INFLUENCE OF MANGANESE AND IRON SALTS ON THE OXIDATION OF ORGANIC MATTER AND RELEASE OF PLANT NUTRIENTS.

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INTRODUCTION.

It was shown in a previous communication on the subject (Harihara Iyer, Rajagopalan and Subrahmanyan, *Proc. Indian Acad. Sci.*, 1935, **2B**, 108) that treatment of the soil with manganous sulphate in large amounts did not produce any appreciable increase in the yield of crops. The possibility was, however, indicated of getting adequate crop return if this chemical be used in smaller doses.

The present paper relates to further work done on the subject to elucidate the behaviour of manganous sulphate and potassium permanganate on application to the soil: how they react with soil and how crops respond to such treatments. The work also deals with the effect on growth of dressings of ferrous sulphate and ferric sulphate, in view of the beneficial effects obtained on using ferric oxide. (Harihara Iyer, Rajagopalan and Subrahmanyan, *Proc. Indian Acad. Sci.*, 1934, **1B**, 106).

Considerable amount of work has been done on the use of soluble manganese salts to improve crop yields. Most of it, however, deals with the study of manganese as an essential element in water cultures or to its use to combat deficiency diseases (Hiltner, *Ras. Intern. Agron.*, 1926, **450**, 3; Gilbert, McLean and Hardin, *Soil Sci.*, 1926, **22**, 437; Gilbert and McLean, 1928, *Soil Sci.*, 1928, **26**, 27; Schreiner and Dawson, *Ind. Eng. Chem.*, 1927, **19**, 400; Samuel and Piper, 1928, *Jour Dept. Agric. S. Austr.*, **31**, 696; Willis, *N. C. Agric. Expt. Sta. Fertilizers*, 1928, **9**, 17; Clark, *Plant Physiol.*, 1933, **8**, 157; Saegar, Amer. J. Bot., 1933, **20**, 234; also, Brenchley, Inorganic Plant Poisons and Stimulants, 1927, Camb. Univ. Press).

Very little information is available regarding the use of soluble manganese salts to improve crop growth on normal soils, though the possibility of manganese aiding the oxidation processes in the soil has been recognised for a long time. (Kelley, *Hawaii Sta. Bull.* 1912, **26**, 7; *Bot. Gaz.*, 1914, **57**, 213; Skinner, Sullivan *et al.*, *U. S. Dept. Agric. Bull.*, 1914, No. 42: 32: Skinner and Reid, *U. S. Dept. Agric. Bull.*, 1916, No. 441: 12). Indeed, the oxidizing power of good soils has been attributed to their larger content of manganese as dioxide (Stuart, *Proc. Hawaiian Sug. Planters' Assoc., 47th Annual Meeting*, 1927, 134).

Work on soluble iron salts has also been mainly confined to the study of the physiological role of iron in plant nutrition. Where iron salts have been used in agriculture, it has been mainly with a view to cure 'chlorosis' and such deficiency symptoms (Gile, *Porto Rico Agric. Expt. Sta. Bull.*, 1911, No. 11; Johnson, *Jour. Ind. & Eng. Chem.*, 1917, **9**, 47; *Hawaii Sta. Rept.*, 1918, No. 23; Gile and Carrero, *Jour. Agric. Res.*, 1920, **20**, 33).

EXPERIMENTAL.

Pot trials with tomatoes to study the effect of manganese and iron salts on crop growth.—Pots were made up in the usual way with mixtures of red earth (20 lbs.) and sand (10 lbs.) and treated with hongay cake (30 gms.) and complete minerals consisting of potassium sulphate (1.5g.), potassium nitrate (2g.), and superphosphate (concentrated, non-acid, 3 g.). The following were the different treatments:—(1) potassium permanganate (1.5g.), (2) manganous sulphate (1.5g.), (3) manganous carbonate (1.5g.), (4) ferrous sulphate (1.5g.), (5) ferric sulphate (1.5g.), and (6) untreated (control). The chemicals were all applied as basal dressings along with the manure.

The two varieties of tomatoes, grown for the present study, were King Humbert and Alice Roosevelt, both being heavy yielders. There were 10 replicates for each treatment with the individual strains.

On 20th November 1935, the tomato seeds were sown at 6 per pot. In a week, germination took place. After the seedlings had grown for a fortnight, they were thinned down to leave 3 uniform and healthy ones in each pot. Fruiting commenced in the last week of February 1936 and continued for nearly two months till the end of April.

General observations during growth indicated the efficacy of all the treatments over the controls, especially of the soluble salts of manganese. The final figures with regard to the yield of fruits are presented in Table I.

TABLE I.

