

felder, as well as important modification of the pre-existing drainage systems.

8. The existing cycle of erosion which is still in its youthful stage.

NOTE ON THE OCCURRENCE OF MANGANESE IN
SOIL AND ITS EFFECT ON GRASS.

By F. B. GUTHRIE, F.I.C., F.C.S., and L. COHEN.

[Read before the Royal Society of N. S. Wales, November 3, 1909.]

A sample of soil was received during last month from the Secretary of the Dubbo Bowling Club representative of a number of small patches occurring throughout the green on which the grass had died down during last winter. It is stated that the green was laid down five years ago, and for the first three years was covered with a splendid coat of healthy couch, but last winter and this winter it died in 40 or 50 small patches, ranging from a few inches to two feet in diameter. As the green receives the same treatment throughout, and as both the soil and the climate of the district are admirably adapted to the growth of couch, the problem presented was an interesting one, especially as there was an absence of the sour condition and shallowness of surface-soil frequently associated with such infertile patches. A sample typical of the soil over the remainder of the green and taken from places within three feet of the dead patches was also obtained. A preliminary examination showed that both the soils were very similar in chemical composition, but the fact was noted by one of us, Mr. L. Cohen, that manganese was present in the soil on

which the grass died down and was absent in the other. The following is the result of the analyses of these soils:—

Examination of soil from a dead patch on Dubbo Bowling Green, forwarded together with portion of the healthy soil by E. R. Hawke, Secretary.

	Soil from normal portion	Soil from part where grass dies off.
Reaction	neutral	neutral
Capillary power	9.3 ins.; excellent	6.6 ins.; good
Moisture	1.76 %	2.09 %
Volatile and organic matter	5.79 "	5.10 "
Nitrogen063 "	.105 "
Total water-soluble salts039 "	.045 "
Lime (CaO) soluble in hot HCl324 "	.329 "
" " in 1% citric acid... ..	.249 "	.220 "
Potash (K ₂ O) soluble in hot HCl038 "	.037 "
" " in 1% citric acid... ..	.010 "	.011 "
Phosphoric acid (P ₂ O ₅) sol. in hot HCl122 "	.105 "
" " in 1% citric acid... ..	.030 "	.017 "
Oxide of Manganese (Mn ₂ O ₃) total... ..	.000 "	.254 "
" " " soluble in hot HCl... ..	.000 "	.022 "
" " " soluble in 1% citric000 "	.033 "

The total manganese was determined by fusion of 2 grms. of the soil with sodium carbonate, the portion soluble in hydrochloric acid was determined in 10 grms of the soil boiled for 20 minutes with hydrochloric acid of 1.1 sp. gr. In the determination of the citric acid soluble manganese, 100 grms. of the soil were shaken with 1 litre of one per cent. citric acid for 20 hours in a mechanical shaker at 50 revolutions per minute.

The only difference shown by the analysis of these two soils is the presence of manganese in the patches on which it is reported that the grass dies down in the winter. It is possible that manganese is present as traces in the other soils, but not in sufficient quantities to give an indication by the methods adopted.

A great number of experiments have been made of recent years, both in pots and in the field, to test the effect of such substances as salts of manganese, zinc, etc., on the growth of plants, particularly by O. Loew and his co-workers at Tokio, and others. A resumé of the work done and references to the original papers will be found in the Annual Reports of the Chemical Society, Vols. I–V. An excellent resumé is also given by G. Pollacci.¹

On the whole, although the results so far obtained cannot be regarded as entirely conclusive, it appears that manganese compounds in the soil in small quantities exert a stimulating effect on the growth of many crops, but whether that effect is due to the direct action of manganese as plant-food or to a secondary action upon other constituents in the soil is not yet satisfactorily determined. Some chemists state that the presence of manganese is necessary to the growth of the plant, and that it is present in minute quantities in all soils. In the particular case of meadow-grass, G. Salomone² found that the pasture was greatly improved by the addition of small quantities of sulphate of manganese, 1 grm. of the metal per square metre (about 27 lbs. of sulphate of manganese per acre) produced a more vigorous growth and of a darker green, the yield of hay calculated to the hectare being 760 kilos greater in the case of the plot which had received the manganese than in the other. The effect on other crops of small quantities of manganese will be found by consulting the references already referred to.

Mr. Cuthbert Potts of the Hawkesbury Agricultural College has also been conducting experiments in this direction, both in the field and in pots. Mr. Potts has experimented with wheat for hay in the field by manuring with

¹ *L'Industria Chimica*, Anno 9, No. 5, p. 65, March 10th, 1909.

² *Le Staz. Sper. Agr. Ital.*, Vol. XL, p. 108.

20 lbs. sulphate of manganese per acre, applied after the seeds had germinated, and although the season was not a favourable one, and the figures are not conclusive, and in some cases the treated plots did not yield any better than the untreated, he finds that on the average the yield from the untreated plots is somewhat better. In the pot-experiments also, Mr. Potts reports a slight average increase with wheat, tares, and oats on treating the soil with '001, '002, and '005% manganese sulphate. Oats are stated to show the greatest increase.

