ON THE DISTRIBUTION OF PHOSPHORUS IN A VERTICAL SECTION OF BLUEGRASS SOIL¹

By

ALFRED M. PETER, *Chief, Department of Chemistry, Kentucky Agricultural Experiment Station.*

The most important chemical action concerned in the disintegration of limestone rock to form soil is the combination of the free carbonic acid contained in natural waters with the calcium carbonate and magnesium carbonate of the limestone to form calcium and magnesium bicarbonate, substances soluble in water [$\text{CaCO}_3 + \text{H}_2\text{CO}_3 = \text{CaH}_2(\text{CO}_3)_2$]. Thus the calcium and magnesium carbonates, which compose the greater part of most limestones, may be dissolved and carried away by percolating water, leaving behind the less easily soluble constituents of the limestone, such as sand, clay and other silicates, ferric oxid, etc. It is this residue of nearly insoluble material which finally becomes converted into soil. In regions of abundant rainfall, such as our Bluegrass country, this disintegration of the limestone and addition of the residuum to the soil is going on almost continuously at the surface of the rock beneath the soil. The rain water, as it falls upon the ground, already contains a little dissolved carbon dioxide derived from the air. In sinking through the soil it acquires more from the oxidation of organic matter in the soil. While passing through the soil, the water takes up more or less soluble material until its downward passage is arrested by the underlying limestone. Here the water may be supposed to collect for a time and be in contact with the limestone long enough to become fully saturated with calcium carbonate before it finds its way to the surface of the ground, at some lower point, in the form of a spring. Such waters carry in solution, besides calcium and magnesium bicarbonate, appreciable quantities of sodium, potassium, iron, silica, sulfates, chlorids, nitrates and phosphates, showing that even the less soluble or soil-making substances are attacked to some extent. The amount of phosphate carried away by the water of springs has recently been studied by Mr. J. S. McHargue, of the Kentucky Agricultural Experiment Station, and reported upon in a paper read at the 1915 meeting of this Academy. Mr. McHargue's analyses show that this amount is relatively small, as compared with the amount of calcium and magnesium

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carbonate present in these waters. The average from the analyses of the water of six different springs in Fayette and Woodford Counties shows one part of tricalcium phosphate to about 100 parts of calcium and magnesium carbonates, taken together, the extremes being 1:71, and 1:133. This phosphate may have been taken up either from the soil through which the water has percolated or from the limestone with which it has come in contact, or both. The relatively small solubility of tricalcium phosphate leads to the inference that, when a highly phosphatic limestone is acted upon by natural waters, the greater part of the phosphate contained in the limestone will be left in the resulting soil, after practically all the calcium carbonate has been dissolved away. Thus, if there is in a given limestone more than one part of tricalcium phosphate to 100 parts of calcium and magnesium carbonates, the excess of phosphate would remain undissolved and be added to the soil. The distribution of phosphorus in a column of soil, however, must be affected by the phosphate continuing to go into solution after all carbonate has been removed, thus reducing the amount in the upper part of the column. Again, in a very phosphatic soil, the fact that the percolating water has an opportunity to become saturated with phosphate before reaching the bed rock would greatly diminish or wholly nullify its solvent action upon the phosphate of the underlying limestone, thus tending all the more to preserve in the newly made soil at the bottom of the column the differences in phosphate content existing in the original limestone.

There are numerous analyses which show that the several layers of the limestone underlying the soil in the vicinity of Lexington differ greatly with regard to their phosphorus content. Published analyses give percentages of phosphorus ranging from 0.3 or less to about 14 per cent, the latter being in a very thin layer of limestone. The ratio of tricalcium phosphate to calcium and magnesium carbonate ranges from 1:60 to 1:1, or, from $1\frac{2}{3}$ parts to about 100 parts of phosphate to every 100 parts of carbonate. The natural inference from these facts and the considerations already stated is that when such limestones, lying in horizontal strata, are converted into soil by natural processes, there would result a soil having horizontal bands of very different phosphorus content, corresponding in a rough way to the several layers of the original limestone, and that these differences would be best preserved in the lower part of the column where the soil is comparatively new.

A series of samples, taken vertically through such a soil, should contain very different proportions of phosphorus. To test this hypothesis, several borings were made on the Experiment Station farm at Lexington, some years ago, by the writer, assisted by Mr. Robert Hart. The soil from each six inches was stored separately and analyzed for phosphorus by Mr. O. M. Shedd, of the Experiment Station. A graphical representation of results of two of these borings is presented herewith. The dif-

ferences shown are just such as would be expected in a soil derived from the highly phosphatic layers of the Lexington limestone and they appear to even a more marked degree than was anticipated. It may be added that small pieces of nearly pure, soft phosphate could be distinguished in several of the samples.

It has been argued that some of the phosphate taken by the soil water from the upper part of the soil column may be deposited again when the lower part of the column is reached, where calcium carbonate is still present in effective quantity. The fact that tricalcium phosphate is less soluble in carbonated water in the presence of calcium carbonate than it is if calcium carbonate is absent, would favor this view. Such a process would tend to produce a maximum of phosphate at a short distance above the bed rock, as was found in the first boring; it would hardly account for the existence of two maxima, as found in the second boring. Besides, the large percentages and the magnitude of the differences found suggest strongly that the distribution of the phosphate in the limestone before it became soil, is the controlling factor, even if leaching and redeposition of phosphate has played some part. The fact that plates of phosphate similar to those occurring in the limestone may be found in the more phosphatic parts of the soil column supports this view.

It should be stated in this connection, also, that the amount of calcium carbonate in this soil is small. Analyses by Dr. Blumenthal of this Station on the soil from the first boring show the maximum of 0.135 per cent of calcium carbonate in the third six inches above the rock and the minimum 0.020 per cent in the fourth sixth inches from the top.

