1431 Issued April 8, 1912.

HAWAII AGRICULTURAL EXPERIMENT STATION,

E. V. WILCOX, Special Agent in Charge.

Bulletin No. 26.

THE FUNCTION AND DISTRIBUTION OF MANGANESE IN PLANTS AND SOILS.

BY

W. P. KELLEY,

Chemist.

UNDER THE SUPERVISION OF

OFFICE OF EXPERIMENT STATIONS,

U. S. DEPARTMENT OF AGRICULTURE.

WASHINGTON:

GOVERNMENT PRINTING OFFICE.

1912.

HAWAII AGRICULTURAL EXPERIMENT STATION, HONOLULU.

[Under the supervision of A. C. TRUE, Director of the Office of Experiment Stations, United States Department of Agriculture.]

WALTER H. EVANS, *Chief of Division of Insular Stations, Office of Experiment Stations.*

STATION STAFF.

E. V. WILCOX, *Special Agent in Charge.*
J. EDGAR HIGGINS, *Horticulturist.*
W. P. KELLEY, *Chemist.*
D. T. FULLAWAY, *Entomologist.*
C. K. MCCLELLAND, *Agronomist.*
WM. MCGEORGE, *Assistant Chemist.*
ALICE R. THOMPSON, *Assistant Chemist.*
C. J. HUNN, *Assistant Horticulturist.*
V. S. HOLT, *Assistant in Horticulture.*
C. A. SAHR, *Assistant in Agronomy.*
F. A. CLOWES, *Superintendent Hawaii Substations.*
J. DE C. JERVES, *Superintendent Homestead Substation.*

LETTER OF TRANSMITTAL.

HONOLULU, HAWAII, *October 12, 1911.*

SIR: I have the honor to submit herewith and recommend for publication as Bulletin No. 26 of the Hawaii Agricultural Experiment Station a paper dealing with The Function and Distribution of Manganese in Plants and Soils, by W. P. Kelley, chemist of the station. For three years the station has been investigating the soil conditions in the chief pineapple districts of the Territory with special reference to getting satisfactory growth of pineapples in certain localized areas. The cause of the poor growth of pineapples in these areas is found to be the manganese in the soil. This element occurs in much higher percentages than have heretofore been reported in other countries. The paper contains an account of the peculiar distribution of manganese, the chemical and physical forms under which it occurs, its apparent origin from the lava rock, and the peculiar effects which it exercises upon pineapples and other plants. The whole problem presented by the occurrence of a high percentage of manganese in soils has been investigated, and important steps in advance have been taken on various parts of the field of investigation. The paper is therefore a decided contribution to the literature of this comparatively new field.

Respectfully,

E. V. WILCOX,
Special Agent in Charge.

DR. A. C. TRUE,
Director Office of Experiment Stations,
U. S. Department of Agriculture, Washington, D. C.

Recommended for publication.
A. C. TRUE, *Director.*

Publication authorized.
JAMES WILSON, *Secretary of Agriculture.*

CONTENTS.

THE FUNCTION AND DISTRIBUTION OF MANGANESE IN PLANTS AND SOILS.

THE FUNCTION OF MANGANESE IN PLANT GROWTH.[1]

INTRODUCTION.

The rôle played by the several elements that occur in plants is a subject of much interest, and one that has been investigated for many years. For about a century it has been recognized that mineral substances are essential in the normal growth and development of plants, and are connected in some vital way with the phenomena of life. In addition to the elements essential to growth there are others found to a greater or less extent in all soils.

Growing plants have the power of absorbing these accessory substances to a considerable extent, but in general the occurrence of small amounts of such elements in plants has been looked upon as being somewhat accidental. The soil moisture dissolves various chemical substances which by osmosis pass into plant sap, and thus ultimately find their way to the several plant organs. The occurrence of small amounts of certain elements in plants, therefore, has been considered as having no special significance.

While it is well known that only about 10 elements are essential to the normal growth and reproduction of the higher plants, certain observations and experiments in recent times suggest that at least some of the accessory and supposedly unnecessary elements that occur in plants may perform some useful function in the economy of nature.

Inquiry has arisen concerning the explanation of the fact, for instance, that while iodin occurs as a minor constituent of sea water, certain marine plants have the power of storing up in their tissues relatively large quantities of this element. Similarly, chlorin [2] occurs to the extent of not more than 0.01 per cent of ordinary soils (in many cases even less), but some plants have the power of extracting this element in rather large amounts. Instances are known where the soil contains only a trace of chlorin and yet some plants absorb from it more chlorin than phosphorus, an element universally considered to be necessary to plant growth. The same may be said in reference to the occurrence and absorption of manganese.

---

[1] Presented to the faculty of the graduate school of the University of California in partial fulfillment of the requirements for the degree of doctor of philosophy, September, 1911.

[2] Chlorin is considered by some authorities to be essential to the growth of plants.

Hilgard [1] as early as 1860 pointed out that the ash of the long-leaf pine from Mississippi contains in some instances a relatively large percentage of manganese.

In 1878 J. Schroeder [2] reported the ash of the Norway spruce, *Picea excelsa*, to contain 35.53 per cent Mn_3O_4 in the case of the needles, and 41.23 per cent in that of the bark, and while he did not report the per cent of manganese in the soil, it is safe to conclude that the amounts present were small; so far as is known, highly manganiferous soils do not occur in that region.

THE OCCURRENCE OF MANGANESE IN PLANTS.

The earliest record reporting the occurrence of manganese in plants is furnished us by Scheele,[3] who pointed out that the ash of the seed of the wild anise contains a small amount of manganese, while a considerably larger portion occurs in the stems of the same plant. Herapath,[4] in 1849, determined the presence of manganese in the ash of the radish, beet, and carrot; and according to the same authority, Richardson found it to be present in the ash of sugar cane. In the same year Salm-Hortsmar [5] reported manganese as occurring in the ash of oats. In 1851 Liebig [6] found that tea contained manganese. By evaporating an infusion to dryness and igniting the residue a green ash was obtained, which color Liebig attributed to the presence of manganate of potassium. In 1872 Leclerc [7] published analyses of various plants and soils and concluded from his investigations that manganese is a universal constituent of soils and likewise occurs in the ash of most plants. From his researches it would appear that certain forest trees, particularly the firs, birches, and elms contain rather large amounts of manganese, while the herbaceous plants contain it only in small amounts. In the various soils analyzed he found manganese in every instance, although none was found which contained more than a few tenths of 1 per cent. In 1884 Maumené[8] pointed out that the parenchyma of cabbage leaves contains only a trace of manganese, while the veins contain considerable quantities.

Special interest in this question was not aroused, however, until late in the nineteenth century. As a result of some investigations on the latex of the lac tree, *Rhus succedanea*, Bertrand [9] pointed out that the ash of oxidizing enzyms contains manganese. The latex was found to contain two substances which he designated as laccase and

---

[1] Rpt. Geol. and Agr. Miss., 1860, p. 360.
[2] Tharand. Forstl. Jahrb. Sup. I (1878), p. 97; Jahresber. Agr. Chem., 21 (1878), p. 110.
[3] Mémoires de Chymie. Dijon, 1785.
[4] Cited by Rousset, Ann. Sci. Agron., 3. ser., 4 (1909), II, p. 82.
[5] Jour. Prakt. Chem., 46 (1849), p. 193.
[6] Familiar Letters on Chemistry. London, 1851, 3. ed., pp. 458, 459.
[7] Compt. Rend. Acad. Sci. [Paris], 75 (1872), p. 1213.
[8] Compt. Rend. Acad. Sci. [Paris], 98 (1884), p. 1418.
[9] Rev. Gén. Chim., 8 (1905), pp. 213, 214.

laccol. The dark color which is developed in the latex upon its coming in contact with air he found to be due to a change in the laccol, brought about by oxidation, the laccase acting as an oxygen carrier. Laccase, therefore being an oxidizing enzym, is able to effect the oxidation of a large amount of laccol. The phenomenon of autooxidation is by no means confined to the lac tree, but is a general property in varying degrees in plants. The most highly purified oxidase from various sources upon incineration, Bertrand found to contain manganese. In the following year he showed that by the addition of manganese compounds to the oxidases their oxygen carrying power was, within certain limits, increased in proportion to the amount of manganese present. Following this discovery it was soon suspected that the manganese performs some physiological function in the vegetable kingdom, and numerous experiments with the use of various compounds of this metal have since been made.

PREVIOUS INVESTIGATIONS.

EXPERIMENTS WITH MANGANESE.

Historical.—The artificial application of various manganese compounds in soil and culture experiments has given widely differing results. In a large number of cases increased growth with a variety of different plants has resulted. In a number of instances, however, negative results have been obtained, while in certain cases a pronounced toxic effect has been observed.

In 1899 Giglioli [1] applied manganese dioxid at the rate of 1.14 quintals per hectare (about 102 pounds per acre) in some wheat experiments and found in some instances it resulted in an increase, while in others a decrease in yield occurred.

Loew and Sawa [2] in 1903 found that by the addition of small amounts of manganese sulphate to culture solutions a considerable increase in the growth of barley, rice, cabbage, beans, and peas was effected. They also made similar applications to soils in pot experiments and with similar results. In the same year Aso [3] cultivated barley, radishes, wheat, and peas in culture solutions containing manganese sulphate and concluded that in sufficiently dilute solutions manganese exerts a stimulating effect.

Nagaoka [4] applied manganese sulphate in addition to a general fertilizer to soils in boxes, in which he grew rice and obtained approximately one-third increase in the yield. The increased growth of the rice was found to be proportional to the manganese applied up to the

[1] Ann. R. Scuola Sup. Agr., Portici, 2. ser., 2 (1901), p. 133; Centbl. Agr. Chem., 31 (1902), No. 3, p. 206.
[2] Bul. Col. Agr. Tokyo Imp. Univ., 5 (1902-3), pp. 161-172.
[3] Bul. Col. Agr. Tokyo Imp. Univ., 5 (1902-3), pp. 177-185.
[4] Bul. Col. Agr. Tokyo Imp. Univ., 5 (1902-3), pp. 467-472.

amount of 25 kilograms of Mn_2O_3 per hectare, while larger applications brought about practically the same yields. The following year [1] these experiments were continued without any further application, and an increased production of 16.9 per cent resulted. The third year Nagaoka [2] continued these experiments by applying manganese sulphate, chlorid, and carbonate. While the season is reported to have been very unfavorable for the growth of rice, it is significant that in most instances a decrease in yield was obtained. The fact that increased growth had been obtained the two previous years by the application of manganese, the author suggested may have partially exhausted the available plant food, so as to bring about need for a general fertilizer. Nagaoka also suggested that the repeated applications of manganese salts probably produced an acid condition in the soil.

Voelcker [3] in some pot experiments at the Woburn Experiment Station found that a decrease in the growth of wheat and barley followed the application of manganous iodid, while the nitrate and phosphate produced a stimulating effect. Germination and sprouting were retarded by manganese dioxid and sulphate, while a deeper green and more luxuriant growth were obtained from the use of manganous chlorid.

In 1904, Loew and Honda [4] obtained from the use of manganese sulphate a noteworthy increase in the growth of the tree *Cryptomeria japonica.*

Bertrand and Thomassin [5] in 1905 grew oats in a soil containing 0.057 per cent manganese, of which 0.02 per cent was soluble in acetic acid and found that by the application of manganese sulphate a considerable increase in growth was obtained. The general appearance of the treated and untreated plats was very similar at harvest time, but notable differences in yields were obtained. The same year Salomone [6] pointed out that by the use of manganese dioxid considerable increases in the yield of wheat were produced; and in 1907 [7] by the use of various compounds of manganese he again obtained considerable increases in the yields of wheat, beans, oats, and onions, always provided, however, the manganese was not applied in too great quantities.

Bertrand [8] further obtained a considerable increase in the yield of oats by the use of manganese sulphate, but found that the oats did not absorb an additional amount of manganese.

---

[1] Bul. Col. Agr. Tokyo Imp. Univ., 6 (1904–5), pp. 135, 136.
[2] Bul. Col. Agr. Tokyo Imp. Univ., 7 (1906), pp. 77–81.
[3] Jour. Roy. Agr. Soc. England, 64 (1903), p. 348; 65 (1904), p. 306.
[4] Bul. Col. Agr. Tokyo Imp. Univ., 6 (1904–5), pp. 125–130.
[5] Compt. Rend. Acad. Sci. [Paris], 141 (1905), p. 1256.
[6] Staz. Sper. Agr. Ital., 38 (1905), pp. 1015–1024.
[7] Staz. Sper. Agr. Ital., 40 (1907), pp. 97–117.
[8] Compt. Rend. Acad. Sci. [Paris], 141 (1905), p. 1255.

Katayama [1] in 1906 applied a solution containing 0.01 per cent of manganese sulphate as a top dressing, at intervals of about 6 weeks, during the growth of barley, and obtained a slight increase in yield, while more concentrated solutions effectively retarded the growth. Further experiments on the stimulating effects of manganese chlorid on rice were made during this year by Aso,[2] which resulted in showing a slight increase in yield, although of less magnitude than had been observed in former years. Where the manganese was used in addition to a liberal application of other fertilizers, scarcely any effects were produced, while with soils which had been continuously cultivated without a general manure it gave an increase of 23.5 per cent. Summing up the results, Aso states: "On the manganese plats the increase was relatively greatest where the manuring conditions were least favorable." The increases in total harvest for the four years over which these experiments were conducted were as follows: 1903, 41.8 per cent; 1904, 2.2 per cent; 1905, 3.5 per cent, and 1906, 23.5 per cent, without a general fertilizer. With a complete manure no increase was obtained.

In 1907, Molinari and Ligot [3] conducted a series of pot experiments with oats, using soil containing from 0.01 to 0.07 per cent manganese. In addition to a complete fertilizer manganese sulphate was applied in quantities of from 0.05 to 0.20 gram per pot. The maximum increase in yield was obtained by the application of 0.10 gram per pot, while the use of larger quantities produced only slight increases in yield. Some experiments have been made by Belgian agronomists with sugar beets, the results of which are of interest in this connection. Grégoire, Hendrick, and Carpiaux,[4] in addition to a general fertilizer, applied manganese sulphate at the rate of 10 and 50 kilograms per hectare and found that in each instance a decrease in total weight of the beets was obtained. The sugar content, however, was slightly greater where manganese had been applied, so that the total yield of sugar was practically the same in each instance. Garola,[5] at the experiment station in Chartres, on the other hand, obtained notable increases in the yield of beets by the application of 3.5 grams of manganese per square meter applied as chlorid and sulphate. According to Rousset,[6] experiments with beets made in Bohemia by Stoklasa resulted in producing an increase of 15 to 20 per cent by the use of manganese compounds, while Gillin reported a decrease in yield from the use of manganese carbonate, although the percentage of sugar in the beets was augmented.

