese oxides of the two soils studied in the previous section might lie in the presence of different manganese oxides in the soils. This was investigated by extracting oxides of known composition with the above reducing systems and determining the recovery.

Materials and methods

Four oxides of manganese were available: pyrolusite (MnO₂), manganite (MnO(OH)), hausmannite (Mn²⁺Mn₂³⁺O₄) and a synthetic preparation of

'manganic hydroxide'. Two specimens of pyrolusite were used: one a commercial product precipitated from potassium permanganate, and one a naturally occurring pyrolusite. The identity of the various oxides was verified by X-ray diffraction analyses and the purity was estimated by manganese analyses.

The sample of 'manganic hydroxide' was prepared according to the procedure of Meyer & Nehrlich (1921) by bubbling air through an ammoniacal solution of $MnCl_2 \cdot NH_4Cl$. After centrifuging, washing and drying, it had an actual manganese

Figs. 3–6 show the values obtained with the different reducing systems.

The different oxides fall into two contrasting groups, pyrolusite and the synthetic 'manganic hydroxide' forming a highly reducible group, while manganite and hausmannite form another group which is only slightly reducible under these conditions.

There appears to be little difference in the action of pyrolusite, the four-valent form, and the synthetic '$Mn(OH)_3$', although the pyrolusite in general
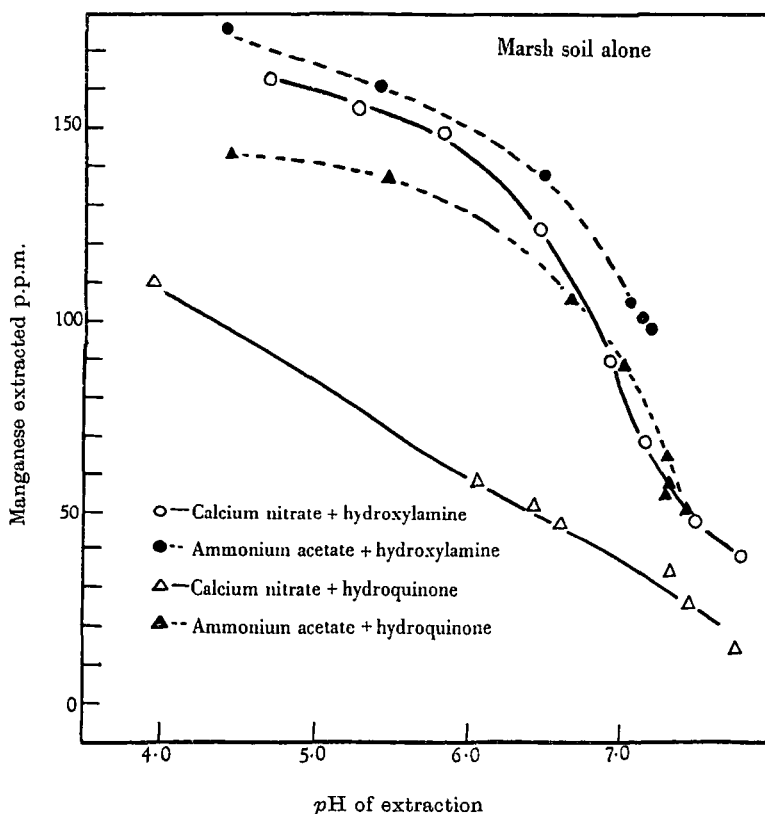

Fig. 2.

content of 68 % and a mean manganese valency of 2·73 instead of the theoretical values of 51·9 % and 3·0 respectively.

The oxides were ground in a mechanical agate mortar, where necessary, and, to simplify the weighing of small quantities, were diluted with nineteen times their weight of Kieselguhr.

Each oxide was added to 5 g. samples of finely ground marsh soil to give 1000 p.p.m. of added manganese. Since the marsh soil used in the previous section was low in both total and reducible manganese, it would not mask the effects contributed by the added oxides.

seems to be slightly more reducible, except in calcium nitrate solution at pH values below 6·0. Recoveries of added manganese are high in all cases up to pH 7·0 with these two oxides, with the single exception of '$Mn(OH)_3$' in calcium nitrate and hydroquinone near the neutral point.

