The results obtained were as follows:

| | Total bromine absorption. | Bromine addition. | Bromine substitution. |
|---|---|---|---|
| Dry, ordinary condition | 110.2 | 104.8 | 2.7 |
| 10 cc. water, ordinary temperature | 108.6 | 104.0 | 2.3 |
| 10 cc. water, cooled | 109.8 | 104.0 | 2.9 |
| 10 cc. water, heated | 113.2 | 103.0 | 5.0 |

It is noteworthy that the results appear to be but slightly affected by the variations introduced and particularly that the presence of water seems to be without serious effect.

## FIXATION OF PHOSPHORIC ACID IN THE SOIL.

By J. T. Crawley.

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It has been known for a long time that when soluble phosphates are applied to the soil, they become fixed by the bases, lime, iron, etc., and are not leached from the soil to any very considerable extent by rain or irrigation waters. By this process water-soluble phosphoric acid is "reverted" or changed to a combination not soluble in water. This is akin to the fixation of potash and ammonia, which are changed into insoluble combinations in the soil.

This is a wise provision of nature and prevents salts and bases in the soil which have been rendered soluble by weathering and other agencies from being washed out and lost from the soil; and it enables the agriculturalist to apply certain forms of soluble fertilizers to growing crops without fear of losing them in the drainage waters. But what becomes of the water-soluble phosphoric acid applied as a fertilizer; is it fixed near the surface, or is it well distributed throughout the soil where the roots of plants can get it?

The following investigation was undertaken for the purpose of determining to what extent water-soluble phosphoric acid is distributed through the soil before it becomes fixed. In certain sections of these islands the cane grows by irrigation; in other sections the rainfall is ample. Where irrigation is practiced the soluble fertilizer is scattered along the cane row, in some cases covered, in other cases not, and followed up within a day or two by irrigation. Three or four inches of water would represent an average irrigation. Usually the water disappears in the soil within twenty or thirty minutes of application. Where rainfall is depended upon, fertilizers are covered up.

## APPARATUS AND METHODS.

The most conclusive and determinate method would be to apply phosphoric acid in water solution to the soil, and then, by making analyses of the soil, find where it has been fixed. This, however, is not practical since our chemical methods are not sufficiently delicate to detect slight differences in the amount of this acid, and were a soil analyzed before and after the application of an ordinary dose of phosphoric acid, this amount would not be detected. The lysimeter method is the next best; a given weight of phosphoric acid is applied to the soil, followed by an excess of water, the drainage water caught and analyzed. The difference between the amount of acid applied and that found in the drainage is the amount abstracted and held by the soil. By varying the depth of soil in this experiment we find the depth at which the phosphoric acid is held. Boxes, 9 in. cube, were made, several holes bored in the bottom for the purpose of allowing the drainage water to escape, and varying depths of soil placed in them. Ten grams of double superphosphate were applied in each case, which is as large an amount as is applied in the cane rows to a space 9 inches by 9 inches. In each case 4800 cc. of water were added, this amount being probably an average irrigation. Notes were made of the time necessary for the water to percolate through the soil, and the total time of draining.

## RESULTS.

I. Experiments with dark-colored soil from Makiki. This soil contains more phosphoric acid soluble in weak vegetable acid solutions than any other Hawaiian soil thus far examined.

(1) Six inches of soil; water began percolating through the bottom of the soil at end of six minutes, and 1790 cc. of water were recovered within one-half hour, when drainage was practically completed. The 1790 cc. of water contained 0.023 gram $P_2O_5$ or 0.57 per cent. of total applied.

(2) Six inches of soil: the phosphate was covered up in the moist soil and allowed to stand over night. Water began drain-

ing within two minutes, and 3300 cc. were drained in forty minutes, containing but a trace of phosphoric acid.

II. Typical red soil from the Honolulu plantation.

(1) Six inches of soil; water began draining in two minutes, and finished draining in forty minutes. Recovered 2072 cc. water containing 0.1113 gram $P_2O_5$ or 2.78 per cent. of total applied.