[1] Bul. Col. Agr. Tokyo Imp. Univ., 7 (1906), pp. 90–93.
[2] Bul. Col. Agr. Tokyo Imp. Univ., 7 (1907), pp. 449–453.
[3] Bul. Agr. [Brussels], 23 (1907), p. 764.
[4] Ibid., p. 388.
[5] Cited by Rousset, loc. cit.
[6] Ann. Sci. Agron., 3. ser., 4 (1909), II, pp. 81–111.

Feilitzen [1] cultivated oats on a moor soil poor in the elements of plant food, to which a general fertilizer was applied in addition to manganese sulphate at the rate of 10 kilograms per hectare, but he failed to obtain any increase in the yield. Grégoire, Hendrick, and Carpiaux [2] also made some experiments with potatoes on a soil very rich in plant food and found that the application of 10 kilograms of manganous sulphate per hectare produced but little effect, while the application of 50 kilograms per hectare brought about a small increase.

In pot experiments in 1908, Garola [3] obtained very large increases in the yield of flax from the use of 1.9 grams of manganous sulphate per pot in one series and 1 gram of manganous chlorid in another. Each pot previously received an application of a general fertilizer, but the increases in yield due to manganese were very great. A similar set of experiments with beans, however, failed to reveal any effect from the addition of manganese.

Sutherst [4] made some pot experiments with corn on a soil from Transvaal, and found that notable increases in the yield followed the application of manganese sulphate, chlorid, or dioxid. The author concluded that manganese exerts a tonic effect, and it is of interest that manganese dioxid stimulated the growth to a greater degree than did the sulphate or chlorid.

Various experiments have been reported from central France,[5] the results of which are by no means concordant. In a number of these tests by-products from certain manganese mines have been applied. These usually contain a mixture of various substances, of such nature that it is difficult to know which constituent is the active one. In certain instances considerable increases in the yields of grapes have been obtained, while in others a decrease was reported.

Malpeaux succeeded in considerably increasing the yield of barley by the use of manganese sulphate, while a similar application produced no effects on oats. Albouy failed to obtain a fertilizing effect in cultures of either wheat or oats. In certain other experiments made under the direction of Marre results uncertain and sometimes contradictory were obtained.

Bernardini [6] in 1910 published a series of experiments, the results of which show that considerable increases in the yield of corn and wheat were obtained by the use of manganese chlorid, and Strampelli [7] reported considerable increases in the yields of various grains from the use of manganese sulphate, carbonate, and dioxid.

[1] Jour. Landw., 55 (1907), pp. 289–292.
[2] Loc. cit.
[3] Cited by Rousset, loc. cit.
[4] Transvaal Agr. Jour., 6 (1907–8), p. 437.
[5] Rousset, loc. cit.
[6] Staz. Sper. Agr. Ital., 43 (1910), pp. 217–240.
[7] Atti 6. Cong. Internaz. Chim. Appl., 4 (1906), pp. 14–17.

In 1910 Bartmann [1] discussed some experiments in which manganese was applied as the chlorid, sulphate, carbonate, dioxid, and two products from manganese mines which consist primarily in a mixture of Mn_2O_3 and Mn_3O_4. Beets, peas, and beans were considerably increased in yield by the carbonate and the manganese mine products. The dioxid, chlorid, and sulphate had but little effect. In a second set of experiments the growth of corn was shown to be stimulated by the application of manganese, from 200 to 400 kilograms per hectare being found to give the maximum effect. Similar amounts appeared to reduce the yields of both potatoes and beets.

From the foregoing experiments the value of manganese as a fertilizer can not be considered as having been established. It is true increased growth in a number of instances has resulted from the application of various manganese compounds, but on the other hand either no effects or a retardation in growth has been reported in so many instances that manganese as a practical fertilizer can not be recommended. In most instances the publications dealing with this subject do not give sufficient data concerning the composition and types of soils used to enable the reader to adequately correlate the effects produced. There is considerable evidence, as will be shown later, however, that the stimulating effects reported were in a large measure due to indirect action. From the experiments in water cultures, on the other hand, there is little doubt of a stimulating effect if manganese be employed in sufficient dilution.

PHYSIOLOGICAL EFFECTS OF MANGANESE.

Historical.—The discovery of the occurrence of manganese in plants naturally suggests the possibility of this element playing some physiological part. Manganese and iron are closely related from a chemical standpoint; they have many properties in common and enter into many similar reactions. This similarity suggested the possibility of substituting manganese for iron in culture solutions. Iron having been known for a long time to be connected in some way with the production of chlorophyll, the first experimental observations with manganese in plant cultures were made with reference to the green coloring matter.

Sachs [2] in 1865, attempted to substitute manganese for iron in the nutrition of various plants, but failed of success. The leaves of the plants became yellow and etiolated.

Birner and Lucanus [3] pointed out that manganese can not replace iron in the production of chlorophyll, and Wagner found that while

[1] Jour. Agr. Prat., n. ser., 20 (1910), No. 47, p. 666.
[2] Handbuch der Experimental-Physiologie der Pflanzen. Leipzig, 1865, p. 144.
[3] Landw. Vers. Stat., 8 (1866), pp. 128–177.

the amount of iron in plants is often less than that of manganese, manganous and manganic phosphates suspended in culture solutions can exert an injurious effect. Field experiments have since shown, however, that sometimes plants take on a deeper green and become more thrifty in appearance following the addition of manganese to the soil. This has been especially noted in cases where stimulated growth has resulted from the application of this element.

In 1884, Maumené[1] found that the ash from the parenchyma of cabbage leaves was white and infusible and did not contain a trace of manganese, while the ash from the veins of the same plant was very fusible and contained manganese in considerable amounts. He also found similar differences in wheat. This author concluded that the larger part of manganese existed as a salt of an organic acid, and that it is only in the sap that manganese occurs.

Following the discovery that manganese occurs in the ash of oxidases, Bertrand[2] found that by the addition of certain soluble salts of manganese to various oxidases, the oxidation of a solution of hydroquinone in a given length of time was proportional to the amount of manganese present. On account of his inability to completely separate the oxidases from manganese, together with the effects produced by the addition of manganese compounds to the sap of lucern, he was led to look upon manganese as being in some way connected with the phenomenon of oxidation in plants. He showed that their oxidizing activity could be considerably increased by the addition of manganese compounds. Not all the salts of manganese possessed this power in equal degrees. The degree of the increased oxygen-carrying power of oxidases under the influence of manganese salts, Bertrand found to be inversely proportional to their degree of dissociation, the nitrate, sulphate, and chlorid being much less active than the acetate, salicylate, and succinate.

Pichard,[3] in 1898 determined the presence of manganese in a large number of plants, and found it to occur in greatest concentration in the leaves and active growing parts. He also found it to be deposited to a considerable extent in the reproductive organs.

In 1901 Coupin[4] found that various chemical substances if present in sufficient concentrations may be toxic to plants. With manganese as nitrate a concentration of one part in 13,000 proved to be toxic to the germination of wheat, and considerably hindered the rate of germination. From some experiments on the oxidases, Trillat[5] found that manganese acts catalytically, and by the addition of a

[1] Loc. cit.
[2] Compt. Rend. Acad. Sci. [Paris], 124 (1897), pp. 1032, 1355.
[3] Compt. Rend. Acad. Sci. [Paris], 126 (1898), p. 1882.
[4] Compt. Rend. Acad. Sci. [Pàris], 132 (1901), p. 645.
[5] Compt. Rend. Acad. Sci. [Paris], 138 (1904), p. 274.

small amount of soluble manganese to the oxidases an increase in their oxygen-carrying power takes place.

At the summer meeting of the American Chemical Society in 1902, Ewell[1] read a paper in which he discussed a soil on which leguminous crops had failed. An aqueous extract of this soil was found to contain about twice as much manganese as calcium, and the legume failure was suspected of being due to the manganese. No further investigation of the question has been reported.

At the meeting of the International Congress of Applied Chemistry in Berlin in 1903, Bertrand[2] read a paper in which he pointed out that in addition to the principal elements that are found in plants, there exist rarer elements which usually occur in small amounts in plants, and that they may perform some physiological function. In this connection he proposed to call such compounds "Supplemental manures" (*Engrais Complementaires*).

In 1903, Loew and Sawa[3] published the results of a number of experiments in water cultures with young pea plants, barley, soy beans, rice, and cabbage. They found that the pea plants in solutions containing 0.25 per cent manganese sulphate were seriously injured in 5 days. The leaves lost their turgor, dried up, and no trace of new rootlets was to be observed. In a 0.1 per cent solution of the same salt, barley seedlings were injured slightly. After 7 days a fading of the green to a yellow was noted; and some water rootlets were developed, although much fewer than in the control. On the ninth day portions of the leaves showed a more pronounced oxidizing enzym reaction than was obtained from the control plants. The increased activity of the oxidizing enzyms, they think, may account for the fading of the green color.[4] In nutrient solutions containing 0.02 per cent manganese sulphate they grew barley and soy beans, and again observed a yellowing of the plants. Subsequent experiments, however, convinced them that if the weather be sufficiently warm, and the manganese present in sufficient dilution a stimulation takes place and no yellowing is produced. With rice seedlings in pots containing 8 kilograms of soil to which 200 cubic centimeters of a 0.1 per cent solution of manganese sulphate was added a stimulating effect was produced; and similar results are recorded with the use of peas and cabbage in soil cultures.

Discussing these results, the authors make the following interesting statements:

> Now it is well known that light retards growth. This hitherto unexplained phenomenon forms a strong contrast to the chemical work the light performs with the aid

[1] Science, n. ser., 16 (1902), p. 291.
[2] Cited by Loew, Bul. Col. Agr. Tokyo Imp. Univ., 6 (1904-5), p. 161.
[3] Loc. cit.
[4] See Woods, Centbl. Bakt. [etc.], 2. Abt., 5 (1899) p. 745.

of the protoplasm in the chlorophyll bodies. One and the same agency, then, increases the organic food, on the one hand, and suspends the utilization of that food on the other. It is in the absence of light that growth proceeds and the products of the sun's work are chiefly consumed. The absence of light has, therefore, the same effect as the presence of manganese. It seems as if under both of these conditions a check is removed which the sun's rays exert. This check might be due to the action of certain noxious compounds produced in the cells under the influence of light. Such compounds are frequently produced in the course of metabolism.[1] It is the office of the oxidizing enzyms, as one of us has suggested, to destroy noxious by-products of the benzene series—a view verbally expressed as follows: "The writer's view on this subject[2] is that as the living protoplasm can oxidize carbohydrates and fat, but does not attack, or attacks with difficulty, compounds of the benzene group; and, on the other hand, as just the opposite takes place with the oxidizing enzyms, it may be inferred that there exists between the protoplasm and the oxidizing enzyms a certain division of labor, the former oxidizing the compounds of the methane series, and the latter those of the benzene series. The former provides for the kinetic energy of the cells; the latter destroys, by partial oxidation, noxious by-products. The oxidations in the former case are generally complete, but in the latter, only partial."

Loew and Sawa summarize their findings as follows:[3]

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. Manganese exerts, further, a promoting effect on the development, still observable in high dilution, while the injurious effects disappear under these conditions. It is probable that soils of great natural fertility contain manganese in an easily absorbable condition and that this forms one of the characteristics of such soils.

Aso[3] found that extracts from the leaves of radishes grown in culture solutions containing manganese also contained a more active oxidase than similar leaves from the control plants. In the case of barley grown in culture solutions containing manganous sulphate a yellowing of the leaves was noticed, and the roots gradually turned brown; also the lower leaves turned brown, especially in spots. Microscopic examination of the epidermal cells showed a browning of the nuclei and colorimetric tests for oxidizing enzyms also gave stronger reactions than were obtained from the green leaves of plants not fertilized with manganese. Similar observations were made with wheat; the lower leaves turned brown, as also did the roots, which in this case the author found to be due to manganese dioxid adhering to the roots. The yellowing of these plants suggested an interference in the assimilation of iron, and in order to provide against this possibility, ferrous sulphate was added to parallel cultures containing manganese, with the result that a partial, although not complete, counteracting of the yellowing was produced. On account of the stimulating effect of small amounts of manganese in field experiments, thus enabling the crop to absorb larger amounts

---

[1] Reinitzer, Ber. Deut. Bot. Gesell., 11 (1893), p. 531.
[2] U. S. Dept. Agr. Rpt. 59, 1899, p. 27.
[3] Loc. cit.

of the essential elements, Loew[1] suggested that its use would ultimately result in a depletion of the soil unless a general fertilizer was also applied. He cited experiments which may be taken as an indication of some indirect effect of the manganese on other substances in the soil. As already mentioned, Aso attributes a part of the residual effects of the treatment with manganese to a possible accumulation of acidity in the soil.

In a series of culture experiments with wheat, Voelcker[1] found that a deeper green color was produced by the application of manganous chlorid, while a retardation in germination followed the use of manganous iodid. The latter salt was also found to greatly hinder root development, small delicate roots with few rootlets being formed. In the solutions containing manganous sulphate good root development took place, although the root hairs were found to be smaller in size than in the check solutions. In a number of these experiments the roots at maturity were observed to be coated with a thin film of manganese dioxid.

In a series of experiments in 1905 Salomone[2] pointed out that injury to the germination of rape and cabbage followed their soaking in dilute solutions of manganous fluorid or iodid. He grew beans in sand cultures to which dilute solutions of these salts were added, and found an increased chlorophyll production and a consequent fertilizing action. With spring wheat, similar cultures resulted in showing a stimulating effect; but when the dose was increased about 50 kilograms per hectare a falling off was observed and maturity delayed.

In 1907 the same author[3] published an exhaustive series of experiments in which he observed that certain manganese compounds exercised a stimulating effect, whereas others produced a toxic effect. By the use of a highly calcareous clay, he grew wheat in field experiments, using dilute solutions of manganese as the iodid, fluorid, nitrate, sulphate, chlorid, and the various oxids. With the oxids the leaves turned slightly yellow and maturity was hastened from four to seven days. The final yield, however, was increased, and there was an increase in the nitrogen content of the grain. By increasing the application of manganese as manganous sulphate, above 50 kilograms per hectare, he observed a decided depressing effect, and when still greater quantities were applied the plants died. The grain from all the treated plats contained a larger quantity of manganese than from the check plats, and increased with the larger applications. Where manganese exerted a toxic effect, when applied in large doses it caused a breaking up of the plasma in the meristem tissues. The growing tips turned yellow and finally died. Plasmolysis ensued in

---

[1] Loc. cit.
[2] Staz. Sper. Agr. Ital., 38 (1905), pp. 1015-1024.
[3] Ibid., 40 (1907), pp. 97-117.

the epidermis and central cylinder of the roots. The protoplasmic vesicles became separated from the cell walls for a distance of about two-thirds of their circumference. Plasmolysis also accrued in the bark and pith of the roots, which were found to be brown in color. The protoplasm drew away from the cell walls and the nuclei became brown. Starch and aleurone grains were less numerous than in the check plants. The protoplasm was altered in some way, as shown by the Millon reaction, which did not give its usual rose-red color. Wheat was grown a second time on the same plats and again a toxic effect was observed, and it was found that the application of lime and basic slag did not diminish this toxic effect.