Effect of various manganese and iron salts on the yield of tomato.

Treatment	Average yield per plant in grams	
	King Humbert	Alice Roosevelt
Potassium permanganate ...	342	317
Manganous sulphate ...	292	314
Manganous carbonate ...	226	287
Ferric sulphate ...	250	278
Ferrous sulphate ...	236	297
Untreated (control) ...	194	241

The above results show that King Humbert responded very well to the applications of potassium permanganate and manganous sulphate, over 50% increases in yield being obtained in both the cases. The treatments with manganous carbonate, ferric and ferrous sulphates, though not so promising, still reveal that beneficial results could be obtained from them. With Alice Roosevelt, there is not much to choose between the different treatments, though even here potassium permanganate and manganous sulphate have scored slightly over the rest.

It is naturally to be inferred from the foregoing that increases in crop yield could be expected from the application of any of the above salts to the soil. In view of the agricultural importance of the problem, it was felt desirable to repeat the experiments, both in pots and plots.

Pot trials in 1936—The treatments were essentially the same as in the previous season excepting that manganese dioxide (7.5g.) was used in place of manganous carbonate ; also, only one iron salt (ferric sulphate) was employed for the experiments. The trials were carried out with King Humbert, a heavy yielding variety of tomatoes and Improved Golden Wax, a pure strain of French beans (*Phaseolus vulgaris*). For each treatment, there were six replicates. Tomatoes were grown at three per pot and French beans at two per pot. The experiments were commenced on 20th July 1936 and completed by the middle of December.

TABLE II.

Effect of some manganese and iron salts on the yield of Tomato and French beans.

Treatment	Yield in grams.		
	Tomato per plant	French beans (12 plants)	
		Pods	Stems & roots
Potassium permanganate.	280	93.4	23.9
Manganous sulphate ...	245	91.7	24.5
Manganous carbonate ...	...	86.6	22.8
Manganese dioxide ...	234	...	...
Ferric sulphate ...	213	89.8	23.4
Ferrous sulphate ...	...	88.2	22.1
Untreated (Control) ...	171	75.3	20.4

The results presented in Table II confirm the previous findings very well. They suggest that manganese in any of the forms used here could be employed to promote plant growth.

Pot trials with Ragi (Eleusine coracana).—These were carried out in connection with some vegetation experiments to assess the fertilizing value of manganese and iron ores. As the results pertaining to the ores will form the subject of another communication, only the data relating to the soluble manganese and iron salts are presented here.

A number of plots $10' \times 10'$ were laid out on a uniform area of land which had been previously used for ordinary agricultural purposes. They were manured with hongay cake at 14 lbs. per plot and then subjected to different treatments as follows :—(1) potassium permanganate at 100 gms.; (2) manganous sulphate at 100 gms.; (3) ferric sulphate at 100 gms.; and (4) untreated (control). The chemicals were applied in solution as basal dressings. Five plots were kept for each treatment, the distribution of the plots being by the random method.

Ragi seeds (variety H 22) were sown on 20th July 1936 in a seed-bed and transplanted in the experimental plots on 12th August at 200 seedlings per plot. Ears made their appearance in the third week of September and the crop was ready for harvest by the middle of November. The final figures relating to the yield of grain and straw from 500 sq. ft. (the five plots allotted to each treatment) are presented in Table III.

Thus, it would be readily seen from these results that both potassium permanganate and manganous sulphate exerted a pronounced effect on crop growth and contributed to an increase in the yield of grain to nearly 25%. The result with ferric sulphate too is equally striking.

The various pot and plot trials reported here bring out clearly the value of manganese and iron salts as fertilizers. In order to determine how exactly the manganese salts function on application to the soil to bring about enhanced crop yields, the following studies were carried out in the laboratory.

TABLE III.

Response of ragi to different manganese and iron salts.

Treatment	Yield (dry wt.) in Kg.	
	Grain	Straw
Potassium permanganate ...	15.7	44.9
Manganous sulphate ...	15.1	41.7
Ferric sulphate ...	14.7	38.2
Untreated (control) ...	12.4	38.1

Decomposition of organic matter on the application of potassium permanganate and manganous sulphate to the soil.—For these experiments, soil from an adjoining area which was under cultivation for a considerable period was selected. The soil which can be described as a red loam had a carbon content of 0.49% and nitrogen content of 0.044%. The pH of the soil was 7.2 and its saturation capacity 40%. At no time had the plants raised on the area from where the soil was taken suffered from any deficiency diseases like 'chlorosis' or 'Gray Speck Disease'. After being finally powdered, the soil was passed though a 100 mesh sieve.