In comparing the two diagrams, it is important to bear in mind that the first boring was made near the top of a gentle slope, whereas, the second was near the bottom of such a slope, a slight rise intervening between the two. No doubt some of the older and well leached soil has been removed from the top of the first column, a condition which would account for the high percentage of phosphorus in the first foot, and that soil of a similar character has been added to the top of the second column, thus keeping down the phosphorus content in the upper four feet.

Both borings were started on nearly level ground at approximately the same elevation above sea level, namely, between 990 and 995 feet, as nearly as could be judged from the 5-foot contour lines on the map of the farm.

These considerations suggest that the maximum phosphate in the first diagram and the first maximum in the second should be referred to the same highly phosphatic beds in the original limestone.

It may not be without interest in this connection to speculate a little upon the character and thickness of a section of limestone capable of producing a soil section similar to that described, though it would be impossible to arrive at a definite or exact conclusion, from the data available. Of

PER CENT OF PHOSPHORUS Underlying limestone Underlying limestone

Fig. 1.—Phosphorus in soil sections, Experiment Station Farm, Lexington, Ky.
 Top, Rose St. field, top of gentle slope.
 Bottom, forage plots, bottom of gentle slope.
 Elevation of the top of each, between 990 and 995 ft. above sea level. The two points are about 250 yards apart.

Fig. 2.—Hypothetical section of limestone with the corresponding soil.

great assistance in such a speculation would be a series of separate analyses of each consecutive layer in a vertical section covering a considerable thickness of the more phosphatic part of the Lexington limestone. Unfortunately, no such series of analyses has been made. In the chemical reports of the Kentucky Geological Survey, Dr. Robert Peter published phosphate determinations upon samples of limestone taken from several different layers exposed in the face of the McMeekin quarry on the Newtown road 4 miles north of Lexington, where he first discovered the phosphate, but the thickness of only one layer was reported. This was the principal phosphatic layer, about a foot thick, appearing at the bottom of the quarry face. Analyses of a sample from this layer gave 45.9 per cent of tricalcium phosphate, 49.2 per cent of calcium carbonate, including a little magnesium carbonate, and 4.9 per cent of other materials. The analyses of eleven other samples selected from different parts of this quarry face gave amounts of tricalcium phosphate ranging from 11.0 per cent to 47.9 per cent, the last being from a thin layer. It is evident that, in taking these samples, the more phosphatic layers were selected. Interspersed with these there must have been layers with a much smaller phosphate content. As the amount of carbonate in the other samples was not determined, we will try to estimate the result of the action of carbonated water upon the 12-inch layer of phosphatic limestone first mentioned. During the solution and removal of 49.2 parts of calcium carbonate by the process heretofore described, about 0.5 part of tricalcium phosphate will have been dissolved. Deducting this from the 45.9 parts present leaves 45.4 parts of tricalcium phosphate, with which will remain the 4.9 parts of other materials belonging to the limestone, making 50.3 parts of residuum, containing 90 per cent of tricalcium phosphate. This would be a high-grade phosphate, somewhat better than the richest plates of phosphate which have been picked out of the highly phosphatic soil corresponding to the geological horizon in which this quarry is situated.

We have here supposed a case where the solvent action on the phosphate was arrested as soon as all calcium carbonate had been removed. Under natural conditions, leaching would continue indefinitely, removing both phosphate and other materials and probably lowering the relative amount of phosphate in the residue considerably.

To obtain a residue more of the nature of soil, we may suppose a limestone containing less phosphate, more calcium carbonate and more of the other materials. For example, with 6.5 per cent of phosphate, 78.5 of calcium carbonate and 15.5 of other materials, the residue from 100 parts of limestone would consist of $(6.5 - .785)$ 5.715 parts of tricalcium phosphate and 15.5 parts of other materials, or 21.215 parts, containing $\left(\frac{5.715 \times 100}{21.215}\right)$ about 27 per cent of tricalcium phosphate, equivalent to 5.3

per cent of phosphorus, or about the same as was found in the fifth six inches from the bottom of the second soil section.

To estimate how much of such a limestone would be required to produce a foot of soil, it is necessary to take into consideration the relative weights of limestone and soil. A cubic foot of limestone weighs about 163 pounds and a cubic foot of soil, about 92 pounds. The weight of a cubic foot of limestone, multiplied by the weight of undissolved phosphate and other materials from one pound of limestone ($163 \times .21215$) gives the weight of residuum from a cubic foot of the stone (34.58). Dividing the weight of a cubic foot of soil, by this figure ($\frac{92}{34.58}$) gives the number of cubic feet of limestone required to produce a cubic foot of soil (2.7 cu. ft.) The same figures will represent the thickness of limestone, in feet, necessary to produce one foot of soil on equal areas.

Making the calculation, the result is found to be 2.7 cubic feet; or, it would require approximately a foot and a half of this stone to produce the 6-inch layer of soil in the soil section referred to. The second diagram shows a hypothetical section of limestone which would produce layers of soil corresponding to those found in the lowest four feet of the second section. This part was selected for illustration because it is presumably the newest and least affected by leaching subsequent to the removal of the carbonates.

It is not intended to assert here that the actual section of limestone from which this soil came was constituted as here pictured. An infinite variety of arrangements could be assumed to produce the same result. The problem is indeterminate, from the data at hand.

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SUMMARY

The chief object of this paper is to draw attention to the peculiar distribution of the phosphate in these soil sections and to point out that it corresponds strikingly with the distribution of phosphate in the phosphatic limestone beds of this vicinity.