all of the solvent remaining in the pomace. Steam distillation does not give complete recovery.

V—No commercial value as fertilizer should be assigned to olive pomace, either before or after extraction.

Laboratories of Zymology and Agricultural Chemistry
Agricultural Experiment Station
Berkeley, California

MANGANESE AS A CAUSE OF THE DEPRESSION OF THE ASSIMILATION OF IRON BY PINEAPPLE PLANTS

By Maxwell O. Johnson

Received October 30, 1916

The chief pineapple district of the Hawaiian Islands lies on the Island of Oahu on the sloping tableland between the Koolau and Waianae mountain ranges. Through this district there occur various areas of dark or black manganiferous soils, and it has been known for ten or twelve years that pineapples on such soils make a very poor growth. At almost any age, but usually about flowering time, the leaves of the pineapple plants gradually become yellow, the plants making slight growth and often dying. The few fruits produced are of small size and poor quality. The unripe fruit, which is pink or red in color instead of the normal green, often cracks open and decays. The flesh of the ripe fruit is hard and white, with considerable acidity. As the dark soils where yellowing of pineapples occurs, aggregate from 6,000 to 10,000 acres of the lowest lying, most accessible, and most easily cultivated land of this region and as the water supply is insufficient for the growth of sugar cane, the profitable utilization of these soils is of considerable economic importance.

ANALYSES OF MANGANIFEROUS SOILS

Kelley[1] first showed that this yellowing of pineapple plants is directly related to an abnormal amount of manganese in these dark soils. From a number of analyses made by the method of the Association of Official Agricultural Chemists, he gives the average water-free composition of the normal red soils and of the manganiferous black soils as follows:[2]

Table I—Composition of Normal Red Soils and Manganiferous Black Soils of Oahu

Average Percentage Composition of	Red Soils	Red Sub-soils	Black Soils	Black Sub-soils
Insoluble matter	42.82	41.42	35.26	37.73
Potash (K_2O)	0.59	0.63	0.91	0.87
Soda (Na_2O)	0.27	0.25	0.31	0.41
Lime (CaO)	0.36	0.48	0.97	0.58
Magnesia (MgO)	0.39	0.38	0.47	0.41
Manganese oxide (Mn_3O_4)	0.37	0.20	5.61	4.90
Ferric oxide (Fe_2O_3)	27.82	30.10	22.58	22.96
Alumina (Al_2O_3)	10.04	10.37	15.39	17.20
Phosphorus pentoxide (P_2O_5)	0.08	0.12	0.27	0.16
Sulfur trioxide (SO_3)	0.11	0.08	0.17	0.06
Volatile matter	15.14	13.74	17.61	13.67
Titanium oxide (TiO_2)	2.01	2.49	0.88	1.08
Total	100.03	100.26	100.43	100.03
Nitrogen (N)	0.32	0.24	0.37	0.20
Acidity[1]	1235.00	..	98.00	..

[1] Calculated to pounds of CaO per acre foot.

The writer has analyzed a number of these manganiferous soils, the analyses agreeing in the main with those of Kelley. However, a typical example of the "manganese yellows" with the characteristic red fruit was found to occur on a soil containing only 0.31 per cent manganese (calculated as Mn_3O_4). This manganese was all present as the dioxide.

A number of samples were distilled according to the ordinary Bunsen method for determining available oxygen in pyrolusite, and the manganese dioxide was calculated. Table II shows the results as compared with the total manganese determined by the official method.

Table II—Comparison of Percentages of Total Manganese with the Manganese Dioxide in Manganiferous Soils of Oahu

Laboratory No.	635	636	637	638	639	640	641
Total manganese calculated as the dioxide. (Official method)	0.35	5.48	5.92	5.89	2.86	6.36	3.25
Manganese dioxide. (Calculated from the Bunsen distillation)	0.35	4.85	5.20	5.15	2.66	5.67	1.92

As the Bunsen method gives low results when organic matter and possibly ferrous iron are present, it is safe to conclude that nearly all the manganese in these soils is present as the dioxide.

THE EFFECT ON PLANTS

Kelley[1] and Wilcox and Kelley[2] made an extended investigation of the effect of these manganiferous soils on the pineapple and other plants. Field notes, results of pot experiments, and ash analyses are given, comparing a large number of plants on manganiferous and normal soils.

From this investigation, Kelley[3] concludes:

"That various plants when grown on manganiferous soil are affected differently. Some species are stunted in growth and die back from the tips of the leaves, which turn yellow or brown and frequently fall off, and a general unhealthy appearance results. Other species appear to be unaffected and so far as can be judged vegetate normally in the presence of manganese. Microscopic investigations have shown that in certain instances the protoplasm undergoes changes. Occasionally it draws away from the cell wall, the nuclei become brown, and plasmolysis takes place.