(a) *Loss of carbon.*—In the previous studies (Harihara Iyer, Rajagopalan and Subrahmanyan, *loc. cit.*), it has been indicated that the loss of carbon from the soil system bears a close relation with the evolution of carbon dioxide which, in turn, is an index of the rate of decomposition of humus in the soil (Stoklasa and Earnest, *Centrabl. Bakt.*, 1905, II, **14**, 723). In the present investigation, therefore, the rate of decomposition of organic matter has been measured by following the changes in the carbon content of the soil.

10 g. lots of the soil were weighed out into a number of 200 c.c. Erlenmeyer flasks. To each of a third of the flasks, 4 c.c. of potassium

permanganate solution (2.5g. per litre so as to correspond to about 1 ton of the salt per acre) was added. Another set received 4 c.c. each of manganese sulphate solution of the same concentration while the rest, which served as controls, were moistened with 4 c.c. of distilled water. The flasks were incubated at 30°C. Once in three days, the loss of moisture in the flasks was made good by additions of distilled water. At weekly intervals, samples were analysed for total carbon. The method of estimation employed was the one developed by Bhagvat, Narayanayya and Subrahmanyan (*Proc. Ind. Acad. Sci.,* 1934, **1B**, 49) and, later on, slightly modified by the present authors (Bhaskaran, Harihara Iyer, Rajagopalan & Subrahmanyan, (*Jour. Indian. Inst. Sci.,* 1936, **19A**, 45). An important difference in detail was that N/2 alkali was used for the absorption of carbon dioxide evolved on chromo-sulphuric digestion, the unused alkali being titrated after the addition of barium chloride solution against N/2 acid. The results have been presented in Fig. I. as loss of carbon in mgms. from the system.

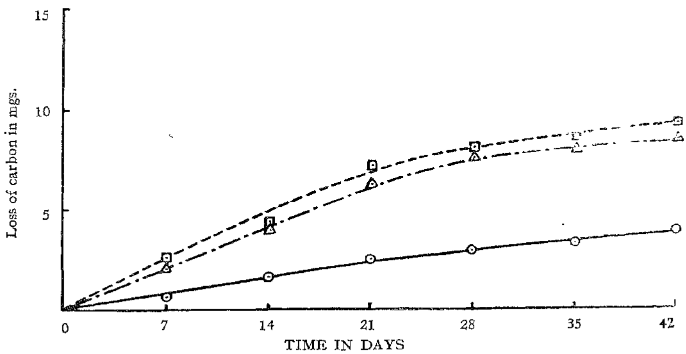

FIG. 1. Unmanured soil

○——○ Control

△-·-△ $KMnO_4$ at 1 ton per acre

□----□ $MnSO_4$ at ,, ,,

The results presented graphically in Fig. I. indicate that both potassium permanganate and manganous sulphate bring about increased

TABLE IV

Manganese transformations on the application of its soluble salts to unmanured soil.

Treatment	Manganese as mgms. in 10 gms. of the soil at the end of									
	1 week		2 weeks		3 weeks		4 weeks		5 weeks	
	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble
Potassium permanganate ..	Traces	3.15	Traces	3.10	Traces	3.10	Traces	2.90	Traces	2.80
Manganous sulphate ...	1.00	2.95	0.05	2.85	"	2.80	"	2.80	"	2.75
Untreated (Control) ...	Traces	2.30	Traces	2.10	Traces	2.10	Traces	1.90	Traces	1.90

oxidation of the organic matter. This would naturally account for the enhanced crop yields reported in the previous sections. The results also suggest that the manganese added in the soluble form gets converted into the higher oxygenated forms and is mainly responsible for hastening the decomposition of organic matter. To find out how far this suggestion is borne out, the distribution of manganese in the water-soluble, acid-soluble and acid-insoluble forms on its application to the soil was followed.

(b) *Distribution of manganese on the application of its soluble salts to the soil.*—The samples for analysis were prepared exactly as for the carbon studies. The determinations were carried out at weekly intervals of (1) water-soluble and (2) acid-soluble manganese by the method laid out in a previous communication (Harihara Iyer and Rajagopalan, *Jour. Indian Inst. Sci.*, 1936, **19A**, 57). The results obtained have been presented in Table IV.

It is quite evident from the foregoing results that soluble manganese, on application to the soil, rapidly gets converted into insoluble forms. A small percentage persists in the acid-soluble condition whilst the rest is insoluble even in 4 N acid. This form would represent manganese dioxide. These data bring out clearly that the increased oxidation of the soil organic matter, on applying the soluble manganese salts to the soil, is brought about by manganese dioxide to which form the added manganese quickly reverts.

