

INVESTIGATIONS ON THE RÔLE OF ORGANIC MATTER IN PLANT NUTRITION.

Part X. Influence of Different Forms of Manganese on the Oxidation of Organic Matter and Release of Plant Nutrients.

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It was shown in the previous communications (Subrahmanyan and Siddappa, 1933; Harihara Iyer, Rajagopalan and Subrahmanyan, 1934; Siddappa and Subrahmanyan, 1935) that small amounts of oxidising agents such as potassium permanganate, hydrogen peroxide, ferric oxide or manganese dioxide, when applied to soil, can improve the growth of plants and increase the yield of crop. Evidence was also adduced to show that such chemicals hasten the oxidation of organic matter and increase the production of carbon dioxide. In the case of manganese dioxide there was a momentary increase in the numbers of bacteria, actinomyces and fungi but subsequent effect was not appreciable. It was not clear, however, as to how far the beneficial effects were due to the bases with which the different chemicals were associated; as to how much was due to purely ionic effects regarding which there is an extensive literature (Brenchley, 1927; Harihara Iyer *et al.*, *loc. cit.*) and how much to oxidation. The mechanism of oxidation is still obscure. Further work is needed to show how far the changes are due to purely chemical action and, to what extent, they are brought about by micro-organisms. Fresh information is also required regarding the comparative merits of the different chemicals used for the purpose and their behaviour under diverse soil conditions. In view of the above and the need for further knowledge regarding the application of oxidising agents as fertilisers, the present enquiry was undertaken. Since the previous study has shown that potassium permanganate and manganese dioxide were highly potent in their action, the immediate research was confined to compounds of manganese.

Experimental.

Plot experiments with ragi (Eleusine coracana).—The trials were carried out on a number of small plots, each measuring 121 sq. ft. in area. The

following were the treatments:—(a) Unmanured (control); (b) manured at 15 lbs. per plot (hongay cake); (c) unmanured and treated with potassium permanganate (150 g. per plot); (d) manured and treated simultaneously with permanganate; and (e) same as (d) but with the permanganate applied as top dressing in two instalments. Four plots were allotted for each treatment except (b) which received eight. They were distributed according to the random method.

A week after the application of manure, the seeds (H₂₂ variety) were sown (12-6-1934). Germination was quite satisfactory and on 6th July, the seedlings were thinned out to 200 per plot. The first instalment of top dressing was given on 6th August and the second on the 13th. Owing to scarcity of rainfall, the plots had to be irrigated with tap water. The growth was, nevertheless, quite luxuriant, especially on the manured plots and the plants were ready for harvest towards the end of October. The grain and straw representing each treatment were dried separately and their weights determined.

In the previous season (1933), similar treatments had been tried on the same plots (Harihara Iyer, *et al.*, *loc. cit.*). The only important difference was that farmyard manure was used in place of the cake and was applied at 22 lbs. per plot (approximately 3 tons per acre). Since the object of that experiment was the same as that of the present one, the two sets of results have been presented together in Table I. The yields have been given as from 484 sq. ft. (1/90th of an acre) in each case.

TABLE I.

| Treatment | Yield (dry wt.) in Kg. | | | |
|--|------------------------|-------|--------------------|-------|
| | Fy. Manure (1933) | | Hongay Cake (1934) | |
| | Grain | Straw | Grain | Straw |
| Untreated (Control) | 1.43 | 1.55 | 5.53 | 15.67 |
| Manure alone | 2.18 | 2.10 | 14.86 | 47.51 |
| Permanganate alone | 2.07 | 1.79 | 8.30 | 15.71 |
| Manure + Permanganate (simultaneously) | 2.87 | 2.80 | 18.79 | 52.00 |
| Manure + Permanganate (top-dressing) | 2.31 | 2.31 | 16.27 | 49.93 |

The meteorological observations for 1933 have been discussed in the previous communication. Analysis of the data* for 1934 would show that the season (July-October) was moderately warm, the maximum temperature ranging from 75-90°F. The nights were comparatively mild, the minimum temperature rarely going below 65°F. As compared with the previous season, rainfall was generally meagre except during the middle of October when there were about 5 inches of rain in the course of one week. There were light showers (generally a few cents at a time) both at the beginning and at the end of July. The showers were more frequent during August, but September (except for a few days in the middle) was comparatively dry. By about the middle of October, the crops had come to harvest, so they derived no benefit from the heavy rains which followed. Relative humidity was generally lower than in the previous years and ranged between 50 and 70 per cents. except for short periods both during and after the showers. The season being comparatively dry, the plots had to be regularly watered almost upto the time of harvest.

It may be noted that, in both the seasons, the yields from the manured as well as unmanured plots were increased as the result of application of permanganate. Of the two methods of application, simultaneous application with the manure yielded better results than top-dressing in instalments.

Although the cake was richer in fertilising ingredients (N, 4.5 per cent.) than farmyard manure (N, 0.8 per cent.), it may yet be observed that the comparatively heavy yield of 1934 was not entirely due to manurial treatment. Even the unmanured (control) plots yielded about four times as much grain and ten times as much straw in 1934 as in 1933. The ratio of grain to straw was approximately as 1 : 1 in 1933 and about 1 : 3 in 1934. The latter observation applies to the yields from all the treatments in each season. It would thus be seen that while the mode of action remains the same, the extent of benefit derived from application of the oxidiser may be greatly modified by the season.

Distribution of manganese in the experimental plots.—Some preliminary observations made shortly after the different treatments showed that there was no free permanganate in any of the experimental plots. This observation suggested that the permanganate was rapidly reduced by the organic matter of the soil. With a view to determining the mode of interaction between permanganate and the soil, the distribution of manganese in the different

* Obtained through the courtesy of Mr. C. Seshachar, Meteorologist to the Government of Mysore, to whom the authors' thanks are due.

experimental plots was studied. Representative specimens (10 g.) of air-dried soil were first extracted with water and the quantities of manganese present in the extracts determined. The residual soil was then extracted with 4 N sulphuric acid and the manganese in the extract estimated as before. Fresh specimens (10 g.) of soil were then treated with sodium sulphite (5 g.) and sulphuric acid (4 N, 100 c.c.) and the total manganese brought into solution on boiling the mixture was estimated. The last procedure was found to be the most suitable for the extraction of total manganese including resistant forms such as manganese dioxide. A number of preliminary trials showed that the extraction was rapid and quantitative. Only small quantities of ferrous iron and other interfering substances were present in solution. Boiling removed the excess of sulphur dioxide.

The estimations of manganese in solution were carried out according to the bismuthate method. Some difficulty was experienced on account of the presence of chlorides in the soil, as also in certain commercial preparations of sodium bismuthate. This was overcome, however, by adding small quantities of mercuric oxide or sulphate (2-3 g.) to the hot soil-bismuthate suspension, just prior to filtration, for estimation. There was not even a trace of chloride in the filtrate. Silver salts were not useful for this purpose, as they formed soluble compounds which interfered with the estimation. Moreover, heating with silver salts (*e.g.*, the sulphate) caused the rapid decomposition of the bismuthate so that there was none left to oxidise the manganese to the permanganate condition. Attention may also be drawn to the small correction to be applied for the oxidising action of water-soluble matter from the bismuthate itself. A simple method embodying the foregoing principles and specially designed for the estimation of manganese in soils and biological media has been developed and will be described in a later communication.

The results have been presented in Table II.

The original soil itself contained fairly large quantities of manganese which was present partly in the acid soluble and partly in the insoluble condition. The added permanganate contributed about a ninth of the original manganese. About half of it passed into the acid soluble condition and the other half into insoluble forms. Since the reaction between soil and permanganate proceeded very rapidly it would appear that the increased yields were largely due to the acid soluble and insoluble products resulting from the treatment.

Effect of Applying Different Forms of Manganese to Soil.