With beans grown in boxes Salomone found that various manganese compounds, in quantities up to 40 kilograms per hectare, produced stimulation, whereas the application of more than 60 kilograms per hectare caused the plants to die. He found that the toxic effect was slightest when the manganese functioned as an electro-positive element and increased in passing from manganous through manganic to permanganic compounds; in other words, when manganese functioned as an electro-negative element it was more toxic than when an electro-positive element. With oats in field experiments, he also observed an increase in the percentage of nitrogen in the grain where manganese was applied. In other experiments with leeks and onions, the use of manganese dioxid at the rate of 1.5 grams of manganese per square meter produced an increased growth. Manganous sulphate at the rate of 1 gram of manganese per square meter resulted in producing a darker green color when applied to meadows, as well as increasing the total yield.

In summarizing these results Salomone concluded that the greatest concentration of the manganese is found in the reproductive organs of the plant. The ash of beans and wheat increased in passing from the roots, through the stems and leaves, to the fruit; and in the top of the stems a greater quantity was deposited than lower down. In the seeds the greatest concentration was found in the embryo. Analyses of different portions of the plant at different stages of growth showed that manganese occurs in the roots, stems, and vegetative portions to a greater extent during the early growth than at maturity; and, therefore, he concluded that it migrates to the grain in a way very similar to the translocation of nitrogen and phosphoric acid in the ripening of grains.

The chemical analogy between manganese and iron suggested to Salomone that the former is probably combined in a weak organic combination. In peas, horse beans, rice, corn, chestnuts, rye, mushrooms, etc., he found manganese to exist in two states: (1) As concretions which he supposed to be formed from the cell sap, in which the manganese was previously observed and (2) in combination with other substances in solution. By macerating these plants with water, he was able to demonstrate its presence in both the solution and the insoluble residue.

Hall [1] holds to the view that the stimulating effect of manganese in field experiments is probably to be explained on the basis of an indirect effect on the dormant bases of the soil, rather than by a direct physiological action, although he considers that the point has not been proven.

In 1909 Guthrie and Cohen [2] described the appearance and subsequent failure of certain crops in Australia, particularly barley and wheat, and concluded that the failure was due to the presence of small amounts of very soluble manganese in the soil.

In 1910 Bernardini [3] published the results of a series of experiments with the use of various manganese compounds, and concluded that manganese acts catalytically on soils increasing their oxygen absorbing power and possibly affecting the soil bacteria. He pointed out that in field trials different manganese compounds frequently bring about increased harvests, although in some instances, negative results have been obtained. He studied the effects of N/5 solutions of sodium, potassium, ammonium and manganous chlorids on soils; and while a certain portion of each of these substances became fixed by the soil, the solution of manganous chlorid had the power of replacing calcium and magnesium from certain silicates to a far greater extent than the other chlorids. He also found that the manganese solution still has the power of replacing the alkaline earths after the soil had been heated for a considerable period, from which he argues that its reaction is in connection with the noncolloidal substances of the soil. He extracted volcanic ash from Vesuvius, mineral hornblende and augite for a period of five days and found in each instance that more lime and magnesia were replaced by the use of the manganese chlorid solution than by the use of the other chlorids. From these results Bernardini concluded that probably the beneficial effects of manganese from artificial applications may be attributed wholly to its indirect effect upon other constituents of the soil rather than its acting physiologically on the plant; and he suggests that a closer examination of the soils previously used in manganese experiments would probably reveal the fact that in those instances where failure has been recorded, the soil will be found to contain large amounts of calcium and magnesium in available forms, perhaps either as the carbonate or in zeolitic combinations.

---

[1] Ann. Rpts. Prog. Chem. [London], 4 (1907), pp. 271-272.

[2] Jour. and Proc. Roy. Soc. N. S. Wales, 43 (1909), pp. 354-360.

[3] Loc. cit.

Recently, Brenchley [1] made a series of water cultures with varying amounts of manganese sulphate. In solutions containing one part in 10,000 the roots of barley turned brown, which she supposed to be due to the deposition of manganese oxid; the leaves gave indication of being diseased and also turned brown and finally died. In dilutions of one in 100,000 parts the effects were less noticeable, while concentrations of less than one part per million produced a stimulating effect. Microscopic examinations showed the affected leaves to be made up of cells of normal size and shape, but with brown cell walls. The dead cells occurred at first in patches which later spread over the entire leaf. The presence of manganese in the leaves was determined by fusion with sodium carbonate and potassium nitrate. Brenchley reported that the time of ripening was retarded especially where the manganese was used in greatest concentration. Toward maturity the manganese appeared to be deposited on the surface of the leaves.

DISCUSSION.

From the foregoing experiments positive conclusions regarding the rôle that manganese plays in plant growth can not be drawn. It seems well established, however, that the addition of small amounts of this element may bring about considerably increased growth, whereas the application of larger quantities is attended by physiological disturbances. From the field experiments there seem to be two well-established facts: First, the addition of various compounds of manganese to certain soils results in stimulating plant growth, whereas similar applications to other soils are without noticeable effects; second, some species of plants are more susceptible to the influence of manganese than others.

From the work of Bertrand, manganese appears to be a necessary constituent of the oxidizing enzyms, although more recent investigations have shown that it is not an absolutely essential element in oxidases.[2] Carefully purified oxidases from several sources have been obtained which did not contain a trace of manganese. There is little doubt, however, that manganese usually occurs as a normal constituent of the oxidizing enzyms; and it has been shown by various investigators that the addition of small amounts of soluble manganese compounds to the oxidases and peroxidases greatly accelerates their oxygen-carrying power. The observations of Bertrand, followed by the work of Loew and his coworkers in Japan; also by Giglioli and Bernardini in Italy, that manganese acts catalytically, stimulating the oxidizing activities of plants, as well as enhancing

[1] Ann. Bot. [London], 24 (1910), pp. 571–583.

[2] A very complete review of the literature dealing with the oxidases is given by Kastle, Pub. Health and Mar. Hosp. Serv. U. S., Hyg. Lab. Bul. 59.

the oxidations of the soil,[1] no doubt have an important bearing on this question; but, as Bernardini pointed out, it has not been shown in field experiments that manganese does not react indirectly on other constituents of the soil, and hence it is unjustifiable to conclude that the entire effect is due to accelerated oxidations.

In practically all of the foregoing experiments, artificial cultures, or the application of manganese compounds to soils, have been made. It is generally recognized that the soil is extremely complex, made up of numerous chemical substances, both organic and inorganic, and contains many species of bacteria and other forms of organized life. It is constantly undergoing chemical changes and may therefore be looked upon as being in a state of semistable equilibrium. The addition of any soluble substance necessarily sets in motion reactions and changes, the exact nature of which, due to the complexity of the soils involved, is extremely difficult to comprehend. The addition of a soluble salt will undoubtedly modify the relative concentrations of the several elements in solution in the soil moisture and will more than likely produce important changes in the biological and physical factors of the soil. In addition, many substances are known to have a "replacing effect," that is, they have the power of setting free other elements which are bound up in less soluble combinations, themselves entering into the less soluble combinations, while still other substances become fixed.

It has been conclusively shown in water cultures that modifications in nutritive solutions, of the order previously referred to in this paper, may be attended by various physiological disturbances, the exact nature of which varies from species to species, and it is by no means the same with equal concentrations of all substances. Consequently the effects produced on crops by the artificial application of chemical substances to soils are extremely difficult to interpret. In previous manganese studies artificial applications have been necessary for the reason that natural soils, containing considerable quantities of manganese, have been unknown.

In some investigations on the pineapple soils of Oahu in 1908[2] it was found that this island contains considerable areas which are characterized by abnormally high percentages of manganese. Soils were discovered which contain manganese in varying amounts from less than 0.1 per cent to as high as 9.74 per cent. Subsequently it has been found that the extent of such soils is relatively great. There is offered here, therefore, a natural soil, which has arisen by the operation of natural causes and which contains manganese as an

[1] Rousset suggests that possibly manganese brings about a decomposition of the toxins of the soil. Loc. cit. Recently Schreiner, Sullivan, and Reid in discussing the action of manganese on soils point out that its office is probably associated with oxidation in soils. (U. S. Dept. Agr., Bur. Soils Bul. 73.)

[2] Hawaii Sta. Press Bul. 23; Jour. Indus. and Engin. Chem., 1 (1909), p. 533.

important constituent. By the use of these soils secondary reactions, due to the introduction of soluble manganese compounds, changes in the concentration of the soil moisture due to the addition of a more soluble substance, and the replacing effects attendant thereto will be obviated. All the experiments and observations hereafter to be reported in this paper were made on these soils without the artificial addition of any substance whatever. Most of the plants have been grown in field cultures under usual field conditions. A series of experiments in pots, using the more highly manganiferous soil and a normal soil for comparison, has also been conducted.

FIELD OBSERVATIONS ON MANGANIFEROUS SOILS.

PINEAPPLES.

The chief crop grown on the manganiferous soils of Oahu is pineapples, and the general appearance and physiological features of the plants are characteristic and clearly differentiate them from pineapples on normal soils. The most pronounced characteristic in these plants is an intense yellowish-white appearance in the leaves, which may appear at any period in the growth, although it usually becomes more intense at from 3 to 6 months after the time of planting, and is always most noticeable during the winter months. The pineapple requires about 18 months from the time of planting to reach maturity and produce fruit. During the winter months the temperature is never very low. Rarely a temperature below 50° F. is recorded; but almost invariably the intensity of the yellowing becomes greater during the months from December to March. The development of this color usually begins to be indicated by a general fading of the green near the margin of the leaves, which rapidly spreads over the entire plant and is followed by a more or less complete blanching of the leaves. Sometimes the yellowing begins as local spots, but these soon spread until the entire plant presents a yellowish-white appearance. This is followed by a cessation of growth; the plant begins to die back from the tips of the leaves; dark brown spots, gradually becoming darker, develop on the leaves, until finally the entire plant dies. Frequently no fruit is produced at all, but that which is formed has a characteristic appearance. The fruit of normal pineapples is deep green in color up to the time of the beginning of the ripening process. Those on manganese soils, on the contrary, are reddish-pink in color throughout the early stages of development and frequently do not contain a trace of green color. On the more highly manganiferous soils the fruit never reaches normal size, and it is difficult to know, by superficial examination, when that which is produced comes to maturity, owing to the similarity in the color between the ripe and unripe fruit.

The interior of the fruit from manganese soil is characterized by a whitish appearance, and usually contains an excess of acidity. Normal pineapples, of the variety grown in Hawaii, are straw colored throughout when thoroughly ripe and golden-yellow on the surface.

The roots of pineapples affected by manganese also present peculiarities worthy of note. Normally the root system is composed of numerous rootlets which branch and subdivide from the larger roots, thus forming a fine network which extends in every direction from the plant to a distance of one or more feet, depending largely upon the physical character of the soil. The root system developed in manganese soil, on the contrary, is much less extensive and contains few rootlets. An examination shows that a large percentage of the roots die some months after formation, although a few live, active roots are usually to be observed, and these are provided with a superabundance of root hairs; in fact, almost every epidermal cell is elongated into a root hair. Such roots are further characterized by a blunt growing tip, which in many instances becomes half as large as a lead pencil, and is frequently swollen into a fleshy enlarged end. The formation of these enlargements appears to mark the end of the growth of the root and death soon follows.

GRAMINEÆ.

Other plants are noticeably affected by manganese, although so far as is known, pineapples are most sensitive to this element. Corn exhibits certain peculiarities. The lower leaves frequently turn brown, die back from the tips, and fall away, and a reddish purple color, sometimes noticed on the stalk and leaf sheath of this plant, forms a pronounced characteristic when grown on highly manganiferous soil. Frequently the purple color extends from the base of the plant to the tassel. The macroscopic examination of the roots reveals no striking variations, except a tendency toward the development of a more pronounced woodiness in the cortex. Without the use of any fertilizing substances, the growth of corn is frequently very scant, the stalk usually small and growth very slow; and in its attempt at reproduction, the tassel is formed when not more than 3 feet high. Sometimes small undeveloped ears are formed. With the use of suitable fertilizers, especially such as contain phosphates, however, corn of normal size and fair yields have been obtained, although a slight browning of the lower leaves, and the development of a purple color on the stalk is not thus entirely overcome.

Panicum molle exhibits certain peculiarities; a general tendency to form less chlorophyll and smaller growth, attended by the formation of a more woody stem, are the most pronounced variations from the normal. The root system seems not to be affected.

Saccharin sorghum shows an appearance similar to that of corn, but perhaps of less intensity.

Rice, when grown as a dry-land crop, becomes yellow soon after germination and shows little tendency to stool or tiller, and appears to be stunted. Its roots are likewise less developed than normally.

Wheat and oats develop a brown appearance on the lower leaves, but are otherwise normal, and a fair growth may be obtained.

Sugar cane appears to be less sensitive to manganese than almost any of the cultivated plants, and shows very slight effects of any sort during the warm summer months. During the winter months, on the contrary, young sugar cane sometimes develops an intense yellowish-white appearance on the leaves, but later this is restored to the normal green, and a thrifty, vigorous growth is obtained. From a practical standpoint the effects of manganese on sugar cane can be ignored, but the development of the etiolated appearance at times indicates some physiological disturbance.

Among the natural grasses in Oahu *Paspalum orbiculare* and *Hydropogon aciculatus* are most abundant in the unplowed areas, and the planters have learned to locate the manganiferous soils by differences in the relative percentages of these two grasses. At the first plowing of this plateau it is not infrequent to find a preponderance of the Hydropogon on the manganiferous soils, whereas Paspalum is by far more abundant on the normal soils. From these differences in the natural growth of these grasses, the pineapple growers have learned to foresee the probable effects of this soil on pineapples; and while it can not be relied upon as an absolute criterion, the indications given by it often furnish a safe guide.

LEGUMES.

In general, the Leguminosæ are affected by manganese somewhat as the Gramineæ. Peanuts become brown in the lower leaves, which subsequently die and fall away, and the stem has a tendency to become purple. The roots show a dark brown appearance.

Jack beans (*Canavalia ensiformis*), likewise, become brown on the lower leaves, which occasionally drop off. The lower part of the stem also shows a purplish color and a stunted growth results. Frequently this plant takes on the appearance of nitrogen starvation, such as characterizes the growth of legumes in the absence of nitrogen-gathering bacteria, although root excrescences indicate the presence of the species that normally infests this plant.

Pigeon peas (*Cajanus indicus*) also appear somewhat stunted, the lower leaves having a tendency to become brown and fall off. In a given length of time the growth of pigeon peas on manganese soil is not more than one-half of that on normal soils. The roots are also more woody and less extensive, but have been found to contain the nitrogen-gathering tubercles in fair abundance.