Effect of manganese salts on soil receiving different amounts of manure.—It is a well recognised fact that the addition of organic manures brings about the greater solubilisation of soil manganese (Brewer and Carr, *Soil Sci.*, 1927, **23**, 165; Willis, *loc. cit.*). To find out whether the presence of large amounts of organic matter in the soil keeps the added manganese in the soluble form to such an extent as to interfere with its usefulness in accelerating the oxidation processes in the soil, the present studies were undertaken. Both the decomposition of organic matter as represented by the loss of carbon and also distribution of manganese in the soil have been followed.

(a) *Loss of carbon.*—The details of the experiment were precisely the same as for the ones before, excepting that the soil received varying amounts of hongay cake : (1) 10 mgms. ; (2) 20 mgms. ; (3) 50 mgms. ; and (4) 100 mgms. for 10 gms. of the soil. These would represent additions of the manure at one ton, 2 tons, 5 tons and 10 tons respectively per acre. The changes in the carbon content were followed for a period of six weeks. The results have been presented in Figs. II. to V.

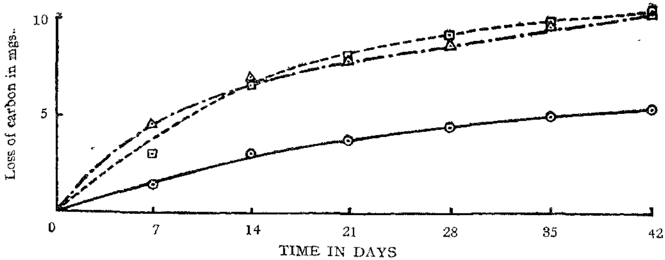

FIG. 2. Soil manured with hongay cake at 1 ton per acre

○——○ Control

△—·—△ $KMnO_4$ at 1 ton per acre

□----□ $MnSO_4$ at ,, ,,

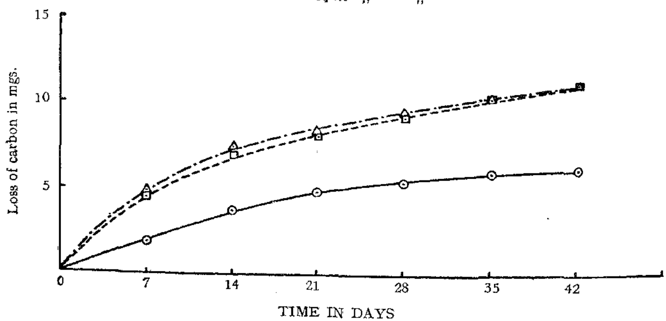

FIG. 3. Soil manured with hongay cake at 2 tons per acre

○——○ Control

△—·—△ $KMnO_4$ at 1 ton per acre

□----□ $MnSO_4$ at ,, ,,

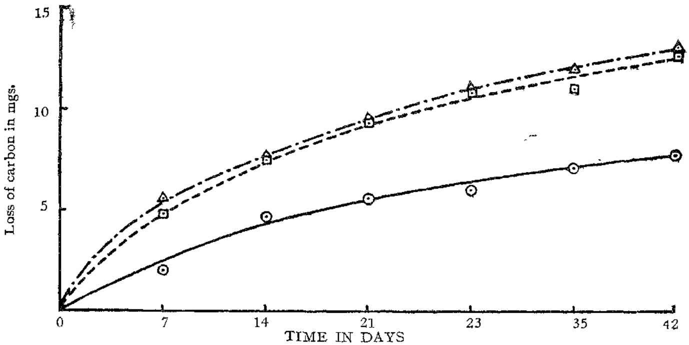

FIG. 4. Soil manured with hongay cake at 5 tons per acre

Control

$KMnO_4$ at 1 ton per acre

$MnSO_4$ at ,, ,,

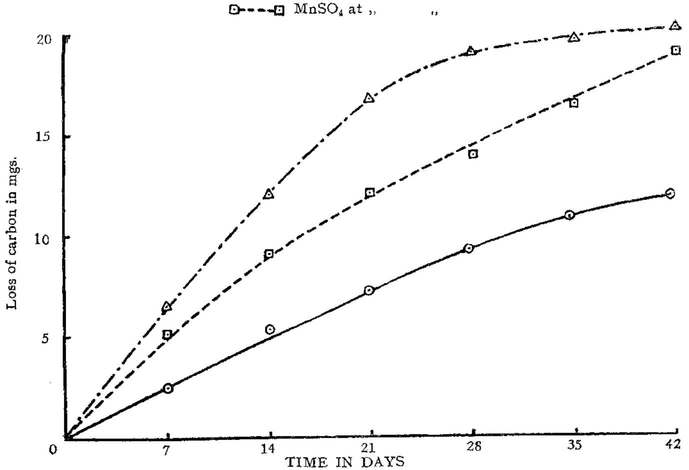

FIG. 5. Soil manured with hongay cake at 10 tons per acre

Control

$KMnO_4$ at 1 ton per acre

$MnSO_4$ at ,, ,,

These results indicate quite clearly that the greater the organic matter content of the soil, the greater is the decomposition brought about by the manganese salts. It is thus apparent that even in the presence of large quantities of organic matter, manganese applications promote oxidation changes in the system to a considerable extent.