(2) Six inches of soil containing 20.72 per cent. moisture; phosphate covered up and allowed to stand over night; began draining in three minutes; finished draining in fifty minutes. 2320 cc. of water were recovered, containing 0.0134 gram $P_2O_5$ or 0.34 per cent. of total applied.

(3) Three inches of soil; began draining in one minute; finished draining in thirty minutes. Recovered 3130 cc. of water containing 0.35 gram $P_2O_5$ or 8.75 per cent. of total applied.

(4) Three inches moist soil; phosphate covered up and allowed to stand over night. 2886 cc. of water were recovered, containing 0.0408 gram $P_2O_5$ or 1.02 per cent. of total applied. The soil and phosphate were allowed to stand two days. Two liters of water were poured over it, of which 1700 cc., containing 0.0048 gram $P_2O_5$ or 12 per cent. of total applied. were recovered. After standing two days this was subjected to a further leaching. the drainage containing but a trace of phosphoric acid.

(5) One inch of soil; began draining in ten seconds; finished draining in nine minutes. Recovered 4260 cc. water containing 1.866 grams $P_2O_5$ or 46.65 per cent. of total applied.

(6) One inch of soil; phosphate covered up and allowed to stand four hours before irrigation. Drainage water contained 0.274 gram of $P_2O_5$ or 6.85 per cent. of total applied.

(7) One inch of soil; phosphate covered up and allowed to stand over night. Drainage contained 0.2928 gram $P_2O_5$ or 7.32 per cent. of total. Same after standing two days and washing with two liters of water, yield 0.033 gram $P_2O_5$ or 0.82 per cent of total.

Putting these results in tabulated form we have:

TABLE I.—SHOWING THE AMOUNT OF PHOSPHORIC ACID HELD BY THE SOIL.

| Depth of soil. Inches. | Black soil, when irrigated. | $P_2O_5$ retained. Per cent. | Red soil, when irrigated. | $P_2O_5$ retained. Per cent. |
|---|---|---|---|---|
| 6 | Immediately | 99.43 | | .... |
| 6 | After fifteen hours | 100.00 | | .... |
| 6 | | .... | Immediately | 97.22 |
| 6 | | .... | After fifteen hours | 99.66 |
| 3 | | .... | Immediately | 91.25 |
| 3 | | .... | After fifteen hours | 98.98 |
| 3 | | .... | Same after two days | 99.88 |
| 1 | | .... | Immediately | 53.35 |
| 1 | | .... | After four hours | 92.68 |
| 1 | | .... | After fifteen hours | 99.18 |
| | | | Same after two days | .... |

From this we see that when the application of the fertilizer is followed immediately by irrigation, (1) more than one-half the phosphoric acid remains in the first inch of soil, more than nine-tenths in three inches, and practically the whole within six inches of the surface; (2) when an interval of fifteen hours intervenes between the application and the irrigation, more than nine-tenths of the phosphoric acid is retained by the first inch of soil and practically the whole by the first three inches. These conclusions are rather startling, inasmuch as it has been heretofore believed that water-soluble phosphoric acid, when applied to the soil, becomes pretty well distributed throughout the first eighteen inches or two feet of the soil when it is easily accessible to the roots of the plants. This bears on the question of the relative value of water-soluble and so-called citrate-soluble or "available" phosphoric acid. At the various experiment stations in the United States the same or very nearly the same valuation is put upon the two forms. Where there is a difference it is rarely more than 1 cent. per pound in favor of the water-soluble. Certainly on Hawaiian soils where the phosphoric acid becomes reverted at the surface, or very near the surface, the two forms have very nearly the same value, for even under the most favorable circumstances the water-soluble phosphates are disseminated throughout the soil but sparingly. On the other hand, in cases where fertilizers are applied and covered up a few hours before irrigation practically all of the phosphoric acid becomes reverted and remains near the surface. Also on plantations depending on rainfall where the fertilizers are applied and covered up, water-soluble and reverted phosphoric acid have practically the same value, as the water-soluble becomes reverted and subsequent rains cannot wash it down to the roots of the plants, nor disseminate it throughout the soil. This is a possible explanation of a fact which I have set forth in former papers; namely, that phosphates have not shown as good results on Hawaiian soils as the other fertilizer ingredients —nitrogen and potash. It takes considerable cultivation to disseminate the phosphates throughout the soil, and although they may be deficient, yet an application is not followed by the immediate results that the planter expects.