Manganite ($MnO(OH)$) can release only a small part (less than 20 %) of its manganese in these reducing systems. Its reducibility varies appreciably with pH.

Hausmannite ($Mn\,Mn_2O_4$) has little or no manganese reducible in these systems at pH 6·0 and above. Below pH 6·0, the amount of manganese

2–2

released by reduction is fairly sensitive to pH, but it remains relatively low even at pH 4·0.

Table 2 gives the values for the amounts of manganese released by the different oxides in the four reducing systems.

manganese deficiency, because pyrolusite is not usually considered to be directly available to plants, and additions of pyrolusite to soils rarely correct manganese deficiencies in crops.
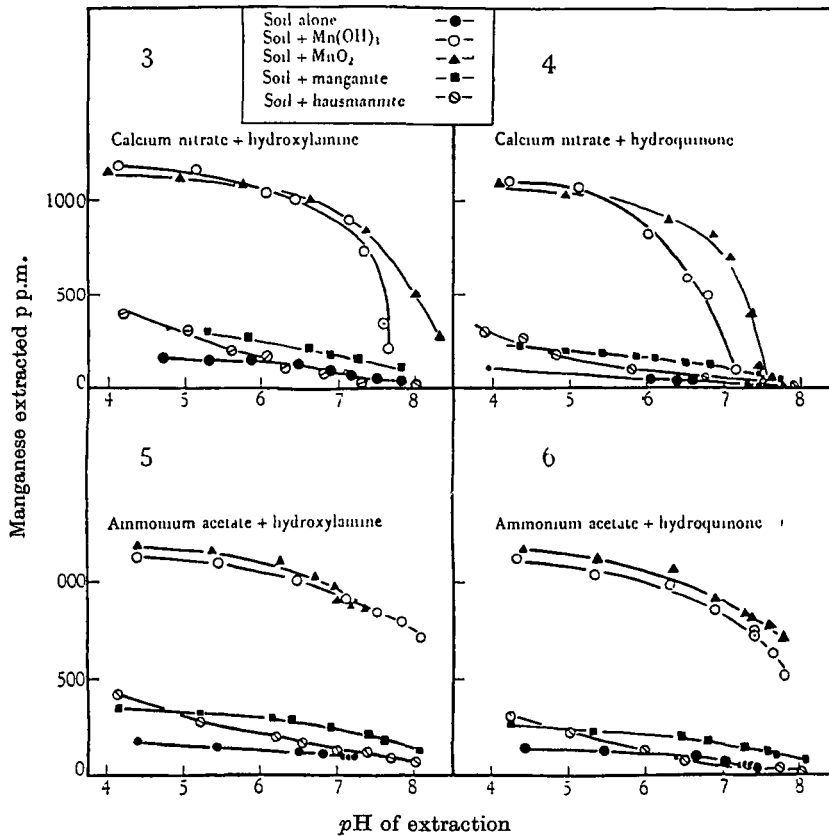
Figs. 3–6.

Table 2. *The reducibility of higher manganese oxides at pH 4·0 and 7·0*

| | Percentage of added manganese recovered | | | | | | | |
| | pH 4 0 | | | | pH 7·0 | | | |
Reducing system	MnO_2	'$Mn(OH)_3$'	$MnO(OH)$	$Mn\ Mn_2O_4$	MnO_2	'$Mn(OH)_3$'	$MnO(OH)$	$Mn\ Mn_2O_4$
$Ca(NO_3)_2$, hydroxylamine	98	102	15	23	83	81	9	−1
$Ca(NO_3)_2$, hydroquinone	100	100	12	27	70	24	7·5	0
NH_4Ac, hydroxylamine	100	96	17	26	83	83	14	2·0
NH_4Ac, hydroquinone	101	99	12	18	81	75	8	−2·0

four reducing systems. The values were obtained from the curves of Figs. 3–6 by extrapolating the curves where necessary and correcting the values for the curves of the soil-plus-oxide by the amount contributed by the soil alone.