Distribution of manganese.—Before conducting a systematic study of the effect of different forms of manganese on organic matter, it was considered

TABLE II.

| Treatment to original soil | Manganese in parts per million | | |
|---|--------------------------------|--------------|-------|
| | Water soluble | Acid soluble | Total |
| Unmanured (Control) | Traces | 89.5 | 360.8 |
| Manured with hongay cake .. | Do. | 85.8 | 371.8 |
| Unmanured + KMnO ₄ | Do. | 118.8 | 398.0 |
| Manured + KMnO ₄ (Simultaneous) .. | Do. | 107.8 | 393.6 |
| „ + „ (Instalments) .. | Do. | 118.8 | 387.2 |

desirable to obtain an idea of the changes that attend their application to the soil. A number of pots were made up with soil-sand mixture (30 lbs. ; proportion, 3 : 1). They were then treated with finely powdered hongay cake (30 g.) and divided into five batches. One set of pots was treated immediately with potassium permanganate at the rate of 4.5 g. per pot. The others were rested for three days and then treated as follows:—(a) manganous sulphate at 4.3 g. per pot ; (b) manganese dioxide (7.5 g.) ; (c) manganous carbonate (10 g.) ; and (d) control (untreated). The quantity of manganous sulphate was equivalent to that of permanganate on the manganese basis and that of manganous carbonate to that of manganese dioxide. Cork-borer samples of soil were taken from the pots at stated intervals and the distribution of manganese determined in the manner outlined already. The results were as follows (Tables III A and III B).

TABLE III A.

| Treatment (Samples taken immediately after treatment) | Manganese in parts per million | | |
|--|--------------------------------|--------------|-------|
| | Water soluble | Acid soluble | Total |
| Soil + Hongay Cake (Control) .. | Traces | 135.5 | 453.9 |
| „ + „ + KMnO ₄ .. | Do. | 147.8 | 569.4 |

It may be noted that, with the exception of manganous sulphate, none of the treatments yielded any water soluble manganese. Even in the former case, more than two-thirds was present in insoluble forms. The water

TABLE III B.

| Form of Manganese applied | Manganese in parts per million | | | | | |
|---------------------------|--------------------------------|--------------|-------|----------------|--------------|-------|
| | After 1 hour | | | After 24 hours | | |
| | Water soluble | Acid soluble | Total | Water soluble | Acid soluble | Total |
| MnSO ₄ .. | 32.3 | 170.8 | 544.8 | 18.5 | 154.0 | 537.0 |
| KMnO ₄ .. | Traces | 150.8 | 540.1 | Traces | 143.1 | 563.2 |
| MnO ₂ .. | Do. | 137.0 | 849.4 | Do. | 132.3 | 864.8 |
| MnCO ₃ .. | Do. | 635.6 | 854.1 | Do. | 587.9 | 843.3 |
| Untreated (Control) .. | Do. | 126.2 | 381.7 | Do. | 127.7 | 386.3 |

soluble manganese tended to steadily diminish and after a week, there was none left in any of the pots. Acid soluble forms which represented a useful proportion of the total manganese in all the cases would include the carbonate, the phosphate and such other compounds. The estimate should also include any manganese that might be present as exchangeable base or otherwise retained by the mineral complex of the soil system. The original soil itself contained fairly large quantities of such forms and there were further additions through the different treatments—especially manganous sulphate and carbonate. In the latter case, the carbonate itself would have contributed to the increase in acid soluble forms. The acid insoluble forms would represent the major part of the manganese in the soil. In two of the cases they were present mostly as manganese dioxide, whereas in the others, especially that of treatment with manganous sulphate, the position is still obscure. Further systematic research is needed to throw light on the mode of interaction between soil and different forms of manganese and its bearing on the various chemical and biological transformations in the soil.

The immediate effect of some of the soluble forms of manganese on soil bacteria.—It has already been shown (Harihara Iyer, *et al.*, *loc. cit.*) that in both the manured and unmanured soil, application of manganese dioxide causes a momentary increase in the number of bacteria and actinomyces,

With a view to determining the effect of applying the other forms of manganese the following experiment was carried out. To 10 g. lots of soil, powdered seed-cake (0.2 g.) was added and the mixtures treated as follows:—(a) Manganous sulphate (0.43 g.); (b) potassium permanganate (0.45 g.); and (c) control (untreated). They were then moistened with water (4 c.c.) and left at the laboratory temperature (25-28°C.) so as to simulate the field condition. Samples were taken out at intervals and plated on Thornton's medium (1922). The bacterial counts were as follows (Table IV).

TABLE IV.

| Treatment | Bacterial numbers per gram of soil | | |
|-------------------------|------------------------------------|-----------------------|-----------------------|
| | At the commencement | 4th day | 10th day |
| MnSO ₄ | 92 × 10 ⁴ | 10 × 10 ⁵ | 50 × 10 ⁶ |
| KMnO ₄ | 16 × 10 ³ | 15 × 10 ⁵ | 60 × 10 ⁶ |
| Untreated (Control) | 25 × 10 ⁶ | 120 × 10 ⁶ | 135 × 10 ⁶ |

Unlike manganese dioxide, the two soluble forms caused an immediate depression in the number of bacteria. Thus, in the case of samples treated with permanganate, the numbers at the commencement were less than a thousandth of those in the control. Later on, there was steady recovery and on the 10th day, the numbers were just under half of those in the untreated samples. Although the quantities of permanganate and manganous sulphate added in the above experiment were rather large, it should nevertheless be admitted that those two forms act as partial sterilisers and that bacterial action would, at any rate momentarily, be retarded. Further work is needed to throw light on the significance of the above in relation to field practice. In the case of permanganate it has already been observed (Harihara Iyer, *et al.*, *loc. cit.*) that the maximum benefit can be obtained only when it is applied together with the manure, a few weeks before sowing or transplanting as the case may be. Whether similar observations would apply to manganous sulphate still remains to be determined.

Decomposition of organic matter in presence of different forms of manganese.—It has already been shown that treatment with oxidiser is attended by fairly rapid loss of carbon (Harihara Iyer, *et al.*, *loc. cit.*). With a view to determining whether (a) the changes follow a similar course in presence of

different forms of manganese and (b) the extent to which purely chemical action accounts for the various transformations, the following experiments were carried out. The soil (red sandy loam similar to that used for the various pot and plot experiments) was weighed out in 10 g. lots into a number of Petri dishes and treated with finely powdered hongay cake (0.2 g.). The dishes were then divided into five different batches and treated as follows:— (a) manganous sulphate (0.43 g.); (b) potassium permanganate (0.45 g.); (c) manganese dioxide (0.75 g.); (d) manganous carbonate (1.0 g.); and (e) untreated (control). Half the number of dishes receiving each treatment were left as such while the others were sterilised by autoclaving for 1 hr. at 20 lbs. followed by dry heating at 110° for 4 hrs. The heating was not carried out at a still higher temperature because it was feared that such a treatment might seriously alter the composition of the soil. The heated samples were moistened with sterile water (4 c.c.) and the others with distilled water. The dishes covered with lids were then spread out on a number of tables, in positions where they received a portion of the day's sunlight. This was done with the object of simulating, as far as possible, the conditions prevailing in the experimental pots. At stated intervals, the entire contents of representative specimens were washed down with minimum quantity of water, into digestion flasks and their carbon contents estimated according to Subrahmanyam, Narayanayya and Bhagvat (1934). The results have been presented in Figs. 1 and 2.

Total carbon in soil, 0.43 per cent.; in cake, 35.1 per cent.; total quantity of carbon at the beginning in the control and in the samples treated with different forms of manganese except the carbonate, 113.2 mg. each; in samples treated with manganous carbonate, 198.6 mg. each.

It may be noted that in both the sets, the maximum loss of carbon occurred in the case of specimens treated with potassium permanganate or manganese dioxide. The latter was slightly more, but the difference was not considerable. Manganous carbonate came next, but it is difficult to state as to what part of the carbonate itself was decomposed in the process. Manganous sulphate followed later and was not very different from the control, which came last.

A comparative study of the two sets of results would show that microbial activity would account for the major part of the loss of carbon. There is nevertheless evidence of considerable amount of decomposition through purely chemical action. The latter effect is most pronounced in the case of specimens treated with the permanganate or manganese dioxide. This would show clearly that chemical oxidisers can act independently of micro-organisms and bring about the decomposition of organic matter. Even the

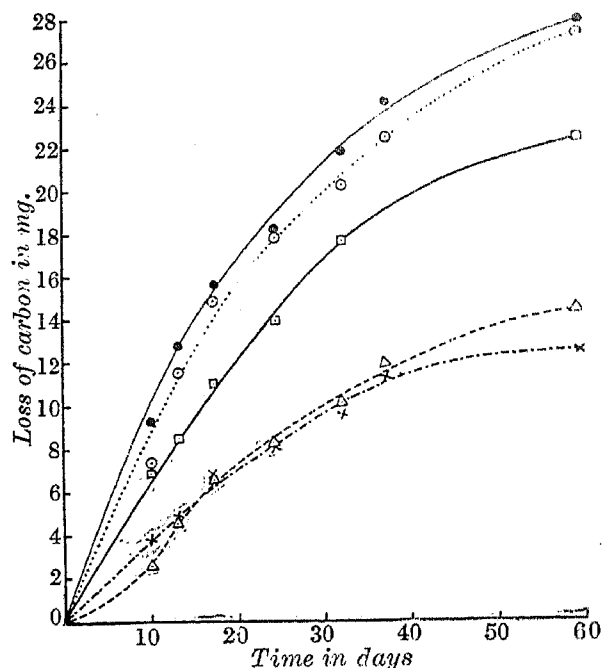


FIG. 1. Non-sterile (ordinary) soil.

x-x Control Δ-Δ MnSO₄ ○-○ KMnO₄ ●-● MnO₂ □-□ MnCO₃

FIGS. 1 and 2. Loss of carbon consequent on the application of different forms of manganese.