Cowpeas (*Vigna catjang*) seem to be the most sensitive of all the legumes observed. The lower leaves, one after another, turn brown and fall away. The stems become purple and a yellowish, stunted appearance results. The roots appear normal and the small amount of seed that is formed seems to be normal.

Kidney beans (*Faba vulgaris*) have been observed to behave very much as jack beans. The lower leaves have a tendency to turn brown and fall away, and a general stunted growth results.

A common species of Crotalaria, from a superficial examination, is unaffected by manganese and grows luxuriantly as a weed throughout the cultivated sections of the islands, and so far as can be observed presents no evidences of any effect from the manganese.

MISCELLANEOUS PLANTS.

Certain weeds, as, for instance, the sow thistle and *Waltheria americana*, also show no effects from manganese.

Cotton grows fairly well and while usually somewhat slower in taking a start the development proceeds normally. Likewise sisal (*Agava sisalana*) is without external effects from the manganese and grows normally. Similarly potatoes, cabbage, and turnips are unaffected in their grosser appearance.

It is claimed that the entire plateau was formerly heavily wooded, but the intervention of the axe and the lack of protection against cattle has resulted in the almost complete destruction of timber throughout this section. Guava bushes are to be found scattered over the unplowed portion, but these have been so eaten by cattle and held in check by intermittent droughts that no deduction relative to the effects of manganese can be drawn. Likewise, *Lantana camara* is found in places, but it also affords no indications.

POT CULTURE EXPERIMENTS.

As will be shown in the second part of this paper, the manganese occurs as a surface accumulation in the soil, being usually much more abundant in the first 10 to 12 inches than in deeper lying strata. Some of the plants previously mentioned are rather deep rooted and have a well-developed taproot system, while still others are cultivated in Hawaii by planting in deep furrows, sometimes 15 inches below the surface of the soil. It was suggested, therefore, that possibly the roots of such plants would penetrate below the manganese layer, and might therefore not have their absorbing surfaces entirely in manganiferous soil. Such could not be the case with surface-rooted plants such as pineapples, the cereals, cabbage, turnips, etc., but with cotton and sugar cane, the latter of which is planted in deep furrows, this supposition appears to have some foundation. In order to study this point, as well as have a more strict control and afford easy means of observation with various plants, a large number of pot cultures have been made, using a manganiferous soil, which upon analysis was found to contain 9.5 per cent manganese as Mn_3O_4. For purposes of comparison a normal soil from the grounds of the experiment station, containing 0.2 per cent manganese as Mn_3O_4, was used in a parallel series of pot cultures. The several species of plants were grown in series of three pots of each type of soil. These cultures were made in an open glass house at the experiment station, where close observation was possible, and notes were taken from day to day. The cultures were planted on February 3, and after germination were thinned to a uniform stand of three plants per pot. The following observations on the general appearance and growth of the several species were made and have reference to those in manganiferous soil, except as otherwise noted.

GRAMINEÆ.

After germination normal growth of corn was maintained for about 2½ weeks, after which the leaf sheath around the stalk began to turn purple, the color gradually spreading to the leaves. The lower leaves turned yellow and died back from the tips and one after another dried up and ceased to function, and a very small stalk was formed. The tassel was formed at a height of about 2 feet and no gain was produced. The root development was found to be more extensive than in the normal soil.

No effects from the manganese were observed in the general appearance of wheat other than a slight retardation in the growth.

Oats germinated well and grew to a height of about 6 inches, after which a general retardation in the growth was noticed on the manganese soil, followed later by the development of a pinkish-purple color on the lower part of the stalk. Later on the stunting effect previously noticed seemed to give way to a more normal growth, the usual color and appearance being restored, and the heading time and maturity were practically the same as on the normal soil.

Barley, after reaching a height of 6 inches, stood without making any growth for several weeks; the tips of the leaves turned yellow and gradually died back. Later a partial recovery was noticeable with the development of the normal green color. At maturity the growth was practically the same as on the normal soil.

Paspalum orbiculare made fair growth and showed no effects from manganese further than the development of a purple color on the lower leaves, which seemed to be most pronounced following a period of damp cold weather.

Rice, when cultivated as a submerged crop, turned yellow on the manganese soil and made practically no growth. Repeated trials were made and very little growth was obtained in any instance. The seedlings usually died in 10 days to 2 weeks from the time of transplanting. In the normal soil good growth was secured.

LEGUMES.

Kidney beans developed normally during the first 6 weeks, after which a slight yellowing took place, although vigorous growth was obtained. At harvest time the roots were observed to contain no bacterial tubercles, whereas those from the check soils were well supplied with them. The roots were also found to be brownish in color.

Cowpeas, after germination, turned yellow, and subsequently became very unhealthy in appearance. The lower leaves turned brown and dropped off. The plants remained throughout their growth about one-half the size of those on the normal soil. At harvest time they were found to be fairly well supplied with nitrogen-gathering nodules.

MISCELLANEOUS PLANTS.

Radishes grew normally in each type of soil and showed no visible effects.

Cotton, after reaching a height of 4 or 5 inches, turned slightly yellow, followed by a browning of the lower leaves, especially on the margins, and a general unhealthy appearance resulted.

Mango and avocado seedlings were transplanted to manganese soil in pots and were found to grow normally, and presented no peculiarities.

Tobacco seeds were planted in pots and after germination and the development of four leaves, the plants in the manganese soils ceased to grow for some weeks. Later these plants made considerable growth and became fairly normal, the only noticeable difference at maturity being an apparent thickening of the leaves.

Sugar cane developed a slight yellow color on the lower leaves, but was otherwise normal.

Onions grown from seeds made normal growth during the first 6 weeks, after which the tips of the leaves turned yellow and growth ceased. A very slight bulb formation resulted in the manganese soil, whereas normal bulbs were produced in the checks.

From these observations on the growth of various plants on manganiferous soil, practically the same conclusions may be drawn as in the instances previously noted. A study of the gross characters of these plants seems to justify three conclusions: (1) Some plants may be injuriously affected by manganese; (2) other species are checked in growth but present no further evidence of physiological disturbance; and (3) still other species are apparently unaffected by manganese. It should be noted that in none of the species mentioned, and so far as the author's observations extend in no species of plant, was any tendency toward stimulated growth on these soils manifested. It should be stated, however, that the ordinary soils of the islands on which comparative observations have been made, contain in every instance at least a small amount of manganese, and as will be shown subsequently, it is usually in a comparatively soluble form, and therefore doubtless exercises some influence on growth. Hence it is not justifiable to conclude from these observations that the small amount of manganese in natural soils is without any significance in plant growth.

PHYSIOLOGICAL EFFECTS OF MANGANESE.

It will be noted that among the plants that show the most pronounced effects from manganese are pineapples, rice, cowpeas, peanuts, kidney beans, pigeon peas, corn, broom corn, and sorghum. With each of these species, and also to a slight extent with certain others, the development of a peculiar color was noticed. A microscopic examination has shown that in each instance this is due to an accumulation in the epidermal cells of colored sap which varies from pink, through various shades, to a deep purple. The brown discoloration previously noted will be subsequently shown to be due to other causes.

With pineapples, however, we are dealing in the main with an utterly different phenomenon, and on account of the economic importance of this crop, together with the fact that it affords examples of the toxic effects of manganese which are to be observed at all times of the year, a detailed study of the chemistry, physiology, and anatomy of this plant has been made. It was thought that on account of the extreme sensitiveness of the pineapple, a careful study of the effects of manganese on it might give a clue as to the effects produced in other plants, still observed in slightly different manifestations and in less intensity. In this investigation a microchemical study of the entire pineapple plant and its several stages of growth, from soils containing varying amounts of manganese, has been made.

MICROSCOPIC STUDIES.

EFFECTS ON THE PROTOPLASM.

The microscopic examination of the several parts of various species of plants has revealed the fact that there is an apparent alteration in the protoplasmic contents of the cells throughout the plant, although the change can not be detected in every cell and it varies in intensity in the different organs of a given plant. Beginning with the roots, the outer three or four rows of cells, in the case of the pineapple, have a tendency to develop a yellowish-brown appearance in the cell walls. When the plant is grown on a manganese soil, the number of rows of cells thus affected is considerably increased, and sometimes small bodies, dark brown in color, are deposited on the cell walls. These bodies are insoluble in hydrochloric acid of various strengths.

The roots of potatoes also showed a slight brown appearance in the central woody tissue. Likewise, the roots of avocados show a dark-brown ring around the cortex when grown on manganese soil. The appearance of the mango roots, however, is even more pronounced. A dark-brown discoloration in the cell walls and throughout the cell contents is shown in a cross section of these roots; the cell contents are less abundant and the root hairs are light brown in color throughout. The roots of the strawberry show a similar dark appearance in the central canal, the cell walls of which contain dark brown or black incrustations, perhaps MnO_2, as in this instance, they were completely soluble in a 1 to 4 solution of hydrochloric acid. The roots of various other plants were found to contain a somewhat larger percentage of cells with specially thickened tissue adjacent to the cell wall when grown on manganiferous soil. The enlarged tips of pineapple roots, previously referred to, are primarily made up of cells containing this abnormal thickening, and the root hairs are usually shorter.

The growing tips of plants in general begin to die back as one of the first evidences of toxic effect, and this is usually accompanied by a browning of the cell walls and darkening of the cell contents. The pineapple leaf shows an irregular surface when grown under the influence of excessive manganese, giving it the appearance of containing small prominences. A microscopic examination has shown this to be due to a shrinkage in the tissue, which is brought about by the loss of water. These prominences, however, often become dark brown, with a browning of the cell walls, and in some instances there is a disintegration and partial decomposition of the protoplasm itself. Later these spots become larger, until in some instances, the normally liquid contents of the palisade cells become coagulated into a formless mass, which draws away from the cell walls. The protoplasm in the cells which normally bear chlorophyll also breaks away from the cell wall in places, contracting into irregular-shaped bodies. Plasmolysis, therefore, takes place and in a few instances the nuclei have been observed to be brown.

EFFECT ON CHLOROPHYLL.

The first appearance of the effects of manganese is shown in the fading of the chlorophyll, which may be observed in the field in every degree of development from the normal deep green on the one extreme, to yellowish-white plants containing scarcely a trace of chlorophyll on the other. Microscopic examinations show that the fading and ultimate disappearance of the green color is attended by a decomposition and finally the complete disintegration of the chlorophyll bodies. Cross sections of the etiolated leaves show that at first there is a fading of the green color, a change in the intensity of the green color of the chlorophyll granules, without their utter disintegration, but that in successive stages the entire protoplasmic bodies in the cells and all organized arrangement of the protoplasm are broken up. The protoplasm draws away from the cell walls in places and completely loses its organized structure, and in advanced stages there is no trace of a granular structure, such as characterizes normal chloroplastids.

The chloroplastids in the higher plants ordinarily contain two pigments, a green, true chlorophyll, and a yellow, xanthophyll, both of which are soluble in alcohol. After extracting pineapple leaves with alcohol the colorless plastids remaining were found to be somewhat smaller in the plants from manganiferous soil. Upon separating the pigments in the alcoholic extract by means of ether or benzin, it was noted that the chlorotic plants contained very small amounts of the green pigment as compared with the normal, while the occurrence of xanthophyll was about the same in the two instances.

From these facts it seems justifiable to conclude that the etiolation of pineapples is caused by some fundamental change in the protoplasm, which change, however, is not concerned with the yellow pigment, and which does not result in the formation of an increased amount of xanthophyll in the plant. Pineapples in common with other members of the Bromeliaceæ are characterized by a number of rows of palisade cells immediately beneath the epidermis, which cells contain no chlorophyll or only traces of it. In the etiolated plants sometimes these cells seem to be given over to the storage of calcium oxalate; and throughout the entire plant from the tips of the roots through the stalk and fruit into the crown the occurrence of oxalate of lime crystals is greatly in excess of that in normal plants.

EFFECT ON STARCH.

The disappearance of chlorophyll naturally suggested an interference with the formation of carbohydrates, and from a microchemical examination the suspicion is well borne out. The chlorophyll granules, in normal pineapple leaves, are shown by the iodin tests to contain starch in considerable quantities, and frequently the entire granule becomes intensely blue. Near the base of the leaf, starch is stored in considerable quantities, while the stalk is given over very largely as a repository for this reserve source of energy.[1] Chlorotic leaves, on the contrary, contain very limited amounts of starch, the amount present being in direct proportion to the amount of chlorophyll. In the more advanced stages of chlorosis no trace of starch was detected in the parts of the leaves which normally contain chlorophyll. Near the base of such leaves and in the stalk and roots, however, starch, stored up before the decomposition of the chlorophyll, occurs in abundance, and it is perhaps from this reserve store that the plant very largely derives the energy by which it continues its feeble hold on life.

Pineapples show the most marked effects in starch formation brought about by the toxic effects of manganese; but other species of plants are also affected in this particular. The stems of barley and jack beans were found to contain starch in diminished quantities when grown on manganese soil. As previously pointed out, the growth of onions was particularly affected by manganese, and a microscopic examination of sections of the leaves of this plant failed to show the presence of a trace of starch, whereas it is found in appreciable quantities in the normal plant.

OXIDIZING ENZYMS.

The discovery, by Bertrand, of the presence of manganese in oxidases, suggested to Loew and his associates in Japan the possibility of an increased oxidase and peroxidase activity in plants grown under the influence of manganese compounds, and they have reported the presence of more active oxidizing enzyms in such plants.

As before stated, some plants are much more sensitive to manganese than others; and in some of the lower forms of plant life, especially the fungi,[2] manganese appears to be incapable of bringing about stimulation. These effects suggest that the function performed by manganese is different in different species of plants. Loew [3] pointed out that tobacco showed no increase in the activity of its oxidizing enzyms after having been watered with a dilute solution of manganous sulphate. It has been previously pointed out by the writer [4] that sometimes the etiolated pineapple leaves from manganese soil contain a more active oxidizing enzym than green leaves from normal plants.

A more extensive investigation of this question, however, has shown that the phenomenon previously observed is by no means of universal occurrence. The activity of oxidases and peroxidases in etiolated pineapple leaves is sometimes greater, and sometimes less, than in

[1] For a more complete discussion of the pineapple plant see a forthcoming bulletin of the station.
[2] Molisch, Sitzber. K. Akad. Wiss. [Vienna], Math. Naturw. Cl., 103 (1894), I, p. 554.
[3] U. S. Dept. Agr. Rpt. 65, 1900, p. 22.
[4] Loc. cit.

normal leaves; and while an increased activity sometimes occurs in the etiolated leaves, the total oxidizing power of such extracts is not greater than that of similar ones obtained from normal leaves. Upon standing for a period of 10 minutes, the total oxidation, as measured by the intensity of the color produced in alcoholic solutions of guaiacum or aloin, was equally great with the extract from plants from the two types of soil. These tests have been applied to all parts of the pineapple plants from soils containing manganese varying from 0.1 per cent to 9.75 per cent, and with plants at every age and in the various stages in the development of the chlorosis; and when thus applied to a large series of samples, no correlation could be made between the development of chlorosis, on the one hand and the activity of oxidizing enzyms on the other. Of the many samples tested, oxidases, in limited amounts, and peroxidases, in still greater amounts, occur; but no relation was found between the activity of the enzyms and the appearance of the yellow color. Frequently the normal plants contain a more active oxidase than do the chlorotic plants.