A point of interest that arises out of a comparison of the Figs. II to V with Fig. 1, (which represents as explained before the loss of carbon on the application of potassium permanganate and manganous sulphate to unmanured soil) merits some consideration here. This refers to the greater oxidisability of the added manure to that originally present in the soil, by the manganese treatments. Thus, when the unmanured soil lost only 9.4 mgms. of carbon in six weeks out of its total content of 48.6 mgms. (Fig. I), the loss amounted to as much as 19.1 mgms. in the same period on raising its carbon content to 77.10 mgms. by adding hongay cake (Fig. V). In other words, though a strictly mathematical expression is not quite warranted, only 9.4 mgms. out of 48.6 mgms. of the soil organic carbon was oxidised in the period in which 9.7 mgms. out of 28.5 mgms. of the carbon added as hongay cake got oxidised. It is evident, therefore, that hongay cake is more easily oxidised by the manganese applications than the soil organic matter. These results suggest that the chemical composition of the soil humus will have a pronounced bearing on the extent to which manganese facilitates the oxidation changes in the soil.

(b) *Distribution of manganese.*—Under the same conditions as described in the previous case, the distribution of manganese on application of potassium permanganate and manganous sulphate to soil receiving different quantities of hongay cake was followed. The results are given below in Tables V to VIII.

It is evident from these results that when manganous sulphate is added to the soil, an appreciable part of the manganese remains in the soluble condition for some time in the presence of large quantities of organic matter. This would probably account for the slightly lower rate of oxidation of organic matter prevailing in the first few weeks after

TABLES V & VI.

Manganese transformations on the application of potassium permanganate and manganous sulphate to soil receiving different amounts of manure (hongay cake).

Treatment	Manganese as mgms. in 10 gms. of soil at the end of									
	1 week		2 weeks		3 weeks		4 weeks		5 weeks	
	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble
TABLE V										
Soil manured at 1 ton.										
Potassium permanganate ..	Traces	3.30	Traces	3.15	Traces	2.00	Traces	3.00	Traces	3.00
Manganous sulphate ...	0.90	3.00	0.05	2.90	"	2.85	"	2.85	"	2.85
Untreated (Control) ...	Traces	2.30	Traces	2.20	"	2.00	"	2.00	"	2.00
TABLE VI										
Soil manured at 2 tons.										
Potassium permanganate ..	Traces	3.65	Traces	3.60	Traces	3.40	Traces	3.30	Traces	3.20
Manganous sulphate ...	1.35	3.55	0.10	3.45	"	3.30	"	3.10	"	3.10
Untreated (Control) ...	Traces	2.40	Traces	2.20	"	2.80	"	2.00	"	2.00

TABLES VII & VIII.

Manganese transformations on the application of potassium permanganate and manganous sulphate to soil receiving different amounts of manure (hongay cake).

Treatment	Manganese as mgms. in 10 gms. of soil at the end of									
	1 week		2 weeks		3 weeks		4 weeks		5 weeks	
	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble
TABLE VII										
Soil manured at 5 tons.										
Potassium permanganate ..	Traces	3.90	Traces	3.60	Traces	3.40	Traces	3.30	Traces	3.30
Manganous sulphate ...	1.45	4.00	0.40	3.80	0,05	3.40	"	3.40	"	3.40
Untreated (Control) ...	Traces	2.40	Traces	2.30	Traces	2.15	"	2.10	"	2.10
TABLE VIII										
Soil manured at 10 tons.										
Potassium permanganate ..	Traces	4.65	Traces	4.10	Traces	3.80	Traces	3.60	Traces	3.60
Manganous sulphate ...	1.60	4.50	0.65	4.00	0.15	3.80	"	3.80	"	3.80
Untreated (Control) ...	Traces	2.45	Traces	2.35	Traces	2.30	"	2.30	"	2.20

the addition of manganous sulphate as compared with that obtaining with the permanganate application to the soil, when the latter is heavily manured (cf. Fig. V). But, very soon even in the former case, the entire amount of manganese is converted into insoluble forms, the concentration of the soluble manganese falling below the toxic limits and thereafter the decomposition of the organic matter proceeds quite rapidly as with the potassium permanganate treatment.