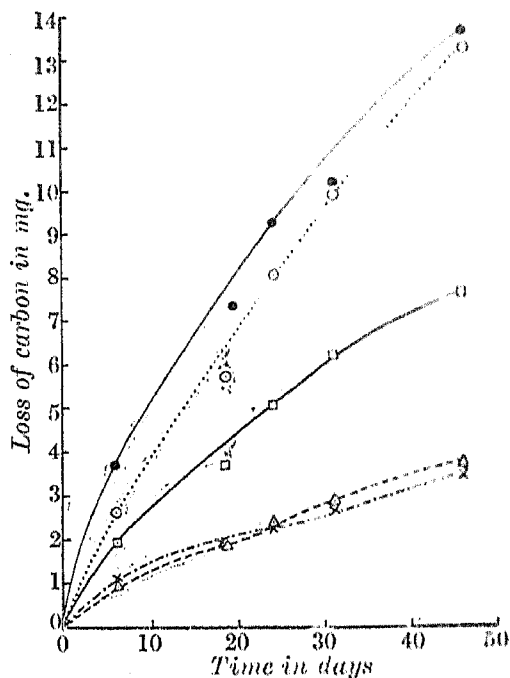


FIG. 2. Sterile soil.

controls (untreated samples) showed some loss of carbon. This is to be expected when considering that the original soil itself contained useful quantities of oxidative minerals such as ferric oxide (Harihara Iyer, *et al.*, *loc. cit.*).

It would thus be seen that there were at least three agencies concerned in the decomposition of organic matter—the mineral matter of the soil, the added chemical and the micro-organisms. The first and the third would depend largely on the nature of the soil and the conditions prevalent in it. The chemical action would be partly determined by the composition of the soil. The added chemicals would, in turn, influence the activity of micro-organisms. Allowing for the above, it should still be possible to obtain estimates of the decomposition brought about, directly or otherwise, through the agency of the added chemicals. The results thus obtained have been presented in Table V.

It may be noted that there was generally greater loss of carbon from non-sterile samples than from the corresponding sterile ones. The available evidence is not sufficient to explain this observation, but it is probable that the chemical oxidation was facilitated by microbial activity which resulted in a preliminary disintegration of organic matter.

TABLE V.

Decomposition of Organic Matter through purely Chemical Oxidation.

| Form of Manganese | Carbon lost (in mg.) at the end of | | | | | | | |
|---------------------------|------------------------------------|-------------|---------|-------------|---------|-------------|---------|-------------|
| | 10 days | | 20 days | | 30 days | | 40 days | |
| | Sterile | Non-sterile | Sterile | Non-sterile | Sterile | Non-sterile | Sterile | Non-sterile |
| Manganous sulphate .. | 0.2 | 0.3 | .. | .. | 0.3 | 0.5 | 0.3 | 0.8 |
| Manganous carbonate .. | 1.4 | 3.4 | 2.4 | 5.5 | 3.5 | 7.5 | 4.0 | 8.5 |
| Potassium permanganate .. | 2.5 | 5.4 | 4.9 | 9.3 | 7.1 | 10.4 | 8.8 | 11.9 |
| Manganese dioxide .. | 3.8 | 5.8 | 6.1 | 10.3 | 8.2 | 11.9 | 9.6 | 13.5 |

Among the different treatments, that with manganese dioxide was the most effective under both sterile and non-sterile conditions. Permanganate came a close second. Its action followed very nearly the same course as that of manganese dioxide. This was due to the rapid decomposition of permanganate resulting in the formation of manganese dioxide. There was fairly rapid loss of carbon from samples treated with manganous carbonate, but since no separate determinations of the residual carbonate were carried out, it is difficult to state as to what part of the loss was due to organic carbon. Manganous sulphate came last and was in fact no better than the untreated control.

Production of carbon dioxide.—The treatments were the same as those in the previous experiment. The only difference was that ten times the previous quantities were taken. The samples were kept in Erlenmeyer flasks (cap. 1 litre) fitted with two-holed rubber stoppers. Carbon dioxide was estimated by displacement with (CO₂ free) air followed by absorption in excess of alkali, a Truog trap (1918) being used for the purpose. The results have been presented in Figs. 3 and 4.

Production of carbon dioxide followed nearly the same course as loss of carbon. As in the previous series, manganese dioxide was the most active with permanganate following as a close second. Manganous carbonate was the third, while manganous sulphate was just better than the control. As

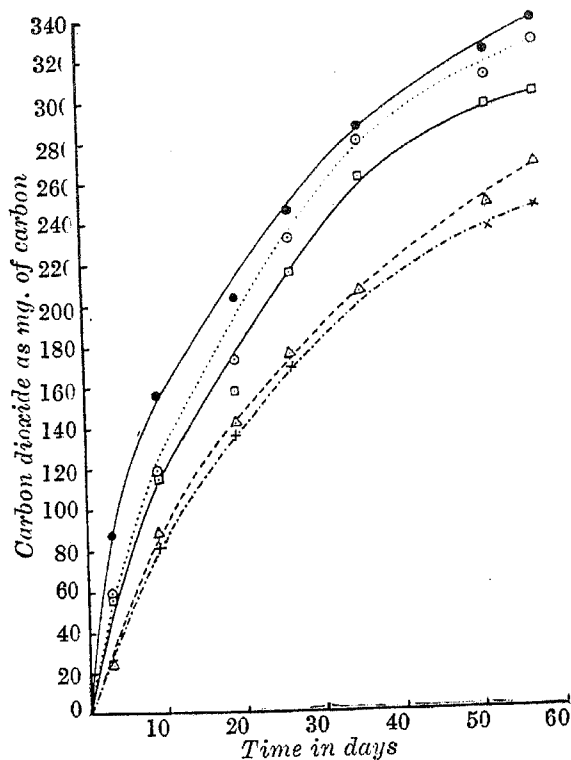


FIG. 3. Non-sterile (ordinary) soil.

x-x Control Δ-Δ MnSO₄ ○-○ KMnO₄ ●-● MnO₂ ◻-◻ MnCO₃

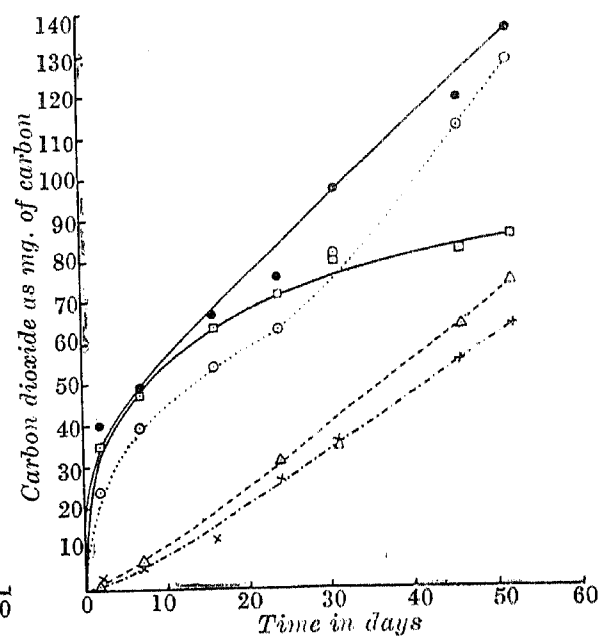


FIG. 4. Sterile soil.

FIGS. 3 and 4. Production of carbon dioxide on treatment with different forms of manganese.

may be naturally expected, the major part of the gas produced from the non-sterile soil was through biological activity. A useful proportion was formed through purely chemical action with the original minerals of the soil. Allowing for these, the quantities of carbon dioxide formed through the agency (direct or otherwise) of the added chemicals may be estimated as follows (Table VI). As in the previous series, the chemical action was more pronounced in the case of the non-sterile samples than in those of the sterile ones. Since the loss of carbon and production of carbon dioxide are inter-related, it may be assumed that the changes indicated in an earlier section would apply to the present series as well.