These tests have been extended to various other plants. The leaves of corn grown on manganese soil gave a strong peroxidase reaction, while only a slight reaction was obtained from such leaves when grown on normal soils. *Paspalum orbiculare* grown on manganese soil gave no reaction for oxidase or peroxidase, while a slight bluing of the guaiacum was brought about by the extract of this plant from normal soil. The intensity of the reaction was about equal in extracts from sugar-cane leaves from both classes of soil. Leaves of Crotalaria from manganese soil gave a strong peroxidase reaction, while a less intensive reaction was obtained from leaves when grown on normal soil. Leaves of the olive tree showed the presence of a more active peroxidase when grown on manganese soil. The leaves of oats showed a strong peroxidase reaction when grown on manganese soil and a weak reaction when grown on normal soil. The leaves of cotton, likewise, showed an increased activity in oxidizing enzyms when grown on manganese soil, the total oxidizing power in this instance, however, was not greater. Upon standing for 10 minutes the intensity of the bluing was about equal for plants from both types of soil. Rice showed a similar effect.

The activity of the oxidizing enzyms in specimens of a given species of plant is by no means uniform when grown on normal soils. It has been found, for instance, that extracts obtained from the fresh leaves of normal sugar cane and pineapples, respectively, varied in their oxygen-carrying power between wide extremes; sometimes the leaves of each of these species were found to give a very weak peroxidase reaction, while in other cases the intensity of the reaction was very striking.

It has been shown that pathological disturbances caused by attacks of aphidæ, the mosaic disease of tobacco, etc., are also associated with accelerated auto-oxidation. The autumnal yellowing of plants incident to maturity and the development of yellow spots on certain plants has been shown by Woods [1] to be associated with an increased activity of the oxidases and peroxidases of these plants. This suggested to Loew et al. that the yellowing of plants under the influence of excessive amounts of manganese may be due to excessive auto-oxidation. These authors did not show, however, that etiolated plants grown under the influence of excessive amounts of manganese contain more active oxidase and peroxidase than the same species of plant when grown under the maximum stimulating effects of manganese.

It seems reasonable to suppose, therefore, that while manganese has the power of increasing the oxygen-carrying power of oxidases and peroxidases, and consequently may, in this way, to some degree bring about plant stimulation, the phenomenon of chlorosis can not be completely explained on the basis of excessive auto-oxidation. The development of chlorosis under the influence of manganese is very probably the result of physiological disturbances of a more deep-seated nature.

EFFECTS OF MANGANESE ON THE ANATOMY OF PLANTS.

The microscopic anatomy of certain plants is modified to some extent by the presence of excessive manganese in the soil. As previously stated, the chloroplasts of pineapples became bleached and ultimately decomposed. The effects of manganese are very gradual, and are best observed in the extreme cases. At first there is a gradual fading of the green pigment and a simultaneous reduction in the size of the chloroplasts. These gradually become smaller and smaller until the spongy parenchymatous cells contain only small, slightly yellow bodies where formerly the chloroplasts were abundant.

With the disappearance of the green coloring matter, the absorption of carbon dioxid ceases, and therefore carbohydrate formation comes to an end. This is clearly shown from the absence of starch grains in the leaves. Ordinary green pineapple leaves contain considerable starch, while in the etiolated leaves scarcely a trace of starch occurs. Throughout the etiolated pineapple leaves there are to be found angular bodies similar in appearance to aleurone grains, but which appear to have resulted from an alteration of protoplasm. These occur adjacent to the cell walls, and are most abundant in the cells which show the most pronounced evidences of plasmolysis.

---

[1] Loc. cit.

The cells in various parts of the plant are also somewhat reduced in size when grown on manganiferous soil, and the cell walls of certain portions of the roots become thickened and fleshy.

The gross anatomy of various species is affected by manganese. As previously stated, corn, cowpeas, pigeon peas, onions, etc., do not attain their normal size on manganese soil. Rice did not tiller as usual. Regarding the effects on root development, mention has been made of the modification in the roots of the pineapple. Certain other plants, as for instance barley, wheat, oats, and jack beans were found to develop an unusual number of fine rootlets. In the case of barley this was especially noticeable. In certain other species, corn in particular, there is a pronounced tendency to form woody roots. The root hairs of the mango were also found to be brown.

COMPOSITION OF THE ASH.

In addition to the effects already mentioned, in studying the function of a given substance in plant nutrition, it is essential to know something regarding its effect on the mineral constituents of plants, and in order to throw some light on this point a large number of ash analyses have been made. If manganese performs a physiological function in connection with the oxidases, or otherwise, it is probable that the composition of the ash will give some indication of this action. For these determinations various plants grown on normal and manganiferous soils were submitted to the usual ash analysis.

Special precautions were taken in selecting the materials for analysis so as to secure representative plants of the same age and stage of development in a given species. In this instance the optional method of the Association of Official Agricultural Chemists,[1] for the preparation of ash from plants was used, and the several determinations were made from samples of the ash thus obtained.[2] Where it was necessary, the samples were leached with distilled water, which was subsequently evaporated to dryness and added to the incinerated residue in making up the ash sample. The table following will show the results.

[1] U. S. Dept. Agr., Bur. Chem. Bul. 107 (rev.), 1908, p. 238.

[2] The plants used for comparison were taken from soils containing various amounts of lime and magnesia.

Ash analyses of plants grown on normal and manganiferous soils.

Plants analyzed.	Silica (SiO_2).	Alumina (Al_2O_3).	Iron (Fe_2O_3).	Manganese (Mn_3O_4).	Lime (CaO).	Magnesia (MgO).	Phosphoric acid (P_2O_5).	Potash (K_2O).	Soda (Na_2O).	Sulphur trioxid (SO_3).	Chlorin (Cl).	Total ash.
Pineapple leaves 5 months old:	*P ct.*	*P ct.*	*P ct.*	*P ct.*	*P ct.*	*P ct.*	*P ct.*	*P ct.*	*P ct.*	*P ct.*	*P ct.*	*P ct.*
Manganiferous soil	9.37	2.12	0.81	2.41	9.01	5.70	2.81	21.09	19.48	2.62	13.37	9.94
Normal soil	8.49	1.20	1.11	1.70	7.14	7.60	3.57	22.97	16.72	2.72	13.33	7.14
Pineapple leaves 18 months old:												
Manganiferous soil	5.72	1.76	.96	2.08	15.66	7.91	1.66	14.35	18.86	2.70	13.91	7.98
Normal soil	7.36	.40	.48	1.40	7.00	6.98	2.70	17.12	22.86	3.58	8.86	6.24
Pineapple stalk 5 months old:												
Manganiferous soil	5.20	.40	.60	.25	36.42	2.60	6.12	16.79	2.65	20.99	6.31	8.85
Normal soil	2.27	1.56	.70	.25	23.87	5.82	8.86	24.18	1.65	16.36	9.36	5.12
Pineapple stalk 2 years old:												
Manganiferous soil	1.72	4.52	T.	.80	14.36	7.75	6.70	32.26	1.10	16.81	11.13	7.78
Normal soil	2.84	6.02	T.	.20	12.96	5.78	8.36	33.11	.50	22.93	8.01	6.60
Corn stover:												
Manganiferous soil	25.55	2.63	2.80	.40	8.60	7.64	5.17	22.67	6.67	5.61	5.05	7.55
Normal soil	39.65	1.02	3.20	.15	3.45	4.60	7.56	25.01	1.95	3.48	4.11	9.18
Cowpea vines:												
Manganiferous soil	10.45	1.75	1.60	3.07	22.72	6.93	2.90	21.63	8.70	7.48	3.12	13.73
Normal soil	22.20	7.37	1.90	.87	17.10	9.13	5.03	23.24	8.04	3.52	5.95	13.44
Cowpeas:												
Manganiferous soil	2.64	5.52		.15	1.47	4.15	15.89	.....	.....	.....	.....	3.93
Normal soil	2.26	5.43		.00	1.13	6.91	22.71	.....	.....	.....	.....	3.53
Paspalum orbiculare:												
Manganiferous soil	66.75	5.21	3.60	2.20	5.30	3.46	2.54	6.04	1.98	4.45	.29	7.88
Normal soil	49.30	6.11	14.00	1.05	6.70	5.05	2.34	4.49	1.87	4.83	.88	7.16
Guava leaves:												
Manganiferous soil	12.00	11.23	3.20	.82	43.02	3.73	4.47	6.15	2.19	9.24	2.31	7.66
Normal soil	11.10	4.52	.48	.28	22.98	10.46	7.70	21.61	2.44	9.73	2.86	6.73
Guava wood:												
Manganiferous soil	4.42	.00	1.28	1.20	52.10	1.51	4.33	10.77	3.82	6.06	.42	5.87
Normal soil	2.05	8.68	.50	.15	26.17	7.22	6.97	28.43	5.28	11.48	1.77	4.02
Sugar-cane leaves:												
Manganiferous soil	39.50	1.62	1.73	.45	14.33	4.41	3.21	17.71	1.38	5.88	3.54	5.57
Normal soil	29.50	.57	2.40	.60	16.60	6.07	4.03	25.10	2.54	6.35	5.67	4.85
Crotalaria:												
Manganiferous soil	16.42	2.90	1.90	1.40	30.80	7.79	4.12	16.27	3.47	8.41	6.85	6.77
Normal soil	13.37	3.60	.80	.05	19.00	21.05	9.13	13.03	4.39	5.96	6.58	6.28
Peanut leaves:												
Manganiferous soil	3.29	2.00	1.30	.25	35.24	5.61	4.49	21.11	.00	3.29	3.54	10.45
Normal soil	5.65	.76	2.41	.04	39.41	10.99	4.97	12.39	.82	2.49	2.20	9.95
Peanut stems:												
Manganiferous soil	7.64	12.00	3.88	2.56	14.80	9.04	2.00	26.57	2.82	4.84	3.54	11.15
Normal soil	4.90	3.13	2.06	.32	21.76	19.02	4.81	26.11	2.92	5.54	1.42	7.12
Ironwood (*Casuarina equisetifolia*) needles:												
Manganiferous soil	3.68	5.62		.66	37.50	4.57	1.62	.....	.....	.....	6.95	.....
Normal soil	.86	5.29		T.	43.12	7.75	4.23	.....	.....	.....	7.87	.....
Olive leaves:												
Manganiferous soil	9.12	7.99	5.60	.64	26.32	1.84	2.63	20.52	5.85	4.34	1.27	.....
Normal soil	15.18	9.70	8.88	.86	17.80	1.53	2.78	17.02	5.79	5.17	1.99	.....
Waltheria americana leaves:												
Manganiferous soil	9.80	7.31	3.84	8.70	31.30	3.81	2.80	11.16	.30	3.32	3.43	.....
Normal soil	6.82	7.89	3.20	.82	29.62	5.44	3.81	16.37	.81	4.43	4.49	.....
Waltheria americana stems:												
Manganiferous soil	2.23	8.40		.56	14.97	11.70	3.67	.....	.....	.....	.....	3.58
Normal soil	2.49	5.96		.45	13.70	11.30	3.46	.....	.....	.....	.....	3.73
Broom-corn leaves:												
Manganiferous soil	29.52	4.77	2.37	2.24	12.08	6.75	.94	20.84	3.98	2.88	5.91	.....
Normal soil	62.40	5.30	2.92	.60	5.44	3.52	1.38	8.96	2.82	1.39	2.62	.....
Broom-corn stalks:												
Manganiferous soil	9.60	5.67	3.39	1.36	2.12	3.12	1.02	.....	.....	6.57	8.01	.....
Normal soil	34.20	4.84	4.12	.52	1.88	2.51	3.72	18.49	11.80	6.44	4.68	.....
Tobacco stems:												
Manganiferous soil	3.17	4.26		.57	9.47	4.08	2.08	.....	.....	.....	.....	7.02
Normal soil	5.17	10.05		T.	1.88	3.27	7.35	.....	.....	.....	.....	8.50
Pigeon-pea leaves:												
Manganiferous soil	25.94	23.90		1.43	16.11	3.25	4.04	.....	.....	.....	.....	12.17
Normal soil	16.53	26.84		.15	7.86	7.66	10.85	.....	.....	.....	.....	7.84
Pigeon-pea stems:												
Manganiferous soil	4.65	5.46		.99	15.29	2.82	4.25	.....	.....	.....	.....	5.81
Normal soil	3.34	16.85		T.	3.79	4.39	9.34	.....	.....	.....	.....	6.22
Oat straw:												
Manganiferous soil	22.15	3.82		.86	9.15	5.16	.73	.....	.....	.....	.....	10.27
Normal soil	33.29	7.97		T.	3.40	3.19	8.81	.....	.....	.....	.....	11.73
Wheat straw:												
Manganiferous soil	29.72	2.90		.22	4.51	4.03	2.96	.....	.....	.....	.....	8.91
Normal soil	63.81	1.98		T.	2.09	2.74	5.56	.....	.....	.....	.....	16.27
Mango leaves:												
Manganiferous soil	29.25	4.27		2.16	33.12	2.15	2.89	.....	.....	.....	.....	9.24
Normal soil	43.66	4.51		.24	17.13	4.90	5.43	.....	.....	.....	.....	8.21

These data show some striking variations in the composition of the ash. Irregular fluctuations in several elements are to be noted. It is well known, however, that a given species of plant, when grown under different conditions, such as different types of soil and climatic variations, give ashes of different compositions. *In practically every instance the absorption of manganese was increased on the manganese soil.* The variations in the composition of the several species above given show that there is a pronounced difference in the percentages of lime, magnesia, and phosphoric acid in the ash of plants from the two classes of soils.

Almost universally with the plants examined, the percentage of lime, both when calculated to a basis of the ash or in terms of the dry weight, was found to be in great excess in the plants from manganese soil over that in normal plants. As regards magnesia, there is a pronounced tendency toward the absorption of a diminished quantity from the manganese soils, while the phosphoric acid is almost uniformly absorbed in considerably smaller quantities per unit of dry matter, or as expressed in percentages of the ash. The plants analyzed showed a wide range of effects from manganese, as judged by their gross appearance. Some are not visibly affected, others little so, while still others show a pronounced toxic effect. Uniformly throughout the tendency toward an increased absorption of lime, on the one hand, and a decreased absorption of phosphoric acid and magnesia on the other, is noted.