Effect of application of varying amounts of manganese salts to the soil.—So far, attention has been directed to the influence of the organic matter contents of the soil on the behaviour of manganese salts on application to the soil. How the additions of different quantities of manganous sulphate and potassium permanganate aid the oxidation changes in the soil, will be considered at this stage.

(a) *Loss of carbon.*—The experimental details for preparing the samples for analysis were the same as hitherto described, excepting that soil receiving hongay cake at 2 tons per acre was used throughout these studies. Potassium permanganate and manganous sulphate were added in solution to the soil samples in varying concentrations so as to correspond to the application of the chemicals at (1) 10 cwts. ; (2) 1 ton ; (3) 2 tons and (4) 3 tons. The amounts of salts introduced into 10 gms. lots of the soil were thus respectively 5, 10, 20 and 30 mgms. The results pertaining to the loss of carbon have been presented in Figs. VI. and VII.

These results bring out clearly that no useful purpose is served by increasing the dosages of manganese to be applied to the soil. Indeed, the lower rate of oxidation prevailing with the higher amounts of manganous sulphate in the early stages would suggest the necessity for caution in applying unduly heavy dressings of this chemical. The final figures indicate that there is nothing to choose between manganous sulphate and potassium permanganate in the efficacy with which they aid the oxidative decomposition of soil organic matter. This would point out to the mechanism of action of these two salts to be practically identical.

(b) *Distribution of manganese.*—Samples prepared as for the above were periodically analysed for water soluble and acid soluble manganese. The results are given below in Tables IX and X.

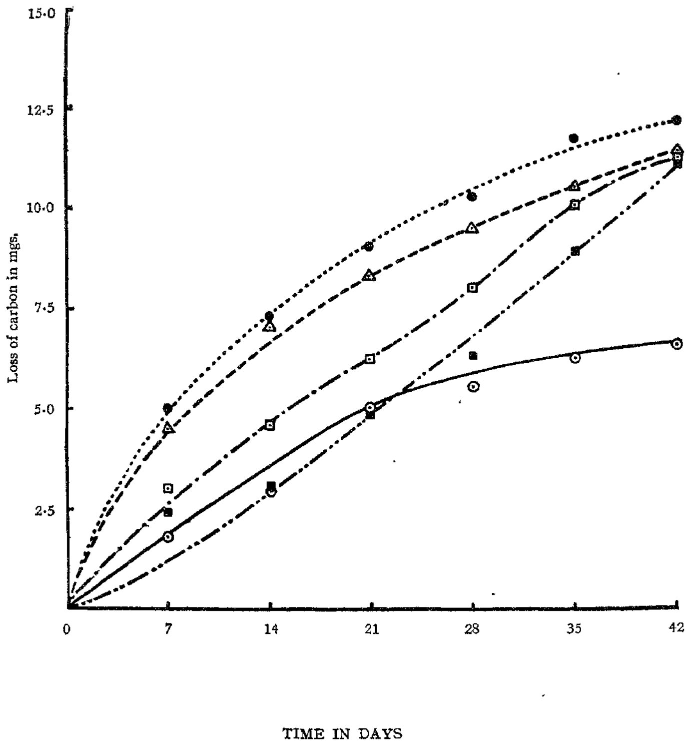

FIG. 6. Loss of carbon of the application of varying amounts of MnSo₄ to soil manured at 2 tons with hongay cake

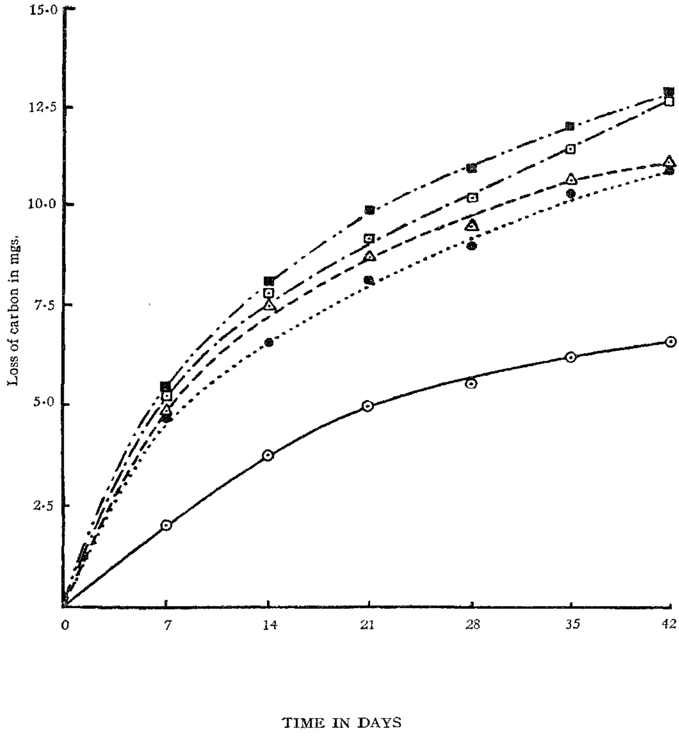

FIG. 7. Loss of carbon on the application of varying amounts of $KMnO_4$ to soil manured at 2 tons with hongay cake

TABLE IX.