Seeing that the water-soluble phosphoric acid is taken up so readily, a further experiment was made to determine the *total capacity* of the soil to fix phosphoric acid. 800 grams of red soil and 50 grams of double superphosphate containing 20.58 grams water-soluble phosphoric acid were thoroughly mixed together. This mixture was kept moist to promote the chemical action, and samples were withdrawn from time to time to estimate the water-soluble acid.

March 26th, 800 grams soil and 50 grams double superphosphate mixed; March 27th, 41.6 per cent. of $P_2O_5$ had become fixed; March 29th, 57.7 per cent. of $P_2O_5$ had become fixed; April 3rd, 73.0 per cent. of $P_2O_5$ had become fixed; April 17th, 85.65 per cent. of $P_2O_5$ had become fixed.

Or, taking 3,500,000 pounds as the weight of one acre of soil to the depth of 1 foot, we find that this soil absorbed:

After one day 35,235 pounds $P_2O_5$ per acre to depth of 1 foot; after three days 48,872 pounds $P_2O_5$ per acre to depth of 1 foot; after eight days 61,431 pounds $P_2O_5$ per acre to depth of 1 foot; after twenty-two days 72,545 pounds $P_2O_5$ per acre to depth of 1 foot.

This latter figure would represent all the phosphoric acid in 181 tons of acid phosphate.

These astonishing figures lead to a consideration of the nature of the soils experimented with, and the reason for the rapid and great fixation of phosphoric acid by Hawaiian soils. On p. 99, *et seq.*, of Maxwell's "Lavas and Soils of the Hawaiian Islands" will be found a comparison of Hawaiian and American soils, in which it is shown that Hawaiian soils are very much more basic than American soils.

TABLE II.

| Soils. | Basic constituents. Per cent. | Acid constituents. Per cent. |
|---|---|---|
| Hawaiian | 63.717 | 36.458 |
| American | 18.980 | 81.014 |

Whereas the American soils from which these figures were drawn contain but 13.250 per cent. iron and aluminum oxides, the Hawaiian soils contain 59.24 per cent.

All Hawaiian soils are very basic, and these bases are probably in a condition to seize at once the phosphoric acid and hold it. The American soils being much older than Hawaiian soils the soluble bases have been washed out, the soils are less basic in character, and will probably hold very much less phosphoric acid than the Hawaiian soils. Following is an average of a number of analyses of dark red soils, and the soil from the Honolulu plantation would not differ very materially from these figures.

TABLE III.—DARK RED SOILS.

| | Per cent. |
|---|---|
| Insoluble matter | 37.20 |
| Moisture | 6.16 |
| Combustible matter | 11.33 |
| $TiO_2$ | 2.59 |
| $P_2O_5$ | 0.19 |
| $SO_3$ | 0.31 |
| $CO_2$ | 0.18 |
| CaO | 0.34 |
| MgO | 0.44 |
| $Fe_2O_3$ | 22.94 |
| $Al_2O_3$ | 16.84 |
| $Mn_3O_4$ | 0.42 |
| $K_2O$ | 0.39 |
| $Na_2O$ | 0.75 |
| | 100.08 |

With soils of this general composition it would be strange if their absorptive power of phosphoric acid were not great.

HONOLULU, H. I.