It has been shown by Loew and others that various plants are affected differently by different ratios of lime and magnesia; certain species of plants will vegetate most advantageously when the ratio of lime to magnesia is as 1 to 1; whereas still other species thrive best when the ratio is as 1 to 3, etc. In the publications dealing with this subject, however, mention is usually made of the effects produced upon the appearance of the plants, and it is to be regretted that so few ash analyses have been made in this connection. From the data obtainable, however, it appears that where the physiological balance between lime and magnesia is disturbed, a corresponding influence is brought about in the composition of the ash.

Under the influence of manganese plants automatically modify themselves in regard to the absorption of these two elements, and as is well known, it is not so much the absolute amount of calcium and magnesium in a given soil as the ratio between these two substances that determines the physiological effects.[1] In order to bring out the relationship more clearly, the relative amounts of calcium and magnesium absorbed from normal and manganiferous soils, respec-

[1] As shown by a number of recent investigations, magnesium appears to be a normal constituent of chlorophyll. This fact may be associated with the development of chlorosis in the pineapple when grown under the influence of excessive manganese.

tively, have been recalculated from the previous ash analyses and are presented in the following table:

The ratio of lime to magnesia in plants (magnesia considered as 1).

Kind of plant.	From manganiferous soil.	From normal soil.	Kind of plant.	From manganiferous soil.	From normal soil.
Pineapple leaves:			Ironwood needles	8.20	5.56
5 months old	1.58	.94	Olive leaves	14.30	11.63
18 months old	1.98	1.00	*Waltheria americana:*		
Pineapple stalk:			Leaves	8.21	5.44
5 months old	14.00	4.10	Stems	1.28	1.21
18 months old	1.88	2.24	Broom corn:		
Corn stover	1.12	.75	Leaves	1.79	1.54
Cow peas:			Stems	.67	.74
Vines	3.28	1.86	Tobacco stems	2.32	.57
Seed	.35	.16	Pigeon peas:		
Paspalum orbiculare	1.53	1.32	Leaves	4.69	1.02
Guava:			Stems	5.42	.86
Leaves	11.53	2.19	Oat straw	1.79	1.07
Stems	34.50	3.62	Wheat straw	1.12	.76
Sugar cane, leaves	3.25	2.73	Mango leaves	15.40	3.49
Crotalaria	3.95	.90			
Peanut:					
Leaves	6.28	3.58			
Stems	1.63	1.14			

An inspection of these data shows that in almost every instance the ratio of the absorbed lime to absorbed magnesia is increased under the influence of manganese.

THE DISTRIBUTION OF MANGANESE IN PLANT ORGANS.

Regarding the deposition of manganese in the various plant organs, authorities are not agreed. Certain investigators have observed it to be present in greatest abundance in the leaves and active growing parts of plants, while still others have found it to be deposited at maturity in the grain. Occasionally it has been reported as in part assuming a concretionary form and being deposited in the cell walls or on the surface of leaves, etc., and finally in some species it is stated to be present in the cell sap only.

The investigations already recorded show that the deposition in various species is not always the same. In certain plants which contain strongly acid sap, as for instance the pineapple, the manganese appears to be in solution in the cell sap. Pineapple leaves were macerated and leached with distilled water, by means of which it was found that practically the entire manganese content was leached out. In addition, no evidence of a deposition of any manganese compound in pineapples was observed in the microscopic studies herein reported.

In certain other plants, strawberries and mangoes in particular, manganese is deposited on the cell walls. In regard to the distribution of manganese in the various parts of plants, the following determinations will be of some interest:

Percentage of manganese in the ash from various parts.

Kind of plant.	Mn_3O_4.	Kind of plant.	Mn_3O_4.
Pineapple:	*Per cent.*	Corn:	*Per cent.*
Leaves	2.08	Leaves	0.66
Stalk	.20	Grain	.00
Fruit	Trace.	Peanuts:	
Guava:		Leaves	.25
Leaves	.82	Stems	2.56
Stems	1.20	Crotalaria:	
Waltheria americana:		Leaves	3.12
Leaves	8.70	Stems	1.48
Stems	.56	Seeds	.80
Broom corn:		Cowpeas:	
Leaves	2.24	Leaves and stems	3.07
Stems	1.36	Seed	.15
Sorghum:		Pigeon peas:	
Leaves	.89	Leaves	1.43
Stems	.79	Stems	.99
Wheat:			
Leaves	1.40		
Stems	1.40		
Grain	.68		

From these data it is apparent that the distribution of manganese in the different parts of plants varies in different species, but is usually greatest in the leaves. In no instance was it found in greatest concentration in the seed.

CONCLUSIONS.

From the preceding investigation it has been shown 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 walls, the nuclei become brown, and plasmolysis takes place.

The chlorophyll in a number of plants is affected. In pineapples it undergoes decomposition, the chloroplasts often becoming completely disintegrated and losing their usual granular structure. Simultaneously with the destruction of chlorophyll starch formation ceases.

The occurrence of oxidizing enzyms in plants appears to bear no relation to the destruction of chlorophyll under the influence of excessive manganese. While the oxidases generally contain manganese as a normal constituent, or at least manganese is closely associated with the oxidases and at the same time their oxygen-carrying power is accelerated by the presence of manganese salts, the foregoing investigations show that there is no correlation between the phenomenon of chlorosis in pineapples and the activity of the oxidizing enzyms. The decomposition of the chlorophyll in this case therefore is not due to excessive auto-oxidation. This does not imply, however, that accelerated auto-oxidation in plants is without effect.

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. Some of the plants analyzed showed a marked toxic effect due to manganese, while others appeared to be unaffected; but in practically every instance a modification of the mineral balance was observed, and this was found to follow the same direction in all species. The ratio of absorbed lime to absorbed magnesia increased under the influence of manganese, regardless of whether the plant showed a toxic effect.

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 effect of the manganese itself. As has been mentioned already, not all species of plants are equally sensitive to modifications in the lime-magnesia ratio, and likewise different ratios are best suited to different species. Therefore the effect of manganese may be very different in different species of plants. With certain plants it is toxic for the reason that the lime and magnesia are thrown out of their optimum ratio for this plant, while with other plants it may exert a stimulating effect by bringing this ratio more nearly to its optimum for these species.

If we are to accept Loew's theory regarding the function of magnesium in plant growth—namely, that it acts largely as a carrier of phosphoric acid—we may come to a better understanding of the data in this connection. According to theory, magnesium phosphate being more easily hydrolizable than the calcium phosphate, a relatively large amount of magnesium in the cell sap prevents the precipitation of phosphoric acid as calcium phosphate, which would tend to remove it from the cell sap, and consequently throw it out of the field of action. Magnesium, therefore, by virtue of mass action, holds in solution this essential for protoplasmic formation. If an excess of calcium should be introduced into the cell sap, however, as is the tendency with plants which grow on manganiferous soils, there would be a tendency to precipitate the phosphoric acid from solution, and thus to interfere with the formation of protoplasm.

The small amount of manganese in natural soils, therefore, probably performs a twofold function in plant growth: (1) It acts catalytically, increasing the oxidations in the soil and accelerating the auto-oxidations in plants; and (2) it tends to modify the absorption of lime and magnesia, perhaps by partially replacing calcium from insoluble combinations, and, by a direct effect on the osmotic absorption of lime and magnesia, increasing the former and decreasing the latter.

The absorption of phosphoric acid is likewise decreased in the presence of manganese. By reference to the table of ash analyses it will be seen that frequently a given species of plant was found to have absorbed not more than one-half as much phosphoric acid from manganese soil as from normal soil. The interference with the absorption of phosphoric acid would also tend to bring about stunted growth, and might be sufficient to account for the differences in the size of plants from the two classes of soil. A possible explanation of the effects on absorption of phosphoric acid is found in the manganese. By reference to the second part of this paper it will be seen that manganese exists in the soil largely as MnO_2, which is quite soluble in organic acids, giving rise to the proto-salts. Phosphoric acid coming into solution in the soil moisture would tend to be precipitated by the manganese as manganese phosphate, a difficultly soluble compound, and hence in this way the absorption of phosphoric acid by plants might be hindered.

In harmony with these ideas are certain experimental demonstrations. It is a matter of common knowledge among the pineapple growers that the application of lime to manganiferous soils results in the production of a more intense yellowing in a shorter length of time than is produced without it. No surer means of pineapple failure can be adopted on manganiferous soils than the application of lime. On the other hand, it has been shown that the application of soluble phosphates [1] tends to ameliorate the effects of an excess of manganese. In practice this is the only means that is known to be efficacious, but in the case of pineapples it does not prevent the development of the yellow color.

Concerning the form in which manganese is absorbed very little can be said definitely. It has been found that a given compound of manganese acts differently with one and the same crop when applied to different soils. This may be partially explained on the basis of an indirect effect on the other bases of the soil. On the other hand, certain compounds appear to be toxic, while others act as stimulants when used in equal concentrations. Salomone found that the toxicity for wheat and barley was greater with compounds in which the

[1] Cf. Guthrie and Cohen, loc. cit.

element played the rôle of an electronegative element (manganates, etc.). Frequently it has been observed that applications of manganese dioxid produced equally as great or greater effects than a soluble salt, like manganese sulphate or chlorid. Recently, in discussing the peculiarities of pineapples on the manganiferous soils of Oahu, James[1] suggested that the manganese is probably absorbed as a manganite of calcium, of which there are a number.

In the presence of the higher oxids of manganese or their hydroxids soluble calcium compounds would probably form one or more of the calcium manganites, and the fact that the application of lime increases the toxicity of manganese, together with the fact that the absorption of lime by plants is increased in manganiferous soils, gives some support to the view that a calcium manganite is formed.

[1] Hawaiian Forester and Agr., 8 (1911), No. 6, p. 176.

THE ORIGIN, COMPOSITION, AND PROPERTIES OF THE MANGANIFEROUS SOILS OF OAHU.

INTRODUCTION.

The island of Oahu is made up of two almost parallel mountain ranges, the Koolau on the east and the Waianae on the west, with a sloping plateau of about 10 miles in width and 40 miles in length between these. The entire island is volcanic, with extinct craters in the mountain ranges, and a number of lateral cones on the coastal slopes, particularly near the southeastern point of the island. The central plateau comprises an irregularly rolling plain, which slopes gently from the mountains on the east and west, toward the central and lower portion, from whence a gentle slope extends to sea level on the north and south, respectively.

This plateau comprises the principal portion of the arable land of Oahu, and rises very gradually from sea level to an elevation of about 800 feet in height from north to south, while there is also a general slope from the mountain ranges on either side. In no considerable area of the plain is there a slope of more than a few degrees. Numerous gulches or deep ravines originating in the mountains traverse the plain, thus furnishing natural water courses for the excessive precipitation of the islands, which is most abundant in the Koolau Mountains.

The depth of the disintegrated detritus, of which the soil is a part, varies from 1 to perhaps 20 or more feet in places, and is underlaid by normal basaltic lava of essentially the same structure and composition throughout, and very similar to that which forms the rock-ribbed foundations and strata of the mountain ranges. The composition and characteristics of the soil vary between wide extremes, the larger portion of which is typical laterite, similar to the red, highly ferruginous soils of the entire island group, and closely resembling the soils of other volcanic islands of the Pacific.

From the evidences at hand, the soil and deeper-lying disintegration products have resulted principally from the primary decomposition of normal basalt, under the influence of the usual weathering agencies incident to a humid subtropical climate. In some localities more drastic chemical agencies may have had a part in the early changes set up in the lava soon after ejection. The ever-present sulphurous vapors around the active volcanoes of Hawaii in recent times may have accompanied the ancient flows that builded up the mountain ranges and plateaus of Oahu, and the sulphuric acid formed from the oxidation of the burning sulphur may at least have taken part in the initial disintegration of the lava; but it is safe to conclude that the main body of disintegrated lava, which is spread out over the entire plain, and a large part of which has been washed down from the greater elevations in the mountains, represent segregation and disintegration products resulting from the operation of normal weathering agencies.

THE LOCATION OF MANGANIFEROUS SOILS.

The natural slope of the plain toward the sea at either end is considerably greatest from the sea level to an elevation of about 650 feet, above which the fall is very gentle. At intervals in this upland plain, and scattered promiscuously from one end of the island to the other over a distance of 15 or more miles, there are areas of various sizes and every shape which are made up of soil quite unlike that surrounding them, and which contain, in many instances, large quantities of manganese. The location of these sporadic manganiferous outliers is usually toward the lower and more central part of the upland portion of the plain, and they are generally found at elevations of from 650 to 900 feet. Sometimes the manganese soil occurs in local areas of not more than an acre in extent, while it is not uncommon to find areas of 20 or more acres in one body; but almost uniformly the manganese soil is located at or near the base of a long, gentle slope, or on a rather level expanse, and sometimes in a shallow basin.

ORIGIN OF THE SOIL.

The occurrence of soils containing such high percentages of manganese, which is, so far as is known, unlike any similar areas elsewhere, naturally calls for some inquiry concerning its origin. More especially is this true when we consider that the entire island group is of volcanic origin and of comparatively recent formation. The lavas throughout the islands belong to the typical basaltic type, and while disintegration and physical segregation of the lava proceeds rapidly under a moist tropical climate, thus rapidly breaking up the lava into a finely divided residuum, true mineralization has not been in progress sufficiently long to affect a very pronounced mineral segregation. Minerals thus understood are a comparative rarity in the islands. In the cooling of the molten magma certain rather definite substances separate into fairly definite mineral forms, such, for instance, as olivine, magnetite, etc., but the disintegration products that have resulted from simple weathering or a combination of weathering and more radical chemical forces, such as the gases accompanying the eruption and flows, are comparatively few in number and may be said to be simple in composition. Mineralogists, as a rule, therefore, have not taken great interest in the islands.

The basaltic lavas of the islands are classified into several classes, but these classifications are in the main based on physical rather than chemical differences. The absolute chemical composition of the unaltered lavas of the islands, while varying from place to place, does not afford fundamental differences sufficiently distinct to form a basis of classification. The unaltered lava then, for our purposes, may be looked upon as a single rock. Particularly is this true of the rock masses that constitute the mountain ranges of Oahu, and the lava-flows which have given rise to the soils of the plain between the Waianae and Koolau Mountains. No detailed geological investigation of the rock masses and formations in these mountains has been published, but numerous geological observations have been made and specimens from various parts examined sufficiently perhaps to warrant the conclusion above drawn.[1]

CHARACTER OF THE SOIL.

The soil that arises from the disintegration of the lava possesses properties that are very characteristic. In general they may be classified as highly ferruginous and of fine texture. The disintegration usually has been complete. Few pebbles or small stones occur in the soil and subsoil, and practically the entire mass is reduced to an impalpable powder. The principal changes that have taken place between the lava on the one hand and the soil on the other, are those of oxidation and solution. There is, of course, every stage of this change represented in these soils, although the main body of the soil and subsoil of this plain represents almost complete decomposition.

COMPOSITION OF THE LAVA.

The lava contains about 11 per cent iron completely disseminated throughout, and in the unaltered condition this is largely in the ferrous state. It is of a dark gray color and usually quite regular. In weathering the iron becomes oxidized, thus taking on a reddish-brown color, which varies owing to different degrees of hydration or the subsequent reduction, under the influence of decaying organic matter in the partial absence of free oxygen.