Distribution of manganese on the application of varying amounts of manganous sulphate.

Rate per acre	Manganese as mgms. in 10 gms. of soil at the end of									
	1 week		2 weeks		3 weeks		4 weeks		5 weeks	
	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble
10 cwts. ...	0.15	2.70	Traces	2.55	Traces	2.40	Traces	2.40	Traces	2.40
1 ton ...	1.35	3.55	0.10	3.45	"	3.30	"	3.10	"	3.10
2 tons ...	1.65	4.25	1.05	3.90	0.25	3.70	"	3.55	"	3.55
3 tons ...	2.80	4.25	2.10	4.25	1.20	4.10	0.30	4.05	"	3.90
Nil (Control) ...	Traces	2.40	Traces	2.20	Traces	2.20	Traces	2.10	"	2.10

TABLE X.

Distribution of manganese on the application of different quantities of potassium permanganate.

Rate per acre	Manganese as mgms. in 10 gms. of soil at the end of									
	1 week		2 weeks		3 weeks		4 weeks		5 weeks	
	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble	Water soluble	Acid soluble
10 cwts. ...	Traces	2.75	Traces	2.55	Traces	2.50	Traces	2.45	Traces	2.45
1 ton ...	"	3.65	"	3.60	"	3.40	"	3.30	"	3.20
2 tons ...	"	4.75	"	4.20	"	3.90	"	3.80	"	3.80
3 tons ...	"	4.75	"	4.40	"	4.20	"	4.10	"	4.00
Nil (Control) ...	"	2.40	"	2.20	"	2.20	"	2.10	"	2.10

It could be readily seen from the foregoing how large amounts of manganese remain in the soluble condition for considerable periods when manganous sulphate is added in appreciable amounts. This would account for the lower rate of oxidative decomposition in the early stages after their application. (Fig. VI). The high amounts of water soluble manganese present in these cases are inimical to the bacterial population of the soil and to the plants alike. This would explain the unfavourable effects on crop growth when heavy dressings of manganous sulphate are applied to the soil. The results also point out that it is only a question of time before the concentration of soluble manganese falls below the toxic limits. This denotes the necessity of allowing sufficient time to lapse before growing crops on soil which has adventitiously received heavy dressings of soluble manganese.

Even when considerable quantities of manganese are applied to the soil, only a very small fraction continues to remain after some time in the acid-soluble condition. The rest is all converted to manganese dioxide, a form in which it is insoluble in dilute acid. It may, therefore, be reasonably assumed from the very low amounts remaining as acid-soluble manganese after some weeks that but for such factors that mechanical aggregation coming into play, the quantities of acid-soluble manganese would be the same irrespective of the amounts applied. If such an assumption be admitted, that amount of the added manganese which remains in the acid-soluble manganous condition will indicate the extent to which manganese enters in the reaction with the soil system to hasten the oxidation processes in the soil.

These and the foregoing results suggest that soluble manganese salts on addition to the soil in moderate amounts are quite efficacious in bringing about oxidation changes in the soil, with ultimate benefit to the growing crop. Further studies will elucidate how to determine the minimum amount of manganese to be applied to different soils to evoke the maximum crop response.

DISCUSSION.

The present enquiry has brought to light many important facts regarding the mode of action of manganese salts on application to the soil.

When added to the soil in a soluble form, manganese rapidly passes to the insoluble condition. Part remains for considerable periods in the acid-soluble state; this will comprise the carbonate, phosphate and lower oxides of manganese as also exchangeable manganese. The rest is converted into manganese dioxide in which form it is insoluble in dilute acids. Thus, it is only to be expected that soluble manganese salts should behave exactly like manganese dioxide on application to the soil, excepting that they will take a little more time to bring about the desired biochemical changes to promote plant growth. Probably this accounts for the necessity of applying soluble manganese salts as basal dressings while manganese dioxide is most useful as top dressing.