It would be difficult to state whether all the carbon dioxide was derived from the added manure. It may be reasonably expected, however, that the major part came from that source, because the manure was readily fermentable and contained more of available carbon and nitrogen than the organic matter of the soil. The quantities of carbon affected by the different treatments varied considerably, but even under the most favourable conditions

TABLE VI.

| Form of Manganese | CO ₂ produced (as mg. of c) at the end of | | | | | | | |
|------------------------------|--|-------------|---------|-------------|---------|-------------|---------|-------------|
| | 10 days | | 20 days | | 30 days | | 40 days | |
| | Sterile | Non-sterile | Sterile | Non-sterile | Sterile | Non-sterile | Sterile | Non-sterile |
| Manganous sulphate | 2 | 5 | 7 | .. | 7 | 5 | 7 | 5 |
| Manganous carbonate | 19 | 32 | 50 | 40 | .. | 50 | .. | 61 |
| Potassium permanganate | 41 | 39 | 41 | 57 | 41 | 70 | 47 | 78 |
| Manganese dioxide | 51 | 59 | 59 | 69 | 61 | 79 | 66 | 86 |

(such as that provided by manganese dioxide) did they exceed half the amount of added organic matter.

The extents to which the different agencies contributed to the oxidation also varied with the treatment, but it may be mentioned that, in all the cases, the micro-organisms were the most active. Thus, chemical treatment was next in prominence in two of the cases (manganese dioxide and permanganate), while in the other two, its effect was not so pronounced. Oxidation by the original minerals of the soil (which was common to all the samples) would account for about a fourth of that brought about by microbial action. Assuming that the other two agencies functioned in the same manner, it would be seen that chemical treatment contributed substantially to the oxidation of organic matter in the soil.

The foregoing observations relate only to conditions prevalent in the absence of the growing plant. It is well known that the presence of vegetation hastens the oxidation of organic matter (Neller, 1922; Siddappa and Subrahmanyam, *loc. cit.*). The penetration of roots increases the air space in the soil and facilitates quicker absorption of oxygen. The production of carbon dioxide would also be augmented by plant respiration. It would be of much practical interest to investigate the action of chemical oxidisers under such conditions.

It would be rather difficult to trace a quantitative relation between the loss of carbon and production of carbon dioxide in the two foregoing sets of

experiments. The containers were of different types. The procedure for the estimation of carbon dioxide involved increased supply of air to the samples used for that study. It would nevertheless be seen (Figs. 5 and 6) that there is close positive correlation between the loss of carbon on the one hand and production of carbon dioxide on the other. The percentages have been calculated on the basis of the total carbon originally present in the soil system.

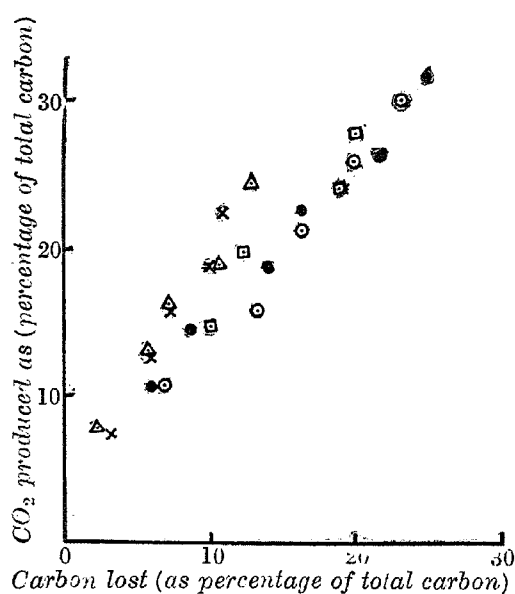


FIG. 5. Non-sterile (ordinary) soil.

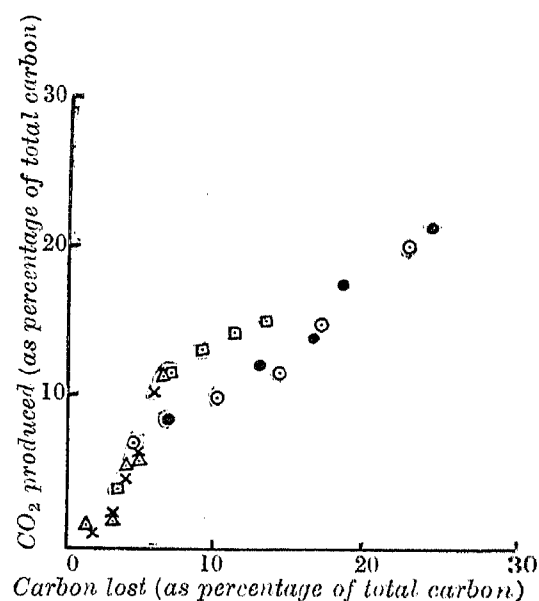


FIG. 6. Sterile soil.

x Control Δ MnSO₄ ○ KMnO₄ ● MnO₂ ◻ MnCO₃

FIGS. 5 and 6. Diagrams showing the correlation between loss of carbon and production of carbon dioxide in samples treated with different forms of manganese.

Although the foregoing observations would point to carbon dioxide as the chief product of chemical as well as biological action, it is nevertheless possible that some of the intermediate products are also of much physiological importance. This inference is further supported by the observation that the increased production of carbon dioxide consequent on the application of chemical oxidisers does entirely account for the greatly improved yield observed in the case of many crops. Similar observations would also apply to nitrogenous compounds. Although there is no perceptible change in total nitrogen (Harihara Iyer, *et al.*, *loc. cit.*) it is yet possible that some of the degradation products of the proteins of the cake may be readily available to plant nutrition.

Effect of application of different forms of manganese on the yield of tomato.— In the previous study (Harihara Iyer, *et al.*, *loc. cit.*) it was observed that tomato responded best to application of manganese dioxide. The observations

showed that the dioxide greatly increased the availability of organic manure; but it was not clear, however, as to whether the beneficial effect was entirely due to oxidation of organic matter. It was considered probable that the response might change with the variety of tomato. The nature of the soil and particularly its reaction might also influence the yield. With a view to obtaining some information regarding the above, the following experiments were carried out. Over a thousand pots were made up with soil-sand mixture (30 lbs.; proportion, 3:1) in the usual way. Half the number of pots were treated with burnt lime at 15 g. each. After a week's rest, all the pots were treated with superphosphate (non-acid, concentrated) at 3.0 g. each. This was followed by application of powdered hongay cake (N, 4.5 per cent.) at 30 g. per pot. A week later, the seeds were sown, 100 pots being allotted for each variety. Six to eight seeds were sown per pot, but as the seedlings came up, they were reduced to two each. A fortnight after germination, all the pots were top-dressed with potassium nitrate (2.0 g. each) and potassium sulphate (1.5 g. each) respectively. A week later, the pots were divided into groups of five and treated as follows: (a) manganous sulphate at 4.3 g. per pot; (b) manganese dioxide at 7.5 g.; (c) manganese carbonate at 10 g.; and (d) left untreated (control). Another set of pots (20 for each variety) was made up similarly, but treated with potassium permanganate (4.5 g. per pot) immediately after application of the cake. Those pots were sown at the same time as the previous series and received similar top dressings of nitrate and potash. In addition to the above, a further control series was started in which all the treatments were the same as those obtained above except that the organic manure was not applied. The following eight varieties were tried:—(1) Ponderosa; (2) Bonnie Best; (3) Globe; (4) Marglobe; (5) Perfection; (6) King Humbert; (7) Cherry Red; and (8) Golden Jubilee. Twelve pots of each variety were allotted for each form of manganese. Of these, six were limed while the other six were unlimed. A similar number was allotted for unmanured controls.

The seeds were sown on 13th August 1934. Germination was generally satisfactory, but the seedlings which came up in the limed pots began dying rapidly, so that they had to be mostly resown. The seedlings were thinned out on 11th September and the top-dressings applied on the 13th and 14th. Flowering began on the 18th September and fruit production from the 13th October. Fruiting stopped towards the middle of January, the season being rather short, as compared with those prevailing in the temperate regions.