"From the ash analyses it was found that manganese was absorbed in considerable quantities, and in nearly every instance was greater in the plants from manganiferous soil. The ash analysis also shows that a disturbance of the mineral balance takes place. The percentage of lime is increased, while the absorption of magnesia and phosphoric acid is decreased * * *

"From these evidences we may believe that the effects of manganese are largely indirect, and are to be explained on the basis of its bringing about a modification in the osmotic absorption of lime and magnesia, and that the toxic effects are chiefly brought about through this modification rather than as a direct result of the manganese itself."

COMPARISON OF ASH ANALYSES WITH OBSERVED EFFECT OF THE MANGANESE

It was thought that it would be of value to attempt some correlation between the ratio of the ash constituents on manganiferous and normal soils and the field notes. The ash ratios for the four constituents mentioned by Kelley,[4] together with those for potash and iron, are given in Table III. The field notes are quoted from Kelley, as they permit an unbiased interpretation of this work. The ash ratios for the leaves of the young plant are used wherever possible, as the chief metabolic disturbances occur there. In cases where the iron and alumina in the ash are reported together, it is impossible to give an iron ratio. No field notes on the ironwood and olive were kept.

A consideration of Table III shows that there is no possible correlation between the observed effects on

[1] Hawaii Sta. Press, *Bull.* **23**; This Journal, **1** (1909), 533; Hawaii Sta., *Rpt.* **1909**, p. 58.

[2] Hawaii Sta. Press, *Bull.* **23**, 3.

[1] Hawaii Sta., *Bull.* **26** (1912).

[2] *Ibid.*, *Bull.* **28** (1912).

[3] *Ibid.*, *Bull.* **26** (1912), 38, 39.

[4] Hawaii Sta., *Bull.* **26** (1912), 36.

TABLE III—RELATIVE PROPORTION OF SOME ASH CONSTITUENTS OF PLANTS GROWN IN MANGANIFEROUS AND NORMAL SOILS

Ash percentage on normal soils taken as 1.0

Plant No.	Plants analyzed	Mn_3O_4	CaO	MgO	P_2O_5	K_2O	Fe_2O_3	Observed Effects of Manganiferous Soil on Plants
PLANTS AFFECTED BY MANGANIFEROUS SOIL								
1	*Paspalum orbiculare*	2.09	0.79	0.69	1.09	1.34	0.26	Very sensitive. Suggested by Kelley as a vegetation indicator of nonmanganiferous soils
2	Peanut leaves	6.25	0.90	0.51	0.90	1.70	0.54	Lower leaves brown, subsequently dying and falling away; stem purple, roots brown.
3	Pineapple leaves, 5 mo. old	1.42	1.26	0.75	0.79	0.92	0.73	Seriously affected. Leaves yellow, fruit small and red
4	Pigeon pea leaves	9.54	2.05	0.42	0.37	....	....	Less than half the growth on normal soil. Lower leaves brown and dying back
5	Sugar cane	0.75	0.86	0.73	0.80	0.70	0.72	Yellow color on lower leaves developed by young cane during winter
6	Broom corn leaves	3.74	2.22	1.92	0.68	2.32	0.81	Pronounced effect
7	Cowpea vine	3.53	1.33	0.76	0.58	0.93	0.84	Very sensitive. Stem becomes purple, lower leaves turn brown and fall away
8	Corn stover	2.66	2.50	1.66	0.68	0.91	0.87	Seriously affected, stalks and leaf sheath purple, lower leaves brown and dying back
PLANTS APPARENTLY NOT AFFECTED BY MANGANIFEROUS SOIL								
9	*Waltheria americana* leaves	10.61	1.06	0.70	0.74	0.68	1.20	No effects
10	Crotalaria	28.00	1.62	0.37	0.45	1.25	2.38	Unaffected by manganese, making luxuriant growth
11	Guava leaves	2.93	1.87	0.35	0.58	0.28	6.67	No visible effects. (Found scattered over unplowed portion.)
12	Oat straw	0.86/T.	2.69	1.62	0.08	..	..	Slight stunting at first, with later normal growth
13	Mango leaves	9.01	1.93	0.44	0.53	..	..	Normal growth
14	Wheat straw	0.22/T.	2.16	1.47	0.53	..	..	Fair growth
15	Tobacco stems	0.57/T.	5.04	1.25	0.28	..	..	Slight stunting at first, with later normal growth

the plants of manganiferous soil and the variations of the individual ash constituents in the case of manganese, lime, magnesia, phosphoric acid, and potash. It is unnecessary to point out the contradictions which these variations exhibit, as they are apparent at a glance. The lime-magnesia ratio also shows no correlation, but in the case of the iron, a remarkable correlation is easily seen. The assimilation of iron is depressed on those plants to which the manganiferous soil is toxic, while it is increased on those where no toxic effect is observed. This is shown further by Fig. I, where the plants are plotted, according to their