The mechanism of action of the manganese salts as indicated by the present studies, may briefly be described as follows:—

The added manganese, on reaction with the colloidal complex of the soil, gets rapidly converted to insoluble manganous hydroxide which is oxidised by atmospheric oxygen to hydrated dioxide. This enters into reaction with soil organic matter to liberate carbon dioxide and in the process is reduced to the manganous condition. Exposure to air reoxidises it to manganese dioxide and the cycle of changes goes on. Thus.—

$$2MnO_2 + C \text{ (organic matter)} \longrightarrow 2MnO + CO_2 \quad \ldots \quad (1)$$

$$2MnO + O_2 \text{ (atmospheric)} \longrightarrow 2\,MnO_2 \quad \ldots \quad (2)$$

Though there is yet no direct proof forthcoming to show that manganese dioxide brings about oxidation of organic matter as represented by equation (1), still all the available evidence points out to such a reaction taking place. Of course, the possibility is there that only certain constituents of organic matter are attacked this way. In this connection the observations of Ingersoll (*Ann. Physiol. Physicochim. Biol.*, 1926, No. 3) may be of some interest. He has demonstrated by carrying out experiments, under sterile conditions, that manganese dioxide oxidises glucose in solution to carbon dioxide on passing a current of air through it.

The present studies also reveal that the addition of large quantities of manganese salts does not necessarily involve more rapid decomposition of organic matter. On the other hand, the presence of water-soluble manganese for long periods when heavy doses of manganous sulphate are applied to the soil would suggest that smaller doses are far more desirable. Further work will have to be directed to determine the minimum amount of manganous sulphate or potassium permanganate that would bring about with different soils the maximum release of plant nutrients with ultimate benefit to the crop.

The chemical composition of the soil humus has been shown to influence the behaviour of manganese salts to a considerable extent. This would mean that manganese brings about the oxidation of certain organic constituents of the humus more readily than of the others. It will therefore be of interest to study the oxidation of different humus constituents of manganese salts and also to follow the composition of organic matter during its decomposition under these conditions.

Why the large amounts of manganese already present in the soil do not promote the oxidative decomposition of humus to any degree comparable with that brought about by the small amounts of added manganese is a question which requires elucidation. Whether mechanical aggregation would account for the inactivity of the soil manganese or whether there are other factors responsible for it, cannot definitely be said in the present state of our knowledge. On the answer to this will depend the devising of ways and means to activate the soil manganese to bring about the desired biochemical changes in the soil.

It may be concluded from the present enquiry that basal dressings of manganous sulphate or potassium permanganate are quite helpful in enhancing crop yields. The same observation holds good in the case of soluble iron salts as well, though to a lesser extent. The results reported in a previous communication (Harihara Iyer and Rajagopalan, *J. Ind. Inst. Sci.,* 1939, **22A**, 171) have shown that such treatments exert no adverse effect on the succeeding crop. Application of such chemicals to the soil is extremely desirable in tropical countries like India to get the maximum release of the plant nutrients during the life time of the crop, thus, indirectly preventing considerable wastage of valuable fertilizing ingredients during summer, when the land is usually fallow, consequent on the high microbial activity prevailing at this part of the year.

It cannot be denied that the effect of addition of manganese or iron salts on crop growth depends also upon the nature of the soil. It is quite possible that when applied to acid soils, they prove quite injurious to the growing crop on account of the large amounts of the metallic ion held in acid solution. Also, their application to alkaline soil may not by itself produce any effect on crop growth, unless combined with suitable treatments that reduce the alkalinity of the soil. In the present enquiry there has been no attempt, therefore, to include such cases within its scope. What has been discussed so far holds good only for normal soils.

SUMMARY.

(1) Basal dressings of manganous sulphate and potassium permanganate, in moderate amounts, considerably enhance the yields of tomato, ragi and French beans. This is true of iron salts also, though not to the same extent.

(2) Soluble manganese salts, on application to the soils, quickly pass into the insoluble condition : a small part of the added manganese remains acid-soluble while the rest is converted to acid-insoluble manganese dioxide.

(3) The decomposition of organic matter is hastened by treating the soils with manganese salts. Evidence has been adduced to show that manganese dioxide that is formed in these cases is responsible for bringing this about.

(4) The extent to which manganese salts hasten the decomposition of organic matter depends to a considerable extent on the chemical composition of the latter.

(5) The greater the organic matter content of the soil the greater is the degree of decomposition brought about by manganese applications.

(6) There is a lag in the oxidation of humus, if heavy dressings of manganese salts are applied ; however, after some time when the concentration of the soluble manganese goes down, the decomposition

proceeds rapidly. The best results, however, could be expected with small dosages of manganese salts.

(7) In the light of the available data, the mechanism of action of manganese in the soil has been explained and the need for further work indicated.

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