The fruits representing the different treatments, as well as varieties, were collected from time to time and their fresh weights determined. The

yields thus obtained at each stage have been presented in Figs. 7-22. The average yields for each treatment have been presented in Tables VII and VIII.

TABLE VII.

Effect of different forms of manganese on the yield of tomato.

| Variety | Average yield per plant (in g.) on treatment with | | | | |
|----------------------|---|-------------------|------------------|-------------------|---------------------|
| | MnSO ₄ | KMnO ₄ | MnO ₂ | MnCO ₃ | Untreated (control) |
| Ponderosa | 355 | 418 | 439 | 301 | 286 |
| Bonnie Best | 257 | 271 | 264 | 248 | 247 |
| Globe | 288 | 310 | 335 | 256 | 258 |
| Marglobe | 248 | 274 | 311 | 238 | 214 |
| Perfection | 241 | 292 | 315 | 176 | 208 |
| King Humbert | 325 | 450 | 424 | 282 | 282 |
| Cherry Red | 217 | 301 | 341 | 141 | 170 |
| Golden Jubilee | 257 | 380 | 435 | 232 | 220 |

TABLE VIII.

Effect of lime on the response of tomato to different forms of manganese.

| Variety | Average yield per plant (in g.) on treatment with | | | | |
|----------------------|---|-------------------|------------------|-------------------|---------------------|
| | MnSO ₄ | KMnO ₄ | MnO ₂ | MnCO ₃ | Untreated (control) |
| Ponderosa | 202 | 213 | 225 | 187 | 125 |
| Bonnie Best | 192 | 223 | 229 | 151 | 141 |
| Globe | 122 | 192 | 150 | 105 | 87 |
| Marglobe | 211 | 233 | 224 | 110 | 114 |
| Perfection | 194 | 265 | 270 | 158 | 132 |
| King Humbert | 146 | 248 | 208 | 134 | 140 |
| Cherry Red | 250 | 298 | 357 | 176 | 223 |
| Golden Jubilee | 111 | 164 | 188 | 101 | 84 |

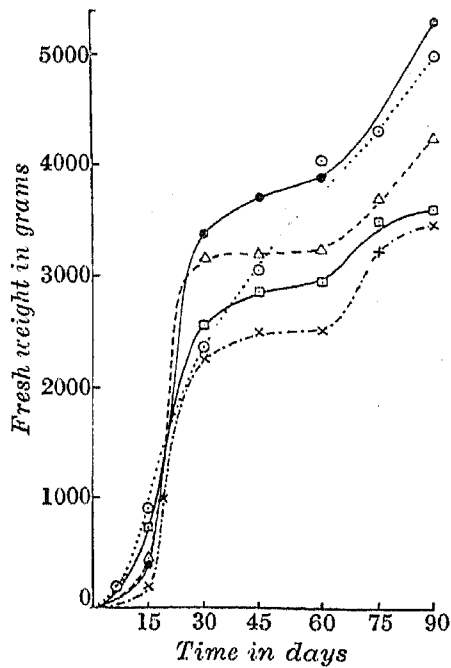


FIG. 7. Variety—Ponderosa.

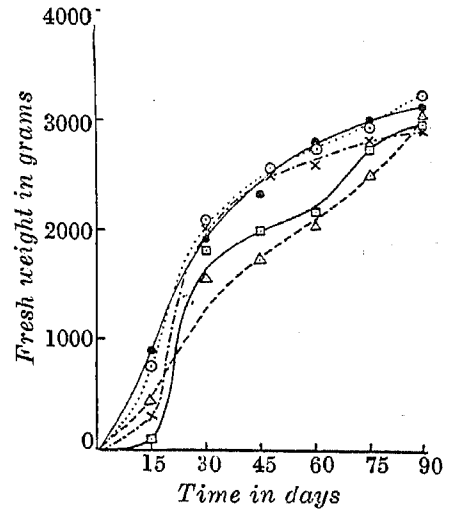


FIG. 8. Variety—Bonnie Best.

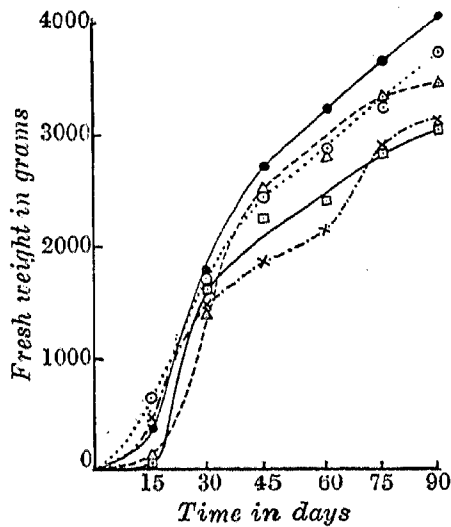


FIG. 9. Variety—Globe.

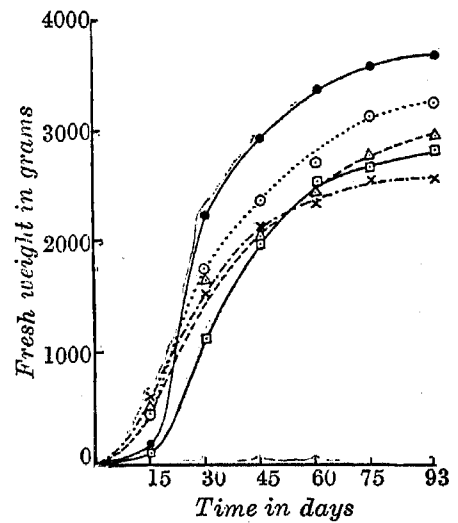


FIG. 10. Variety—Marglobe.

The unlimed plants came out generally better than the limed ones and yielded more fruit. Among the different treatments, permanganate and manganese dioxide were the most effective. It is difficult, however, to decide between the two, some varieties responding better to permanganate and the others to manganese dioxide. Manganous sulphate came out next and was followed by manganous carbonate which was slightly better than the control. Among the different varieties, Ponderosa, King Humbert

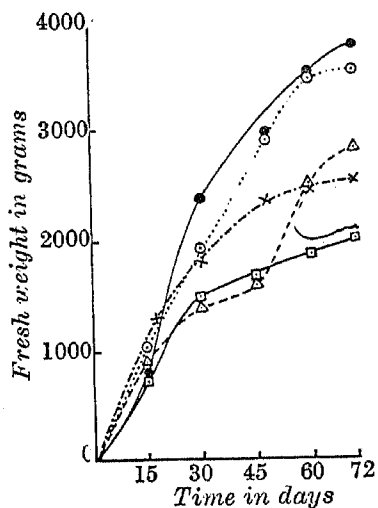


FIG. 11. Variety—Perfection.

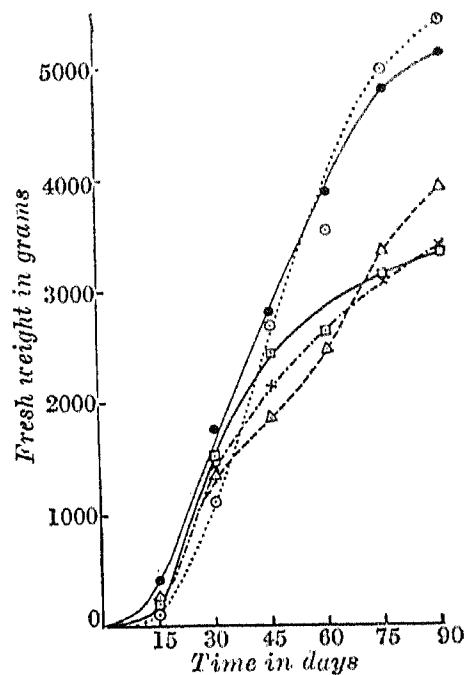


FIG. 12. Variety—King Humbert.

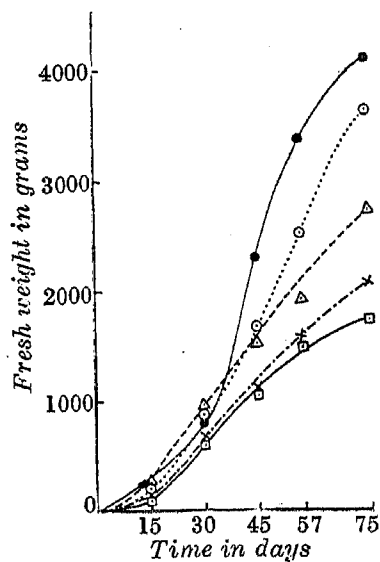


FIG. 13. Variety—Cherry Red.