---

[1] C. H. Hitchcock. Geology of Oahu, Bul. Geol. Soc. America, 11 (1900), pp. 15-60. Hawaii and Its Volcanoes. Honolulu, 1909.

The accompanying table shows the composition of normal lavas taken from different parts of the plain, and may be looked upon as fairly typical:

Analyses of lavas from Oahu.

Constituents.	A.	B.	E.	F.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Silica (SiO_2)	52.45	52.15	51.98	52.24
Alumina (Al_2O_3)	11.49	12.57	15.85	16.00
Ferric oxid (Fe_2O_3)	3.66	3.36	2.90	3.73
Ferrous oxid (FeO)	6.90	7.07	6.84	5.89
Manganese oxid (Mn_3O_4)	.36	.50	.92	.68
Lime (CaO)	10.32	8.54	9.57	9.54
Magnesia (MgO)	5.81	6.51	5.61	5.90
Potash (K_2O)	.89	.84	.97	.86
Soda (Na_2O)	2.44	2.64	2.70	2.65
Sulphur trioxid (SO_3)	.20	.61	.51	.53
Phosphorus pentoxid (P_2O_5)	.38	.28	.22	.11
Titanic dioxid (TiO_2)	4.07	2.07	1.50	1.50
Combined water (H_2O)	1.02	.94	1.04	.54
Total	99.99	100.08	100.61	100.17

For purposes of comparison, samples of soil immediately adjacent to the lava were also analyzed. The strata are frequently made up of large bowlders of lava, which upon weathering show a concentric structure, being apparently made up of successive layers of lava which possibly accumulated during the slow flow, and in part is perhaps due to the cooling of successive layers proceeding from without toward the center. It here affords a good opportunity for a study of the changes that take place in the successive decomposition and weathering of the lava, for successive layers still showing the structures of the lavas, are to be found in every stage of decomposition from the unoxidized and unaltered rock, on the one hand, to completely oxidized and weathered soil, on the other. Recent cuts made by building roads across the ravines and gulches expose these decomposing bowlders in numerous places, and, in addition, give good opportunity for a study of the general question of stratification and decomposition throughout the plain.

COMPOSITION OF LAVA-ALTERATION PRODUCTS; THE EFFECTS OF LEACHING.

The composition of these weathered products is shown in the following table:

Analyses of lava disintegration products.

Constituents.	C.	D.	G.	H.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Silica (SiO_2)	20.29	24.01	26.82	32.00
Alumina (Al_2O_3)	37.97	36.27	30.13	35.28
Ferric oxid (Fe_2O_3)	15.01	14.29	16.86	11.80
Ferrous oxid (FeO)	3.22	3.31	3.03	1.53
Manganese oxid (Mn_3O_4)	.19	.43	.06	.08
Lime (CaO)	.33	.17	.22	.22
Magnesia (MgO)	.20	.09	.11	.14
Potash (K_2O)	.25	.24	.46	.30
Soda (Na_2O)	.27	.31	.57	.61
Sulphur trioxid (SO_3)	.78	.49	.74	.70
Phosphorus pentoxid (P_2O_5)	.23	.34	.19	.04
Titanic dioxid (TiO_2)	4.69	4.82	2.21	2.13
Combined water (H_2O)	16.84	15.61	18.34	15.06
Total	100.27	100.38	99.74	99.89

Sample C was taken from adjacent to lava sample A.
Sample D was taken from adjacent to lava sample B.
Sample G was taken from adjacent to lava sample E.
Sample H was taken from adjacent to lava sample F.

By comparing these analyses with those in the previous table it becomes apparent that great changes take place during this process. The iron becomes oxidized to a large extent; the color consequently changes from a dark gray to a reddish-brown; the calcium, magnesium, sodium, and potassium are very largely leached out as silicates by the heavy rains that frequent the sections, thus giving rise to a soil that contains a large percentage of iron and alumina and correspondingly small amounts of calcium, magnesium, sodium and potassium. Leaching, therefore, plays a greater part in determining the composition of the soil than perhaps any other factor. As further proof of the correctness of this view, Maxwell[1] points out that the waters of the natural streams of the islands contains these elements in large quantities. It is noteworthy in this connection that the percentage of manganese was in every instance found to be less in the soil around these bowlders than in the unaltered lava. It should also be remembered that on account of the great concentration that takes place, due to dissolution of calcium, magnesium, potassium, silicon, etc., those elements not appreciably dissolved would necessarily become concentrated in passing from the lava to the soil; hence, a greater dissolution of manganese than the mere analytical data indicate, must have taken place.

By referring to the analyses of red (and for the present, normal soil (see p. 51), since it represents the usual residuum arising from the

[1] Lavas and Soils of the Hawaiian Islands. Honolulu, 1898, p. 162.

normal weathering of the lava, and is quite similar in composition to the main body of soils throughout the islands), we note a striking similarity between their composition and that of the weathered product collected from around unaltered lava. These red soils constitute the chief arable land of this plain, the manganese areas being localized spots in the general soil.

THE OCCURRENCE OF MANGANIFEROUS SOIL.

The location of manganese soil in the lower parts of the comparatively level portion of the plain and its occasional occurrence in a slight depression suggests solution and segregation as possible factors in the transfer and subsequent deposition of this material. The surface soil throughout the plain is undoubtedly colluvial and alluvial, having been derived from greater elevations; but by no means can the entire mass of disintegrated material, which often extends to a depth of 15 or 20 feet in places, be looked upon as having thus been transferred from the lava of its origin. A sharp line of stratification is shown at many places on the cut edges of the gulches and in excavations made in road building, etc., clearly marking the alluvial layer from that which is sedentary or residual. The alluvium varies in thickness from about 2 to 8 or 10 feet in places, and constitutes the surface soil of the plain.

It is in this alluvium that the manganese uniformly occurs. Nowhere does the decomposed residuum show an accumulation of manganese, neither has a highly manganiferous lava been discovered, although search has been made for such. The manganiferous areas are localized and in no sense continuous, and the percentage of manganese uniformly decreases from the surface downward. Frequently the soil contains 5 per cent manganese, whereas the subsoil at a depth of 30 inches contains less than 1 per cent.

In localities where the alluvium is deepest, highly manganiferous material is found at a depth of 6 to 8 feet. In one location the soil was found to contain 9.7 per cent Mn_3O_4, the entire mass being very finely divided and containing no particles larger than 1 millimeter in diameter; whereas the subsoil at a depth of 36 inches contained 8.50 per cent Mn_3O_4. At this depth, however, the manganese occurred largely in the form of concretions, some of these being $\frac{1}{2}$ inch in diameter. At depths below the alluvial deposit the residuum contains less than 0.5 per cent Mn_3O_4. Within 50 yards from this spot the soil on every side of it, save that of the natural drainage, contains less than 1 per cent of manganese, and successive borings at various depths failed to reveal the presence of more highly manganiferous materials.

Throughout the plain the low-lying areas contain manganiferous concretions of all shapes and sizes, ranging up to a size of $\frac{1}{2}$ to $\frac{3}{4}$ inch in diameter. These uniformly show the concentric shell structure of concretions deposited from solution, and are arranged around a nucleus of some sort, usually of red substance similar to the red soil.

LEACHING OF THE MANGANESE.

Heavy precipitation is a pronounced characteristic of the Koolau Mountain climate, the run-off draining through the natural gulches of the districts. Some of these streams are continuous throughout the year. It has been noticed that the bowlders and pebbles in the bed of these small streams are coated over with a black film, which upon examination has proven to be the higher oxids of manganese. In some instances pieces of vesicular lava lying in the bed of a drainage ditch were found to contain numerous manganese concretions imbedded in the surface cavities. No cavity or vesicle which did not have direct open connection with the surface contained manganese concretions. In these instances the manganese was deposited on these stones from solution in the natural drainage water. Some of these incrustations are of quite recent deposition, and without doubt the drainage waters from lavas that are undergoing disintegration at the present time contain manganese in solution, although it is present in very minute quantities.

In this connection it is of interest that the previously published analyses of Hawaiian lavas [1] show the presence of manganese as a general constituent, and in some instances it has been found to be present in the lava to the extent of 1.91 per cent, expressed as MnO. Other samples taken from Kilauea range from a trace to 1.72 per cent. It is safe to say that manganese is a constituent of all normal lavas of the islands.

In the disintegration and weathering of basalt, therefore, manganese becomes soluble and leaches out. The drainage waters necessarily contain this element, which subsequently becomes oxidized and is precipitated around various nuclei, or as a film on the surfaces of stones in the drainage waters. Thus far this discussion has kept close to experimental facts which are being demonstrated on a grand scale wherever lava is undergoing disintegration under semihumid climate in the islands.

THE PROBABILITY OF SUBMERGENCE.

During the cruise of the "Challenger" expedition in 1873–76 [2] it was found that at various places between Hawaii and Japan, to the south of Hawaii and scattered promiscuously over the southern Pacific, the floor of the ocean contained manganese concretions. In

[1] Hitchcock, Hawaiian Forester and Agr., 8 (1911), p. 27.

[2] Report on the Scientific Results of the Voyage of H. M. S. Challenger, 1873–76. Deep Sea Deposits by J. Murray & A. F. Renard. London, 1891, pp. 337–412.

some instances the reports state that the dredge brought up a ton or more of these, which were of varying sizes and shapes, sometimes as large as cricket balls. In some localities these were much more numerous than in others, and they were entirely wanting in still others. Microscopical and chemical analyses showed these concretions to have almost the same composition as the concretions that occur throughout the manganiferous soils of Oahu. For the sake of comparison, analysis of concretions from each of these regions is submitted in the following table:

The composition of manganese concretions.

Constituents.	From Oahu.	From the Pacific.[1]	Constituents.	From Oahu.	From the Pacific.[1]
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
Silica (SiO_2)	16.74	13.58	Titanium oxid (TiO_2)	3.26	....
Alumina (Al_2O_3)	25.48	3.53	Lime (CaO)	.20	....
Ferric oxid (Fe_2O_3)	9.00	20.64	Loss on ignition less oxygen	18.75	....
Manganese dioxid (MnO_2)	23.08	28.17			
Manganous oxid (MnO)	2.88	....	Total	99.39	....

[1] Average of 34 samples. See Challenger Report, Deep Sea Deposits, p. 370.

A comparison of these data shows a parallelism in the composition of the concretions from the two localities, especially as regards the percentages of manganese, silica, and iron. It should be stated that the composition of the concretions from the floor of the Pacific as well as those from Oahu varies considerably. Some of the concretions are made up very largely of the higher oxids of manganese with only small amounts of other substances, while in other cases the percentage of manganese is relatively less. The nature of the mixture in a given case seems to be somewhat accidental and dependent upon the condition and occurrence of the various substances associated with the manganese. Some of the concretions from the Pacific contained considerable amounts of lime and magnesia. The unreported balance in the above analyses is largely to be referred to these substances.

The sharp line of demarcation separating the alluvial deposit from the sedimentary indicates that at some time since the laying down of the foundation of the plain by lava flows an inundation has taken place. The evidences do not point to a submergence of great depth, for the alluvium becomes of less thickness in passing from the lower to the higher portions of the plain, while in the mountains there is nowhere any sign of there having been submergence.

In this connection it is of interest to note that Hitchcock,[1] in discussing the formation of Oahu, states that at first Kaala, the highest peak of Oahu, made its appearance above the ocean followed by

[1] Hawaii and Its Volcanoes, p. 21.

Koolau, thus forming two islands, which were later connected by subsequent lava flows. On account of its bearing on this point the words of the author will be quoted:

> The Kaala dome existed before the Koolau Mountains were raised very much above sea level. The ocean came, perhaps, half way across the islands, and the trade winds impinged against the basaltic piles, dropping moisture which excavated the eastern side very completely, together with the Waianae Wind Gap. * * * In later times the Koolau came up from the depths and poured over the skeleton ridges on the east side of Kaala so as to conceal them from view and underlaid the plateau with nearly horizontal sheets of basalt.

In addition, the same author points out that in his opinion, based on the occurrence of marine shells in cultivated fields at Waialua, and coraline remains in the crater at Diamond Head, together with such occurrences near Kaimuki and at Kahuku, that Oahu underwent a subsequent depression to the extent of 250 feet.

With the additional observation concerning the occurrence of an alluvial sheet over the principal part of the plateau containing manganese concretions similar in every way to those found on the floor of the Pacific, it is reasonable to suppose that the submergence was greater than formerly believed to have been, and possibly extended over the entire plateau after the time of the lava flows.[1]

If we accept this view, the accumulation of the manganese soils and their origin can be easily explained. The manganese originated from the normal lavas which became dissolved during weathering and disintegration, just as it does at the present time. In solution, probably as carbonate, it was washed down from the mountains, and upon subsequent oxidation was precipitated in the form of concretions, and deposited along with the highly ferruginous sediment which the descending waters must have borne. If originating and transported in this way, the deposition of manganese would naturally be greatest in the low places. In addition the specific gravity of the manganese concretions is less than that of unaltered lava or the ferruginous soil which accompanies it, which would also tend to favor their deposition in the lower altitudes. And probably a final factor in the accumulation of the manganese in the soil is to be found in the solubility of the manganese subsequent to deposition. Further on it will be shown that the manganese is somewhat soluble in water, greatly so in weak organic acids. The heavy rains that frequent the plateau at times naturally leach soluble substances toward the lower levels, where, on account of the greater depths of the detritus, surface drainage is much less than at higher levels. Substances thus dissolved would tend to accumulate in the lowest places, and would naturally become concentrated near the surface through the force of capillary rise of moisture during the long dry seasons, when the upward flow of capillary moisture must be very great.

[1] This idea is in accord with the Tertiary theory of artesian water supply in the islands. See Hitchcock, Hawaiian Forester and Agr., 8 (1911), p. 27.

COMPOSITION AND PROPERTIES OF THE SOIL.

The manganiferous areas are characterized by properties not possessed by the soils surrounding them; they are dark brown or black in color, finely pulverized, and easily tilled; they do not compact by heavy rains, and are naturally well drained. The normal red soils are characterized by extreme heaviness, and have a pronounced tendency to become puddled. Tillage therefore is difficult and the drainage poor.

The accompanying analyses show the composition of these soils:

Composition of manganiferous and normal soils of Oahu.