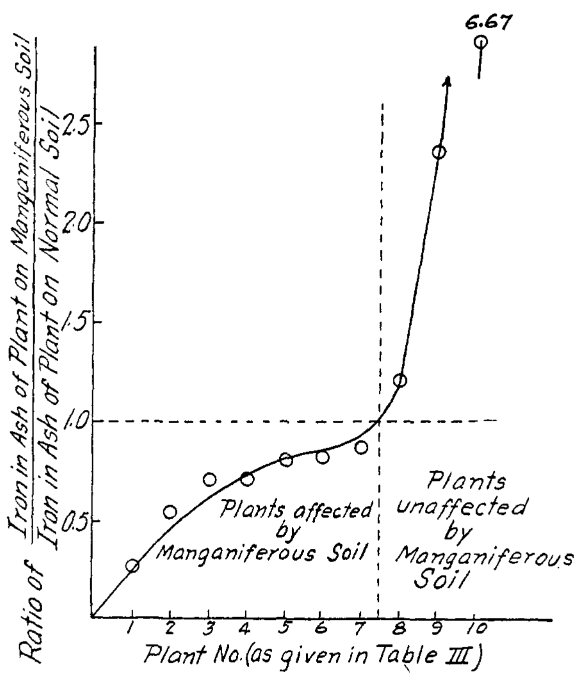

FIG. I—GRAPH SHOWING CORRELATION BETWEEN THE ASSIMILATION OF IRON AND THE EFFECTS ON THE PLANTS GROWN ON MANGANIFEROUS SOIL

number in Table III, on the axis of abscissas, with the ash ratio as ordinates. It would be expected that a significant excess or lack of a constituent would be shown by an opposition of the points plotted in the angles formed by the intersection of the line dividing the plants affected and unaffected by manganiferous soil and the horizontal line for an ash ratio of 1.0.

An inspection of Fig. I shows that the iron content of affected plants is decreased, while that of plants unaffected is considerably increased. Similar graphs for the other ash constituents are without significance. On the basis of this interpretation, the observed physiological derangements are easily explained. The purple, brown, or yellow color, the lack of starch, and other toxic effects are due to deficiency of chlorophyll, for the production of which a proper supply of iron is necessary.

PRACTICAL METHODS OF CONTROL

The theory that this trouble is due to a lack of iron has found striking confirmation in its practical application to the pineapple, the chief economic crop of the region where the manganiferous soils occur. Fields of yellow, unhealthy plants sprayed with solutions of iron salts became green within a very short time. The effect on the fruit was most remarkable. The small, red, stunted pineapples, when sprayed, showed decided improvements within a week, becoming normal dark green and commencing a most vigorous growth within two or three weeks' time. Where iron was applied to one side of the unripe fruit only, that side became green first and made such growth that the fruit soon presented a lopsided appearance. Later the iron appeared to be distributed, as the fruit was fairly symmetrical when ripe. Solutions of iron salts applied to the etiolated leaves of the pineapple plants effected quick relief, while relatively immense quantities of solution and of solid iron salts applied to the soil were without result. Acids applied to the soil and combinations of iron salts with various fertilizing elements were tried without effect. Sodium nitrate gave promising results. Ferrous sulfate sprayed directly on the leaves proved the most economical form of iron to apply. Solutions made slightly acid with sulfuric acid or the waste pineapple juice from the canneries gave slightly better results, the acid tending to prevent precipitation of the basic ferric sulfate.

A convenient and profitable method of treatment has been worked out which has been applied to extensive areas of highly manganiferous soil with immediate success. Good yields of pineapples of excellent size and quality have been harvested from plants sprayed with ferrous sulfate, while on the unsprayed check plats, all the plants were yellow, and many were dead and dying, with fruit of such inferior size and quality as to be scarcely worth picking.

As a result of the writer's experiments, practically all the pineapple plantations have now utilized this spraying treatment on the manganiferous soils. Success has everywhere been reported, and at present there seems no obstacle to the profitable cultivation of these extensive areas of manganiferous soil.

These experiments will be given in fuller detail in a forthcoming publication of the Hawaii Agricultural Experiment Station.