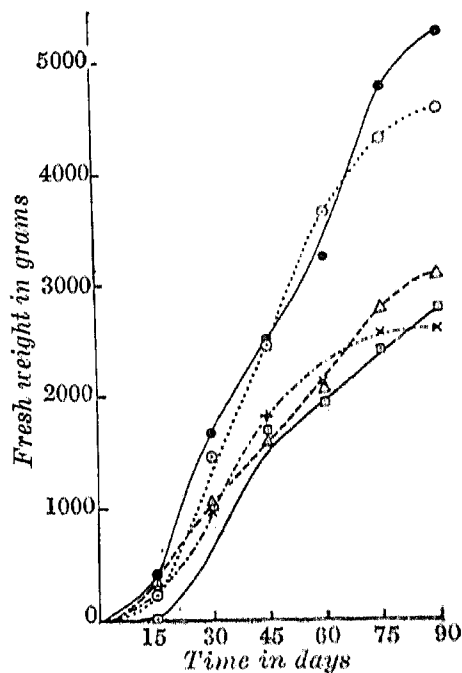


FIG. 14. Variety—Golden Jubilee.

x---x Control Δ---Δ MnSO₄ ○---○ KMnO₄ ●---● MnO₂ □---□ MnCO₃

Figs. 7 to 14. Effect of different forms of manganese on the yield of tomato.

and Golden Jubilee were the heaviest yielders and responded best to treatment with permanganate or manganese dioxide.

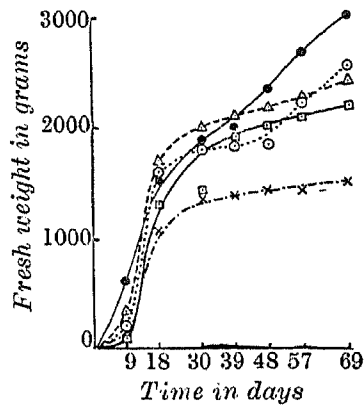


FIG. 15. Variety—Ponderosa.

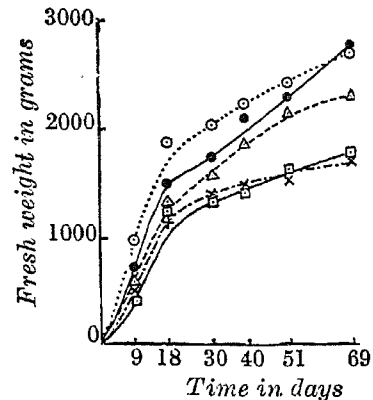


FIG. 16. Variety—Bonnie Best.

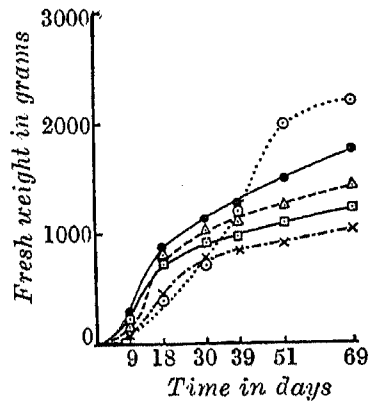


FIG. 17. Variety—Globe.

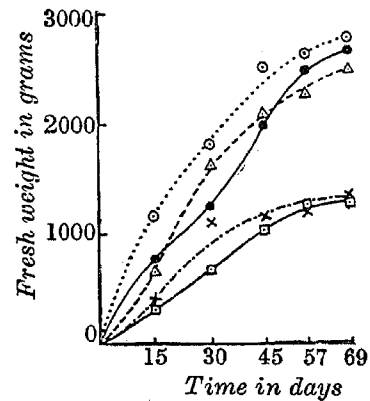


FIG. 18. Variety—Marglobe.

Observations on individual varieties.—

Ponderosa.—In both the limed and the unlimed series, the plants receiving permanganate were the first to bear fruit. They were soon overtaken, however, by those receiving manganese dioxide, which bore very heavily in the course of the first month. After that period there was a short one of rest followed by steady flowering and fruiting almost upto the end. The resting period is noticeable in all the cases, but the effect is least seen in those receiving manganese dioxide. The limed samples followed nearly the same course as the unlimed ones, but the yields were consistently lower than those from the latter.

Bonnie Best.—This variety bore fruit at a steady rate but the yield, when reckoned on the basis of weight, was rather low. As observed previously, the pots treated with permanganate were the first to bear fruit. Later observations did not however bring out any marked difference between the different treatments. In the unlimed series, permanganate and manganese dioxide were only slightly superior to the other treatments. Liming

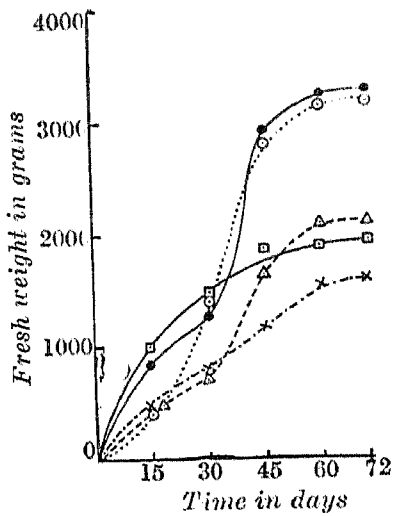


FIG. 19. Variety—Perfection.

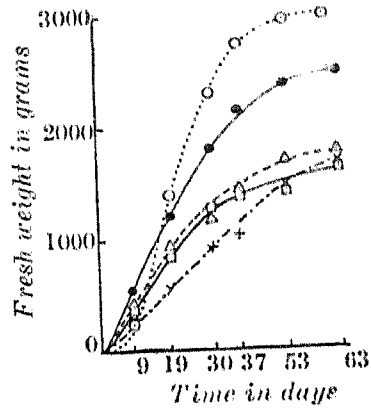


FIG. 20. Variety—King Humbert.

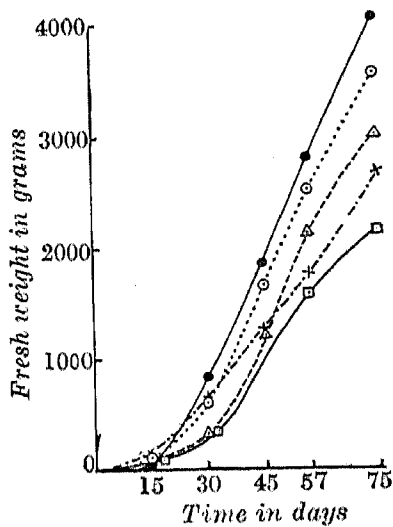


FIG. 21. Variety—Cherry Red.

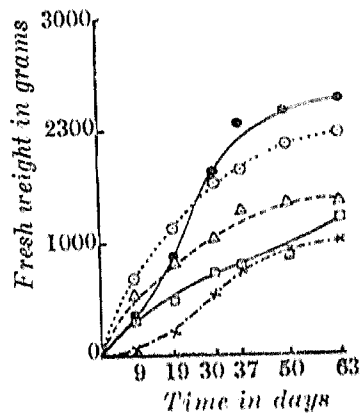


FIG. 22. Variety—Golden Jubilee.

---x Control △-△ MnSO₄ ○-○ KMnO₄ —●— MnO₂ □-□ MnCO₃

Figs. 15 to 22. Effect of lime on the response of tomato to different forms of manganese.

depressed the yield and the adverse effect was most marked in the case of the controls (untreated) and those receiving manganous carbonate.

Globe and Marglobe.—These two varieties behaved more or less similarly. In the unlimed series, manganese dioxide evoked the best response, though the increase in yield (30–50 per cent.) was not so marked as in the case of some other varieties. In the limed series, the yields were, as usual, greatly depressed. Permanganate yielded the best results and was followed by manganese dioxide and manganous sulphate respectively. Manganous carbonate was not much superior to the control.

Perfection.—In both the limed and unlimed series, manganese dioxide produced the best results, with permanganate following as a close second. The adverse effect of lime was most seen in the case of the controls and those receiving manganous sulphate.

King Humbert.—This variety is a heavy yielder. Application of permanganate increased the yield by about 50 per cent. Manganese dioxide was somewhat less effective but it was nevertheless very much superior to the other treatments. Liming reduced the yield by about 50 per cent., but even there the two oxidisers (permanganate and manganese dioxide) produced the best results.