Constituents.	Manganiferous soils.									
	Soil. No. 9.	Subsoil. No. 10.	Soil. No. 11.	Subsoil. No. 12.	Soil. No. 15.	Subsoil. No. 16.	Soil. No. 27.	Subsoil. No. 28.	Soil. No. 51.	Subsoil. No. 52.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Insoluble matter	33.46	36.06	39.02	42.60	33.73	34.53	42.08	42.78	38.78	39.74
Potash (K_2O)	.83	.74	.78	.81	.99	1.07	.65	.64	.83	.76
Soda (Na_2O)	.40	.42	.36	.44	.21	.38	.32	.37	.34	.47
Lime (CaO)	1.39	.86	.64	.60	.49	.37	.19	.21	.24	.26
Magnesia (MgO)	.55	.43	.41	.39	.52	.41	.35	.28	.64	.49
Manganese oxid (Mn_3O_4)	9.74	8.76	4.80	3.50	4.01	2.43	4.14	3.59	4.32	4.24
Ferric oxid (Fe_2O_3)	19.65	21.51	18.24	20.52	26.03	26.85	22.05	21.36	20.40	25.38
Alumina (Al_2O_3)	15.50	15.74	15.40	16.89	15.82	18.98	16.01	19.51	19.35	16.14
Phosphorus pentoxid (P_2O_5)	.21	.16	.36	.13	.35	.21	.13	.11	.11	.14
Sulphur trioxid (SO_3)	.16	.09	.23	.05	.17	.05	.37	.30	.29	.28
Titanic dioxid (TiO_2)	.73	1.09	.40	.58	.85	1.58	[1]	[1]	[1]	[1]
Loss on ignition	17.73	14.45	19.71	13.72	16.68	12.83	14.02	11.31	15.29	12.45
Total	100.35	100.31	100.35	100.23	99.86	99.69	100.31	100.42	100.59	100.35
Nitrogen (N)	.39	.23	.45	.19	.35	.20	.27	......	.24	.13

Constituents.	Normal soils.								
	Soil. No. 7.	Subsoil. No. 8.	Soil. No. 13.	Subsoil. No. 14.	Soil. No. 31.	Subsoil. No. 32.	Soil. No. 49.	Subsoil. No. 50.	Soil. No. 19.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Insoluble matter	40.89	39.25	46.52	46.37	41.73	37.16	42.36	39.82	44.00
Potash (K_2O)	.51	.60	.50	.57	.53	.57	.65	.48	.59
Soda (Na_2O)	.21	.32	.31	.13	.20	.37	.46	.20	.29
Lime (CaO)	.51	.66	.32	.31	.22	.15	.23	.12	.24
Magnesia (MgO)	.37	.38	.40	.42	.36	.30	.47	.44	.42
Manganese oxid (Mn_3O_4)	.22	.06	.33	.35	.22	.39	1.17	.36	.16
Ferric oxid (Fe_2O_3)	35.72	33.28	24.37	24.49	23.29	24.13	20.36	25.87	27.94
Alumina (Al_2O_3)	3.58	8.66	9.15	12.02	16.02	20.87	20.37	19.42	11.91
Phosphorus pentoxid (P_2O_5)	.07	.08	.09	.13	.08	.12	.10	.10	.04
Sulphur trioxid (SO_3)	.09	.07	.11	.12	.46	.33	.23	.42	.11
Titanic dioxid (TiO_2)	3.83	2.74	2.20	2.05	[1]	[1]	[1]	[1]	.28
Loss on ignition	14.22	13.99	15.98	13.17	17.22	16.38	13.22	13.33	13.95
Total	100.22	100.09	100.28	100.13	100.33	100.77	99.62	100.56	99.93
Nitrogen (N)	.34	.25	.38	.25	.29	.20	.27	.14	.29

[1] Titanium was not separated from alumina.

It is worthy of note that the manganiferous soils contain relatively more so-called plant food, and this, as will be shown further on, is in a more soluble state. The mechanical analyses also show the difference that necessarily exists in physical properties. The percentages of clay are considerably higher in the red soil, while there is correspondingly more silt and fine sand in the manganiferous soils. The organic constituents are low in both alike, and the difference in color must be looked for in connection with the manganese rather than the organic matter. It should be noted that the black color of the manganese soil is not destroyed except by prolonged heating at a high temperature, when it becomes changed into a reddish brown by the driving off of oxygen from the manganese dioxid, thus converting it into mangano-manganic oxid. Upon treating the manganiferous soil with hydrochloric acid copious quantities of chlorin are evolved.

SOLUBILITY.

In investigating the functions of manganese in plant growth it is essential to know something of the form and solubility of the various substances in the soil. The mineral plant nourishment comes from the soil moisture, and the concentration and composition of this solution are known to exercise a direct influence on the growth of vegetation. It is, however, by no means easy to reproduce in analytical operations all the conditions that occur naturally in the fields. The soil moisture is a variable complex, which is constantly being further affected by the activities of bacteria in the soil and by the products of root growth and plant decay. Growing rootlets are known to have solvent powers that are not possessed by pure water, and in addition laboratory experiments at best are only approximations of natural processes and should therefore not be looked upon in any other light. Every step leading to a knowledge of the relative solubility of the substances in the soil, however, makes possible a better understanding of the process of absorption and assimilation, and therefore lie at the foundation of functional studies; for, as stated above, insoluble substances must be looked upon as chemically inert so far as vegetable growth is concerned.

With a view of throwing some light on this question, representative samples of soil were extracted with various solvents for a definite period at the ordinary temperature of the laboratory. The solvents employed were water, 1 per cent solutions of citric, oxalic, and acetic acids. In every instance 100 grams of air-dried soil were shaken at intervals for three days with 1,000 cubic centimeters of the solvent, then filtered and 500 cubic centimeters of the filtrate evaporated to dryness, incinerated, and the residue analyzed. The table following shows the results.

Solubility of manganiferous and normal soils.

MANGANIFEROUS SOILS.

Number of soil and solvent used.	Silica (SiO_2).	Alumina (Al_2O_3).	Ferric oxid (Fe_2O_3)	Manganese oxid (Mn_3O_4).	Lime (CaO).	Magnesia (MgO).	Potash (K_2O).	Phosphoric acid (P_2O_5).
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Laboratory No. 128:								
Water soluble	0.00	0.0028	0.00	0.0018	0.0040	0.0012	0.0057	0.00
Citric acid soluble	.036	.440	.086	1.521	.209	.041	.035	Trace.
Oxalic acid soluble	.035	.498	.035	.952	Trace.	.032	(1)	Trace.
Acetic acid soluble	.025	.014	Trace.	.025	.351	.022	(1)	Trace.
Laboratory No. 129:								
Water soluble	.00	.003	.00	.0016	.0054	.0019	.0084	.00
Citric acid soluble	.036	.475	.113	1.692	.120	.046	.028	Trace.
Oxalic acid soluble	.045	.194	.039	1.248	Trace.	.003	(1)	Trace.
Acetic acid soluble	.023	.029	Trace.	.036	.167	.022	(1)	Trace.
Laboratory No. 125:								
Water soluble	.00	.002	.00	.0014	.004	.002	.007	.00
Citric acid soluble	.048	.527	.109	1.634	.138	.035	.050	Trace.
Oxalic acid soluble	.065	.373	.065	1.507	Trace.	.011	(1)	Trace.
Acetic acid soluble	.028	.021	Trace.	.026	.265	.024	(1)	Trace.
Laboratory No. 124:								
Water soluble	.00	.002	.00	.002	.003	.002	.008	.00
Citric acid soluble	.051	.626	.141	1.493	.142	.031	.034	Trace.
Oxalic acid soluble	.065	.370	.069	1.800	Trace.	.029	(1)	Trace.
Acetic acid soluble	.034	(1)	(1)	.029	.193	.019	(1)	Trace.

NORMAL SOILS.

Number of soil and solvent used.	Silica (SiO_2).	Alumina (Al_2O_3).	Ferric oxid (Fe_2O_3)	Manganese oxid (Mn_3O_4).	Lime (CaO).	Magnesia (MgO).	Potash (K_2O).	Phosphoric acid (P_2O_5).
Laboratory No. 127:								
Water soluble	.00	.001	.00	.00	.005	.001	.005	.00
Citric acid soluble	.084	.288	.076	.014	.080	.003	.029	Trace.
Laboratory No. 126:								
Water soluble	.00	.001	.00	.00	.008	.002	.009	.00
Citric acid soluble	.039	.275	.134	.009	.080	.001	.024	Trace.
Laboratory No. 123:								
Water soluble	.00	.001	.00	.00	.004	.001	.006	.00
Citric acid soluble	.107	.347	.045	.165	.081	.002	.036	Trace.
Laboratory No. 7:								
Water soluble	.00	.001	.00	.00	.006	.001	.012	.00
Citric acid soluble	.045	.308	.099	.009	.040	.001	.030	Trace.

[1] Not determined.

The principal difference to be observed in the relative solubility of the manganese soil, as compared with normal soils, is in regard to the manganese, which is uniformly found to be more soluble than other constituents, especially in di- and tri-basic organic acids, such as oxalic and citric acids, which are known to have a solvent effect on manganese dioxid, with the formation of the corresponding proto-salts. Acids of the monobasic series, however, such as acetic, have much less solvent effects on MnO_2, being more difficult of oxidation, and consequently dissolved appreciably less manganese, although the amounts taken up are noteworthy.

The solubility of the manganese in water is of special interest, and the data show that if the absorbing surfaces of growing plants have no other nutrient media than that afforded by water in contact with this soil manganese would be available to them in dominant quantities. In addition to its bearing on the availability of the manganese, the solubility table also affords further evidences that point to the importance of the solubility factor in explaining the occurrence of the manganiferous areas.

PHYSICAL PROPERTIES.

From the standpoint of the physical composition and properties the manganiferous soil is superior to the general soils of the plateau. It contains less clay and more silt, consequently is tilled with less difficulty and maintained in a good pulverulent condition with far more ease. The heavy rains that frequent the section at times produce a baking and puddling of the red soils, which condition is almost entirely absent in the manganiferous soils, so that the texture of these soils is all that the agriculturist desires. Normal root development, so far as the texture is concerned, would therefore be expected to be superior in the manganiferous soil. The following table shows the physical composition of the two types:

Physical analyses of soils.

Kind of soil.	Manganiferous soils.		Normal soils.	
	Serial No. 9.	Serial No. 15.	Serial No. 7.	Serial No. 19.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Gravel	0.00	0.00	0.00	0.00
Fine gravel	.87	2.54	.00	.00
Coarse sand	8.20	6.28	.77	.60
Fine sand	22.44	21.17	3.64	2.31
Silt	13.64	14.57	8.85	6.79
Fine silt	23.13	21.90	34.54	38.42
Clay	13.61	15.50	36.28	37.58
Organic matter and combined water	16.77	16.66	13.14	13.35

From an examination of these data it is apparent that the circulation of air is freer in the manganese soil.

NITRIFICATION AND AMMONIFICATION.

With the view of determining the relative rates of nitrogen transformation taking place in the two classes of soil, samples were collected in sterilized containers, carefully protected from the direct influence of light, and used in nitrification and ammonification experiments. These experiments were carried out in large beakers, using 100 grams of soil with the addition of ammonium sulphate, in one series, and solutions of peptone in another, in quantities containing 100 milligrams of nitrogen per beaker. The soil was brought to a two-thirds saturation with sterilized water, and allowed to stand in the dark for a period of four weeks. Additional water was added at the end of each week in sufficient quantities to replace that lost by evaporation. At the end of this period nitrogen as nitrates and ammonia was determined in each sample. The results are recorded in the table following.

Nitrification and ammonification in soils.

Class of soil.	Milligrams of nitrogen in 100 grams of soil.				
	As nitrates.			As ammonia.	
	Original soil.	With the addition of ammonium sulphate.	With the addition of peptone.	Original soil.	With the addition of peptone.
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
Normal soil, No. 127	0.66	1.68	1.44	2.80	90.22
Normal soil, No. 126	2.00	.50	2.08	2.00	87.70
Normal soil, No. 7	.72	.50	.80	2.20	87.98
Normal soil, No. C	1.00	1.24	1.00	2.80	84.06
Average, normal soils	1.09	.98	1.33	2.45	87.49
Manganiferous soil, No. 9	.40	5.00	2.00	5.60	86.30
Manganiferous soil, No. 15	.43	1.68	.80	4.20	83.44
Manganiferous soil, No. 128	.28	2.00	2.20	3.50	76.76
Manganiferous soil, No. 129	.47	1.25	1.80	3.10	84.62
Average, manganiferous soils	.40	2.48	1.70	4.10	82.78

It will be seen that nitrification took place more rapidly in the manganese soil, while ammonification was about equal in the two classes of soil. These results are in harmony with the physical composition of the soil. Aeration and consequent oxidation would be expected to take place more rapidly in the manganese soil, and the fact that nitrification is more active in the manganese soil may be taken as evidence of the noninterference in the growth of nitrifying and ammonifying bacteria by the manganese.

DISCUSSION AND CONCLUSIONS.

The manganiferous soils of Oahu are located on the upland plateau between the Waianae and Koolau Mountain ranges, at an elevation of from 650 feet to 900 feet. Their occurrence in local areas as surface accumulations in the alluvial sheet and never in the sedimentary strata below it is such as to indicate that the concentration of manganese has come about through the action of solution and leaching, followed by subsequent oxidation and deposition.

The normal lava, which is the original material from which all the soils of the islands are derived, contains manganese in greater quantities than does the decomposition residue arising from it. The drainage water from the mountains at the present time contains a small amount of manganese in solution, from which it becomes slowly deposited on the surfaces of objects in the streams. Manganese, therefore, becomes soluble in the normal weathering of the basaltic lavas of the islands. The occurrence of the manganiferous soil in the lower altitudes, etc., together with the fact that the manganese of the normal lava becomes soluble during weathering, indicates that the transfer and ultimate deposition of the manganese has been affected through the agency of water.

The occurrence of manganese concretions, the largest in size of which being some depth below the surface, and deposited in the lower levels in the alluvial sheet, but not in the sedimentary or residual soil, together with the sharp line of stratification separating the alluvial from the residual strata, indicate that there has been a submergence, during which time the deposition of the alluvial soil and the accumulation of manganese concretions took place. Subsequent leaching further accentuated the accumulation of the manganese in the lower places, especially in basins or at the bases of long slopes.

The solubility in weak organic acids shows that the availability of the manganese is relatively high and that manganese probably exists in the soil moisture and in solution around the absorbing surfaces of roots in greater quantities than any other element. Therefore it exists in just the condition to exert its full physiological effects on plants. The physical properties of the manganiferous soils are more nearly ideal than are those of red soils. They contain less clay, and more of the coarser particles. Consequently the circulation of air is greater in the manganese soil.

Nitrification and ammonification appear not to be influenced by the presence of manganese in the soil. That the former has been found to take place more advantageously in the manganese soil can probably be accounted for by the fact that the circulation of air is less obstructed in this type.

Acknowledgments are due and thanks are hereby extended to Dr. E. W. Hilgard for helpful suggestions in this work; and to Dr. E. V. Wilcox, who showed the greatest interest throughout this investigation, offered many suggestions, and in many ways rendered valuable assistance.

ADDITIONAL COPIES of this publication may be procured from the SUPERINTENDENT OF DOCUMENTS, Government Printing Office, Washington, D. C., at 10 cents per copy.