MANGANESE AS THE CAUSE OF A DEPRESSION IN THE ASSIMILATION OF IRON

It is well known that excessively calcareous soils[1] may depress the assimilation of iron and even lead to a chlorosis, but this seems the first case where a manganiferous soil has caused such trouble. That manganese is the cause is evident from the fact that the usual calciphilous legumes are among the most strongly affected.

Many fertilizer experiments with different forms of manganese show a stimulation with small doses and a toxic effect with larger applications. Other experiments show no effects.

Loew and Sawa[2] in 1903 published results of water-culture experiments where they observed a yellowing of pea plants, barley, and soy beans with solutions to which manganous sulfate had been added. The addition of manganous sulfate to the ordinary iron-containing nutrient solution caused an increased growth but later a yellowing took place. This yellow color they think may be due to the increased activity of the oxidizing enzymes. In their conclusions they state that "manganese exerts in moderate quantity an injurious action on plants, consisting in the bleaching out of the chlorophyll. The juices of such plants show more intense reactions for oxidase and peroxidase than the healthy control plants."

Aso[3] in similar water cultures with young radish, barley, and wheat plants observed a yellowing with solutions containing (*a*) 0.02 per cent $MnSO_4$ + trace of $FeSO_4$, (*b*) 0.02 per cent $MnSO_4$ + 0.02 per cent $FeSO_4$, (*c*) 0.02 per cent $FeSO_4$ and in these three solutions diluted with 10 times their volume of water. The ordinary mineral constituents were supplied. With the solution containing only a trace of $FeSO_4$ and diluted ten times, the yellowing suggested an interference in the assimilation of iron. Pea shoots grown during the first stage of development, without mineral salts, in solutions containing 0.002 per cent of ferrous and manganous sulfates singly and in combination found the greatest stimulation with the manganous sulfate. No yellowing was observed during this first stage of development.

This observation seems to be the only intimation the writer can find from a brief review of the literature of any association of the depression in the assimilation of iron with the toxic effect of manganese.

SUMMARY

I—It has been shown that the manganese of the highly manganiferous soils of the Island of Oahu is nearly, if not all, in the dioxide form.

II—From a study of ash analyses of plants grown on these manganiferous soils, it appears that the toxic effect observed is due to a depression in the assimilation of iron.

III—The pineapple plant, the chief economic crop grown on these manganiferous soils, has recovered from the toxic effects of the manganese when supplied with iron through the leaves.

IV—A commercially successful treatment has been worked out, and the profitable utilization of these highly manganiferous soils seems assured.

HAWAII AGRICULTURAL EXPERIMENT STATION
HONOLULU, H. I.

[1] See Gile, Porto Rico Sta., *Bulls.* **11** (1911) and **16** (1914).

[2] *Bull. Col. Agr. Tokyo Imp. Univ.*, **5** (1902–3), 161–172.

[3] *Ibid.*, **5** (1902–3), 177–185.

THE FERTILIZER VALUE OF CITY WASTE
I. THE COMPOSITION OF GARBAGE

By W. J. O'BRIEN AND JOHN R. LINDEMUTH

Received September 5, 1916

In connection with its investigation of the fertilizer resources of the United States, the Bureau of Soils has undertaken the study of the various city wastes to discover if there may be found therein a source of those materials which have value as fertilizer ingredients. The study has involved the origin, composition and methods of disposal of these. It has had to do with the statistical, economic, engineering and sanitary features of the problems of the collection, disposal and utilization of city wastes. Most of the work has been done in the field. In the laboratory various classes of substances have been examined analytically to determine their composition; the availability of the ingredients of potential fertilizer value has been studied and new methods and apparatus for the more economical commercial treatment of these waste materials have been devised. It is proposed to present the results of the laboratory investigations in the present series of papers.

The work has been carried out under the direction and with the collaboration of J. W. Turrentine.

In the commercial rendering of city garbage for the recovery of fats and the preparation of tankage for fertilizer use, the success of the undertaking depends largely on the quality of the raw materials. Due to the wide diversity existing between the methods of handling city wastes in vogue in the various cities, it by no means follows that because the rendering of the garbage of one city is commercially profitable, that of any other city will be. If segregation is effected with equal skill and the richest portions of the garbage are not diverted from the rendering plant, success in one city connotes success in another.

The ingredients of segregated garbage in which a prospective renderer is interested are fats, bone phosphate, combined nitrogen and potash. The first named is the ingredient representing the main value to be recovered. And among those of fertilizer importance, combined nitrogen has the greatest value.

The large quantities of garbage available, the expense to which most urban communities are put in disposing of it, and the profits realizable from its