Cherry Red.—The response of this variety to treatment with different forms of manganese was similar to those of others. Manganese dioxide yielded the best results with permanganate as the second. The effect of lime was however rather unexpected. In three cases, there was distinct increase in yield consequent on that treatment, while in the other two, it remained (permanganate and manganese dioxide) more or less the same. The significance of this observation is rather obscure but it would be of considerable scientific as well as practical interest to compare the chemical composition and physical properties of the tissue fluids of this variety with those of others (especially Golden Jubilee) which are adversely affected by lime.

Golden Jubilee.—This variety was a good, steady yielder and showed practically no lag during the three months of production. It responded best to manganese dioxide. Permanganate was a fairly distant second while the other treatments came very much behind. Liming had the worst effect on this variety, the yields being reduced to less than half by that treatment.

It would thus be seen that all the varieties responded very favourably to treatment with permanganate or manganese dioxide, the yields (as compared with the manured controls) being increased by 30-100 per cent. depending on the nature of the variety. Some varieties responded more favourably to a basal dressing of permanganate than to a top-dressing of manganese dioxide. Since both those treatments are chemically of the same order and yield similar products, it would appear to be advantageous to combine them. The quantities to be thus applied, the influence of season and soil conditions on such treatments would require further study. Except in the case of Cherry Red, liming was consistently unfavourable, but it would nevertheless be useful to determine whether similar observations would apply to other organic manures and to different types of soils.

Unmanured series.—The results of these experiments have not been recorded as the growths were generally poor and the yields low and unsteady. It was observed, however, that both in the limed and the unlimed series, the plants receiving permanganate or manganese dioxide came out better and yielded more fruit than the others.

Effect of treatment with different forms of manganese on the quality of tomato.—The market value of tomato depends largely on the size, shape and colour of the fruit. The popular taste in regard to sweetness and flavour, as also for fleshy or juicy fruits, is highly variable, but it may be stated in general, that sweet and juicy fruits are more favoured than the others. The activity of the digestive ferments present in the fruits, as also their contents of Vitamins B₁ and C are factors determining the nutritive value of fruits.

Specimens of fruits representing different varieties and treatments were compared from time to time. It was observed that shape and colour were essentially varietal characteristics. The size was partly dependent on the manuring. Thus, those receiving cake without lime were generally bigger than those with lime. The latter were, in turn, better than those raised in unmanured pots. No special distinction could be noticed, however, between the different treatments of manganese when the variety and the manuring were the same. The plants receiving permanganate or manganese dioxide bore larger number of fruits than those on other treatments, so this would account for the heavier yields obtained from the former.

The taste and flavour of the fruits representing different treatments were compared in the following manner:—Fruits of nearly the same size and at about the same stage of ripeness were collected at the same time and cut into slices which were kept separately. A number of volunteer tasters, "A", "B", "C", "D", . . . were invited to sample the slices and place them in order of taste and flavour. The opinions thus collected were entered separately for each variety and then analysed for their significance. It was found however that the results thus obtained were rather discordant. No special distinction could be found between taste and flavour. The order of preference varied with the individual and there was no clear majority in favour of fruits derived from any treatment. As an instance of the above, the order of taste and flavour as placed by four independent tasters in regard to one variety (King Humbert) may be cited below. (Table IX).

It may be seen from the table that the variations, if any, resulting from the different treatments were not so marked as to call for at least a majority opinion. The subtle distinctions observed by the individual tasters should be traced to certain personal factors which are obscure. It has to be

TABLE IX.

| Tasters | | | Treatment | | | | |
|---------|----|----|------------------------|-------------------|-------------------|------------------|-------------------|
| | | | Untreated (control) | MnCO ₃ | MnSO ₄ | MnO ₂ | KMnO ₄ |
| A | .. | .. | 2 | 4 | 3 | 1 | 5 |
| B | .. | .. | 3 | 5 | 4 | 2 | 1 |
| C | .. | .. | 3 | 4 | 2 | 5 | 1 |
| D | .. | .. | 4 | 2 | 1 | 3 | 2 |

inferred therefore that the chemicals, by themselves, had no perceptible effect on the taste and flavour of the fruit.

Vitamin contents.—Vitamin B₁ was assayed colorimetrically, the colour index as defined by Ghosh and Dutt (1933) being determined. It was found, however, that the values thus obtained were variable, even parallel samples showing a difference of 20-30 units. Even after allowing for this, some slight difference could be noticed between the controls and the different treatments. Thus, in the case of one variety (Cherry Red), the values were as follows:—Control (untreated), 570; MnCO₃, 478; MnSO₄, 504; KMnO₄, 454 and MnO₂, 463. When different varieties receiving the same treatment (KMnO₄) were compared, results of the following type were obtained:—King Humbert, 240; Perfection, 230; Cherry Red, 450; Peach, 440. It may thus be seen that the varietal differences were much greater than those introduced by the treatments.

Similar observations were also made in regard to Vitamin C contents which were titrated according to Birch, Harris and Ray (1933). Each variety had its own small range within which the different values lay. The values represented as mg. of ascorbic acid per c.c. of juice were as follows:—Ponderosa, 0.22-0.23; Bonnie Best, 0.22-0.25; Globe, 0.26-0.28; Marglobe, 0.20-0.21; Perfection, 0.20-0.22; Cherry Red, 0.25-0.29; King Humbert, 0.14-0.17; and Golden Jubilee, 0.26-0.28. The following were some typical values for individual treatments.

Variety, Cherry Red.—Control (untreated), 0.28; MnSO₄, 0.26; KMnO₄, 0.25; MnO₂, 0.28; and MnCO₃, 0.29.

Golden Jubilee.—Control, 0.27; MnSO₄, 0.26; KMnO₄, 0.26; MnO₂, 0.26; and MnCO₃, 0.28.

Bonnie Best.—Control, 0.23; KMnO₄, 0.22; MnO₂, 0.25; & MnCO₃, 0.22.

Perfection.—Control, 0.20; MnSO₄, 0.22; MnO₂, 0.22; and MnCO₃, 0.21.

Effect of varying dosages on the yield of French beans and tomato.—In the previous experiments, the different forms of manganese were compared on a more or less arbitrary basis. Thus, permanganate was applied at one-third of a ton per acre and compared with manganous sulphate applied on equivalent manganese basis. That this comparison is not justified is shown by the fact that whereas manganous sulphate continues to remain, at least for a short period, in water soluble form, the permanganate turns almost immediately into manganese dioxide. If manganese in soluble forms has any adverse effect on plant growth, it would naturally be more prominently seen in the case of manganous sulphate than in that of permanganate. It was considered desirable therefore to compare varying dosages of manganous sulphate with another form—manganese dioxide—which was more effective in the previous series. Some pot-culture experiments were accordingly carried out with French beans and tomatoes which had responded favourably in the earlier studies. The details relating to the preparation of the pots were the same as in the previous series except that larger quantities of cake (45 g. per pot) were applied. After applying the usual top-dressings, the pots with the seedlings were divided into six batches of 50 each and treated as follows:—(a) MnO_2 at 3.0 g. per pot; (b) MnO_2 at 6.0 g. per pot; (c) MnO_2 at 7.5 g.; (d) $MnSO_4$ at 1.5 g.; (e) $MnSO_4$ at 3.0 g.; and (f) control (untreated). Half the number of pots were allotted to French beans and the other half to tomatoes.

It was observed that the vegetative growth was favoured by increasing quantities of manganese dioxide whereas the reverse was observed in the case of manganous sulphate. The yields were also correspondingly affected as may be seen from Table X.

It may be noted that the yields obtained with 1.5 g. of manganous sulphate were nearly as high as those with 7.5 g. of manganese dioxide.

The foregoing experiments were carried out during the period, May-September, 1934. There were fairly heavy rains during June (18th-30th) when the tomatoes came to flower and the French beans were bearing. It may be expected that the adverse weather conditions had a depressing effect on the yield, but it is hardly probable that it affected any single treatment to a greater extent than the others. It has to be inferred therefore that manganous sulphate in minute quantities may be as beneficial as manganese dioxide or permanganate in much heavier doses.

The conditions relating to the application of soluble forms of manganese and the mechanism of their action on organic matter will form the subjects of later communications.

TABLE X.

| Treatment | Total yield in grams | |
|--------------------------------------|---------------------------------|--------------|
| | Tomato (var.—Golden Jubilee) | French Beans |
| | (Fresh weight) | (Dry weight) |
| MnO ₂ (3 g. per pot).. .. | 4995 | 565 |
| „ (6 g. „).. .. | 5798 | 630 |
| „ (7.5 g. „).. .. | 6113 | 710 |
| MnSO ₄ (1.5 g. „).. .. | 5858 | 705 |
| „ (3.0 g. „).. .. | 4125 | 610 |
| Control (untreated) | 3908 | 530 |

Discussion.