The results differentiate clearly between 'easily reducible' and 'difficultly reducible' manganese. If the form of manganese dioxide occurring in the soil behaves in the same way as added pyrolusite, it is unlikely that the determination of 'easily reducible' manganese will be of much value in diagnosing

The effect of particle size and time of extraction on the reducibility of pyrolusite

Since Leeper (1935) considered 'colloidal MnO_2' to be one of the active forms of soil manganese, it was thought that ammonium acetate and hydroquinone at pH 7·0 might discriminate 'colloidal MnO_2' from larger inactive particles. An estimation which differentiated between size fractions might also be sensitive to time of extraction.

An experiment was designed to test this proposi-

tion; two size fractions of the pyrolusite obtained by sieving the commercial sample through bolting cloth were added to marsh soil and extracted at a final pH value of 7·0 in the manner already described for periods of 1, 3 and 6 hr. with hydroquinone as reducing agent. The results appear in Table 3 In

Table 3. *The effect of particle size and time of extraction on reducibility of* MnO_2 *added to the soil*

| Extracting system | Time hr. | Mn extracted p p m | |
		'Coarse' MnO_2	'Fine' MnO_2
Ca(NO$_3$)$_2$, hydroquinone	1	720*	800*
	3	890	965
	6	1095	1080
NH$_4$Ac, hydroquinone	1	860†	890†
	3	940	975
	6	1010	1010

* Including 40 p p m. from soil alone.
† Including 90 p p m. from soil alone

Table 3, again showing no difference in reducibility with ammonium acetate and hydroquinone at pH 7 0.

While the data in Table 3 do not suggest that ammonium acetate and hydroquinone at pH 7·0 is effective in differentiating between large and small particles of MnO_2 in soils, there is definite indication of a time effect in the extraction. The curves in Figs. 3–6, showing the great influence of pH on the reducibility of MnO_2, could possibly be explained on the basis of a pH control of the *speed* of the reduction To test whether slow reduction was responsible for the relatively small amounts of MnO_2 made soluble under alkaline conditions, mixtures were shaken for periods of 2, 4 and 6 days with final pH values in the range 6·8–8·5. The results appear in Fig 7.

It is apparent that above pH 7·0 the longer periods of shaking actually extract less. This may result

Marsh soil with 1000 p p.m
Mn added as MnO_2

× 1 hour figures
○ 2 day figures
○ 4 day figures
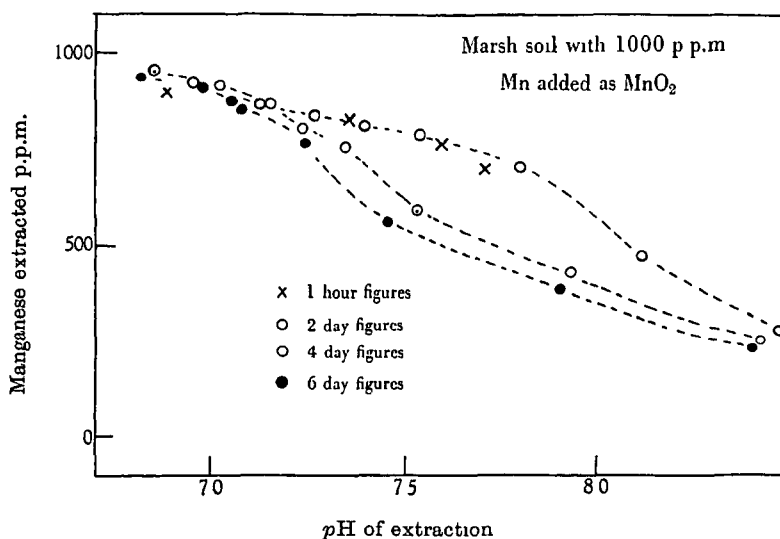● 6 day figures

pH of extraction

Fig. 7.

ammonium acetate and hydroquinone, there seems to be no appreciable difference in the behaviour of the 'coarse' and 'fine' fractions, irrespective of the time of extraction. In calcium nitrate and hydroquinone, the 'fine' fraction seems to be reduced a little more rapidly than the 'coarse', although the result at the end of 6 hr. is the same. In both reagents, however, the recoveries are high in all cases.