In larger quantities manganese compounds have been found to act as plant-poisons. G. Salomone¹ finds as the result of experiments in the field, that 50 kilogrammes of manganese sulphate per hectare (about 44 lbs per acre) produce the most favourable results in the case of wheat. Above this quantity the development of the plant is retarded and the proportion of grain and straw diminished. With 80 to 85 kilos per hectare the plants died before flowering, and with 90 kilos per hectare the plants only attained a height of a foot and then suddenly wilted. He finds also that the toxicity of the different salts of manganese increases in those in which it acts as an electronegative element, being greatest in the manganates and permanganates.

A series of interesting experiments has been published by W. P. Kelley² of the Hawaii Experiment Station, into the effect of manganese upon the growth of pineapples. He finds that certain areas of the soil in Hawaii on which the plants do not develop, turning yellow in colour and producing inferior fruit, always contain excessive quantities

¹ Le Staz. Sper. Agric. Ital., Vol. xxxviii, p. 1015, and Vol. xl, p. 97. In the first paper will be found a good bibliography of previous work on this subject up to 1905.

² Journal of Industrial and Engineering Chemistry, Vol. i, No. 8, p. 533 (August 1909).

of manganese compounds. Analyses of these soils show that those on which the pines become yellow contain on the average as much as 5.61% of manganese (calculated as Mn_3O_4) in the surface-soils as against 0.37% in the soils producing the healthy pines. In this case it is to be noted that both soils are highly ferruginous, containing over 20% ferric oxide, the good soil being of a red colour, while the infertile soils are black. He has shown a further interesting point which bears upon the question immediately before us, namely, that on soils containing an intermediate proportion of manganese, (1.36% Mn_3O_4), the pines become distinctly yellow during the winter months, but sometimes recover completely with the return of the warm weather.

Although the quantities of manganese found in the poor soil examined by us is not nearly so great as that in the black Hawaiian soils (containing only .245% calculated as Mn_3O_4), yet it is possible that the peculiarity noticed in this soil, that the grass dies down in the winter, is due to the same cause, namely, the presence of an amount of manganese not sufficient to kill the plants when growing vigorously, but sufficient to affect them when in a less vigorous state of growth. Aso¹ has also pointed out that the toxic effect of manganese salts on wheat and barley is greatest in the cold weather, the plants recovering themselves completely with the return of warm weather.

That the cause of the failure of the grass in these patches is due to the presence of manganese is only put forward as a suggestion. It is to be noted that the Dubbo soil is not particularly rich in iron, and that the soils do not differ in colour, both being of a brownish colour becoming red on ignition. The peculiar fact that the grass showed no sign of the effect of the poison for the first three years is also

¹ Bulletin, College of Agriculture, Tokio Imperial University 5, No. 2, p. 177.

noted in the case of the Hawaiian soils. W. P. Kelley (*loc. cit.*) reports that the first crop of pines showed but little yellow colour during the first twelve months when grown on the black soils. Later, however, the plants became yellow and refused to grow. The soil itself also appears to become darker in colour with the continued growth of the pines. He concludes from this that there is possibly some change brought about in the soil by the crop itself, resulting in a change in the state of oxidation of the manganese.

Speaking generally concerning what is known of the action of manganese in the soil, it may be regarded as proved that in small quantities it is beneficial to some crops, that in larger quantities it acts as a plant-poison, but whether this is due to the direct action of the manganese itself or to some secondary action on the soil-constituents is not established. A quantity of manganese which is toxic to some plants may be harmless towards others. Thus Aso (*loc. cit.*) finds that barley and oats are not affected by doses of manganese which are injurious to rice, and Kelley states that the soils which do not grow pineapples give good crops of sugar cane. The toxic action is greatest in winter, and if the quantity of manganese present is not excessive the affected plants often recover with the warm weather. The compounds in which manganese plays the part of an electro-negative element are the most toxic, and it appears that some process goes on by which the manganese is converted in the soil from an originally innocuous compound to a more poisonous one, so that its presence is not noticed in the soils for the first year or two. This process is probably one of oxidation, as the higher oxides are found to be more toxic than the lower.

Corroboration of these results has been afforded by the examination of patches of land at Milton (South Coast) in

which barley would not grow. Comparison of the manganese content of this soil and of adjacent land in the same paddock, on which barley grows satisfactorily, showed that in the case of the bad land a higher percentage of manganese was present. The quantities in both cases were again small, but was larger in the bad soil both in the fusion, hydrochloric and citric acid solutions. The amounts soluble in hydrochloric acid were 0·038% in the good soil, and 0·087% in the bad, the amounts soluble in citric acid being 0·034% in the good soil, and 0·062 in the bad. Judging from these results alone, which is perhaps premature, it would appear that couch grass is affected by a proportion of manganese which has no appreciable effect upon barley.

A further case of soil-poisoning probably due to manganese, has been afforded by the examination of samples of soil from the Experiment Farm at Bathurst, on which wheat died down before reaching maturity. The soil on which the crop died was found to contain ·114% Mn_3O_4 (soluble in hydrochloric acid) as against ·026% in soil from the same paddock in which wheat grew normally.

The sample of bad soil was found to contain small fragments (1/10 gram to 1 gram in weight) of a manganiferous iron compound of a black colour and very soft.



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