The present enquiry has brought to light a number of facts of scientific as well as practical importance. It has also indicated certain promising lines of future research.

The plot experiments with ragi have shown that while the yield can be improved by application of either permanganate or manganese dioxide, the extent of benefit to be derived from the treatment is largely determined by the season. This observation is in keeping with the other known facts in fertiliser practice. It is nevertheless important to determine the precise nature of the effect of climatic conditions on the action of oxidisers in the soil. The details relating to the application of the oxidisers in different seasons have yet to be standardised. The nature of the agencies determining the ratio of grain to straw will have to be studied and the conditions modified so as to ensure the best return to the producer.

The mode of interaction between soil and the different compounds of manganese and the subsequent changes in organic matter would suggest that in field practice (*a*) the ionic effect, if any, is much less important than the oxidising action, and (*b*) the resulting insoluble compounds are primarily responsible for the beneficial effects observed. The mechanism of the related changes is still not clear, but some evidence has already been obtained to show that manganese dioxide is one of the products formed in all the cases. Some of the manganese is also present in acid soluble form, but further work is needed to show whether it occurs as compounds such as carbonate and

phosphate or is otherwise associated with the mineral complex of the soil. The present study was carried out with only one type of soil. The observations should be extended to other types, as well, before any definite conclusions can be drawn. The influence of various factors such as reaction, temperature and moisture on the distribution of manganese should be studied. The relation of these changes to the oxidation of organic matter should also be followed.

The observations on the partial sterilising action of some of the compounds of manganese are highly suggestive. It is not clear as to whether the action is selective. The subsequent rapid recovery in numbers and the increased oxidation of organic matter would show that the adverse effect, if any, is only momentary and that the ultimate changes are beneficial to the crop. The action of these compounds is, in some respects, similar to that of those employed to combat soil sickness. It would be of much interest therefore to determine whether the two types of action are identical. It would also be of much practical value to determine whether chemical oxidation can be utilised to combat soil sickness and, better still, to remove the causes which lead to it.

The experiments with tomatoes have conclusively shown that basal dressings of permanganate or top-dressings of manganese dioxide lead to greatly increased yields. Addition of lime has a general depressing effect, but since, even, then the two oxidisers have given the highest yields, it may be expected that their application in field or glass-house practice (as the case may be) will always be attended by beneficial effects. The later observations have shown that small dressings of manganous sulphate can also lead to increased yields, but further work is needed to standardise the conditions for its application.

Tomato is a crop of much economic importance. The fruit is highly nutritious and is consumed in large quantities in all parts of the world. The crop is grown in the open in tropical countries, but in the colder regions it is largely raised under glass. The tomato requires heavy manuring and, at any rate in many parts of Europe and America, is an expensive crop to produce. It may be naturally expected therefore that any treatment which increases the yield by even a small margin should lead to useful returns to the producer. Treatment with oxidisers—especially with minerals such as manganese dioxide or ferric oxide—is comparatively cheap and since the present observations have shown that increased yields ranging from 30 to 100 per cent. (depending on the nature of the variety) can be obtained, such compounds should find ready application both in the field and in glass-house practice.

The beneficial effect of added mineral oxides raises a fresh issue of much scientific as well as practical interest. Every soil contains a useful quantity of ferric iron, at least a part of which is present as the oxide. Many soils are also naturally rich in manganese. These compounds are, no doubt, useful in bringing about a part of oxidation changes as may be seen from the results of the present study. They are not, however, so effective as their total quantities would suggest. They are indeed less useful than the much smaller quantities of fresh oxides applied as top-dressings. It would appear, therefore, that long periods of weathering, as also association with the silicates of the soil, combined with mechanical aggregation, have rendered them comparatively inactive. This, in turn, would naturally suggest that, if by some process, the mineral oxides of the soil can be activated, addition of fresh oxidisers would be largely unnecessary. A number of experiments have accordingly been started, subjecting the soil to a variety of treatments, some of which are similar to those adopted for effecting partial sterilisation. It is hoped that the results of these and other trials will form the subject of a later communication.

In addition to the above, further work is needed to determine the particular form or forms in which a chemical oxidiser would be most effective. Thus, there are several forms of ferric oxide or manganese dioxide all of which may not be equally useful. The method of preparation (if produced in a factory) and the state of division would be important factors determining the efficiency of the oxidiser. When a quarried mineral is used, the associated compounds would also have to be taken into consideration when assessing the fertilising value of the oxidiser.

The previous researches (Bhaskaran, Narasimhamurthy, Subrahmanyam and Sundara Iyengar, 1934; Sundara Iyengar and Subrahmanyam, 1935) have also shown that soluble ferrous iron is steadily precipitated in the soil and finally oxidised to the ferric condition. It may be naturally expected that, in such cases, the precipitate will occur in finely divided condition. The resulting oxide may thus prove to be more reactive than any other form which may be directly applied to the soil. Some experiments have therefore been started, comparing the oxidative efficiency of different forms of soluble ferrous as well as ferric iron with that of pure ferric oxide. Similar trials are also being conducted with different soluble manganese salts comparing them with manganese dioxide.

Although there has been no significant difference in regard to Vitamin B₁ and C contents, it is yet probable that application of different forms of manganese may have produced other profound changes in plant metabolism and modified the nutritive value of the products. The effect on enzyme

activity is still awaiting systematic investigation. Some preliminary observations suggested that there is no appreciable difference in regard to oxidase and peroxidase activities, but further quantitative work is needed before any definite conclusion can be reached. The distribution of manganese between the different parts of the plant will also be of much value, in view of the increasing importance of manganese in animal and human nutrition.

Summary.

(1) Plot experiments with ragi (*Eleusine coracana*) showed that, on both manured and unmanured soil, treatment with small quantities of permanganate led to increased yields of grain and straw. Permanganate applied together with the organic manure was more effective than that applied later as top-dressing.

(2) Permanganate applied to soil passes rapidly into water-insoluble condition. Part of the product is soluble in dilute acid, while the rest is insoluble in that reagent. Other compounds of manganese also behave in a manner similar to that of permanganate. Manganous sulphate is slow to react, but after a few days, that too yields insoluble products.

(3) Application of either potassium permanganate or manganous sulphate causes an immediate reduction in the number of soil bacteria. After a few days, however, the adverse effect is removed and the numbers increase at a rapid rate.

(4) When equivalent quantities of different forms of manganese were applied, the decomposition proceeded most rapidly in presence of manganese dioxide. Permanganate came second and was followed by manganous carbonate and manganous sulphate respectively.

(5) Production of carbon dioxide followed the same order as the decomposition of organic matter. There was close correlation between loss of carbon on the one hand and production of carbon dioxide on the other.

(6) Under the conditions of the present study, less than a fourth of the oxidation of organic matter was due to the action of the mineral constituents of the soil. About a third was due to the oxidiser when manganese dioxide was applied. The rest was due to microbial action. The division is however only arbitrary since the various agencies are either mutually dependent upon or otherwise influenced by each other.

(7) Experiments with eight varieties of tomato have convincingly demonstrated the advantages of supplementing organic manures with chemical oxidisers. Improved yields ranging from 30 to 100 per cent. (depending on the variety) were obtained. Manganese dioxide and potassium permanganate yielded the best results. Manganous carbonate and manganous

sulphate—at any rate, in the proportions at which they were tried—were not much superior to the control (untreated). Among the different varieties, the best response was from Ponderosa, King Humbert and Golden Jubilee.

(8) Liming generally depressed the yield of tomato. The adverse effect was greatly reduced by application of either manganese dioxide or potassium permanganate. The variety, Cherry Red, was, however, an exception as it responded favourably to application of lime.

(9) Treatment with different forms of manganese does not produce any appreciable difference in the quality of tomato. Fruits of the same variety possess about the same degree of flavour and taste and contain approximately the same amounts of Vitamins B₁ and C irrespective of the form of manganese received by them.

(10) The significance of the foregoing and other observations has been discussed. The possibility of applying chemical oxidisers to obtain greatly increased yields of crop—especially of tomato—has been indicated. Certain useful lines of future research leading to (a) improved methods of applying chemical oxidisers and (b) enhancement of the oxidising action of minerals already present in the soil, have been suggested.

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