These extractions were repeated using 'fine' and 'coarse' samples of the naturally occurring pyrolusite, since the precipitated MnO_2 used previously might have consisted of very small particles throughout, the large particles being merely aggregates. However, the results with the naturally occurring pyrolusite agreed very well with those shown in

from either an autoxidation of the reduced manganese or an absorption reaction, possibly involving the oxidation products of hydroquinone. It is obvious, in any case, that the decrease in the reducibility of MnO_2 and '$Mn(OH)_3$' at and above the neutral point in the reducing systems studied is not due simply to a slower rate of reduction.

DISCUSSION

The results presented indicate some of the complexities involved in treating the soil manganese with reducing systems In addition to the nature and amount of the higher oxides present, the nature of the salt solution, the nature of the reducing agent and the time of contact, all seem to exert some effect

on the amount of manganese reduced at comparable pH values. It is probable that still other factors will be found to control the apparent reducibility of the oxides present. In the present stage of our knowledge of soil manganese, it would seem advisable to proceed with caution in using analytical methods for 'easily reducible' manganese until more is known of the nature of the compounds contributing to this fraction, the factors influencing the magnitude of the observed values and of the actual diagnostic value of the method in the field.

It has been shown that pyrolusite is reduced by ammonium acetate and hydroquinone at pH 7 and would therefore be classified as easily reducible manganese. Thus, there is no reason to assume that the easily reducible fraction of soil manganese as determined by this test exists in a colloidal form of high reactivity as suggested by Leeper (1935) and Sherman & Harmer (1942).. If, however, it is possible in certain regions to use this form of manganese to distinguish between deficient and healthy soils, it would appear that the manganese of such deficient soils occurs in a less easily reducible form than pyrolusite.

On the other hand, there are indications that higher manganese oxides in a form more easily reducible than pyrolusite may occur in soils. Thus Heintze (1946) found that when manganese salts were incubated with soils the oxidation products could in general be recovered by calcium nitrate and hydroquinone at alkaline reactions. Since the reducibility of both pyrolusite and 'manganic hydroxide' falls off rapidly at pH values above 7, it would appear that the freshly formed manganese oxides in such soils possess a high reactivity and would thus resemble the active forms suggested by Leeper. It appears possible that this reactive oxidation product could be differentiated either by the use of ammonium acetate and hydroquinone at alkaline pH values or by the use of a weaker reducing agent than hydroquinone or hydroxylamine. Further investigation of this question is in progress along these lines.

SUMMARY

1. In studying the factors influencing the 'easily reducible' manganese in soils, results were obtained to indicate that the estimation is dependent on the pH of the system, the nature of the salt solution, the nature of the reducing agent and the time of contact, in addition to the amount and nature of the higher oxides of manganese present.

2. Pyrolusite (MnO_2) and a synthetic preparation of manganite hydroxide are 'easily reducible' oxides, while manganite ($MnO(OH)$) and naturally occurring hausmannite ($Mn\,Mn_2O_4$) are apparently 'difficultly reducible' forms.

3. Since pyrolusite occurs in the easily reducible fraction, those deficient soils which contain only a small proportion of their manganese in the easily reducible form must contain the larger part in a form less reactive than pyrolusite.

4. The substitution of hydroxylamine hydrochloride for hydroquinone in Leeper's procedure is suggested, to avoid the troublesome destruction of hydroquinone prior to the colorimetric manganese estimation. It gives results of the same general order as hydroquinone in ammonium acetate solutions, but is slightly more efficient in reducing manganese in all cases tested.

5. Some modification is necessary in the methods for estimating reducible manganese if it is required to demonstrate the presence of manganese oxides more reactive than pyrolusite.

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