

STUDY OF THE RELATION OF THE ORGANIC CONTENT OF SOIL TO ITS pH^1

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AN INTRODUCTION TO THE PRINCIPLES INVOLVED

The sources of the soil acids and their behavior.—According to Stephenson (1919), most of the mineral acids in soils may trace their origin back to the rocks from which the soil was formed. The feldspars which constitute sixty per cent of the igneous rocks are the greatest of the soil-forming silicates. On weathering, these are broken up, the alkali metals in them are leached away as soluble salts of the organic acids while the less soluble acid-forming portion is left behind in the soil. The aluminosilicates are relatively strong acid formers. By a simple interchange of radicals these silicate acids may displace and set free small quantities of the stronger acids which have formed salts with the heavier metals in the soil. Small amounts of the stronger mineral acids may be formed in the soil by the oxidation of the elements that produce them; as, sulphuric acid from sulphur, nitric acid from nitrogen, and phosphoric acid from phosphorus. Purely organic acids are derived from carbohydrates or proteins. The carbohydrates may produce acids by fermentation, oxidation, or partial decomposition, while the proteins will yield amino acids on hydrolysis.

Stephenson says (1922), that both the chief mineral and organic acids may act as buffers to prevent any great change in the acid status of the soil. The complex silicate acids may react with the stronger acids to give products that very slightly affect the pH of the soil while the amino acids may unite with considerable quantities of either acid or alkaline substances and still retain their original condition.

The sources and influence of organic matter.—The term organic matter is used to designate those constituents of the soil that were once part of a living organism. Most organic matter is of vegetable origin, while a smaller amount is derived from animal sources.

Organic matter does produce some acids (Stephenson, 1919), but they do not greatly affect the pH of the soil except in peat bogs and mucks. Sandy soils are usually more acid when organic matter is

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absent. This paradoxical statement is explained by the fact that the absence of organic matter allows the soluble basic materials to leach away more readily, leaving the less soluble acid-forming substances.

Measuring the degree of acidity and alkalinity.—We understand that the common property of acids is due to the hydrogen ions and that the relative strength of acids is dependent upon the concentration of these ions. The strength of an acid is not due to the total amount of ions that may be formed by a given quantity of the acid but to the concentration of the ions available for action at a given time. In this study we are concerned only with the degree of acidity, since it determines the p_{H} of the soil.

There have been two, variously modified, methods developed for measuring the degree of acidity, or hydrogen ion concentration. The colorimetric method which consists of adding indicators to a colorless water extraction of the substance to be tested and matching the color produced with the color of the same indicator in a buffer solution of known p_{H} . The electrode method is based upon the fact that when the electrodes are immersed in a solution containing hydrogen ions that a potential develops which is proportional to the concentration of the ions. The quinhydrone electrode, which is considered the best for soil work, owes its action to the fact that quinhydrone dissociates to give a potential directly proportional to the hydrogen ion concentration of the solution. The resulting electromotive force is measured by a potentiometer.

Since the potentiometer readings are in millivolts, it is evident that such units would not be a satisfactory method of expressing the ionic concentration; hence, the term p_{H} has been adopted instead. Numerically it is the logarithm of the reciprocal of the actual hydrogen ion concentration.

Determination of the organic matter.—The organic matter in soils is usually determined by: the colorimetric method, the Kjeldahl process for nitrogen, or combustion for carbon. The first determines all the organic matter directly by comparison with a standard of known organic content, while in the other two only one constituent is found, and the total amount is calculated from that. The Kjeldahl process is the same as used for all nitrogen determinations, and considers soil organic matter five per cent nitrogen. The carbon combustion may be carried out by either the dry or wet method. In the former heat is used to produce the combustion, while in the latter some strong oxidizing solution is used instead of heating. The resulting carbon dioxide may be absorbed by an alkaline solution and determined by weighing, or it may be collected as a gas and measured.

Schollenberger (1927) developed a modified wet combustion method for the rapid determination of organic matter in soils in which he neither absorbed nor collected the resulting carbon dioxide. This process is based upon the fact that a given amount of a standard solution of chromic acid will oxidize a definite weight of carbon. He treated weighed samples of dry soil with an excess of chromic acid in concentrated sulphuric acid, heated the mixture to 170° C.

and titrated the excess chromic acid with a standardized solution of ferrous ammonium sulphate, using diphenylamine as an indicator. From the data obtained he calculated the organic matter present, assuming that organic matter is fifty per cent carbon.

Degtjareff (1930) modified Schollenberger's method in that he first added as much of a 0.3% solution of hydrogen peroxide as he did of the chromic acid solution and did not heat the mixture but shook it well, allowed it to stand till the reaction ceases, then titrated the excess chromic acid. Otherwise the process is the same as Schollenberger's. It can be carried out more easily and more rapidly than any method proposed heretofore. That it is sufficiently accurate for soil work is evidenced by the fact that upon repeated experiments on pure organic substances his results never varied more than 0.07% from the results obtained on the same substances by the classic Liebig-Gustavason dry combustion method. He states that the reaction may be expressed quantitatively by chemical equations, but suggests that it is probably better for each worker to determine the carbon factor for his own solution by running tests upon substances of known composition.

COLLECTION OF SAMPLES AND DETERMINATION PROCEDURES

Sources of soils studied.—All the samples of soil used in this study were collected along Tennessee Highway No. 1, including all new divisions under construction during the winter of 1930-1931. This road extends from the banks of the Mississippi River at Memphis, Tennessee, to the suburbs of Bristol, Tennessee-Virginia. This study covers approximately five hundred and fifty miles; it crosses six major geological divisions of the state: Plateau Slope of West Tennessee, Western Highland Rim, Central Basin, Eastern Highland Rim; Cumberland Plateau, and the Great Valley of East Tennessee; and includes portions of twenty-two counties. A total of one hundred and ninety-three samples—one hundred and two of soil and ninety-one of subsoil—were gathered from one hundred and eleven different stations.

Collection of the samples studied.—In collecting samples an attempt was made to get as nearly representative ones as possible of the areas studied. Samples were taken from bottoms and divides all along the way, and between these when changes appeared, but if the land showed few changes, samples were taken very infrequently. In all cases, collections were taken from places that were not affected by temporary or local factors. All subsoil samples were taken from as deep as possible. The samples varied in size, but usually ran from a half-pound to a pound in weight. The specimens were pressed into balls, wrapped in wax paper, labeled, and carried to the laboratory of George Peabody College for Teachers, where all determinations were made.

Determination of the pH.—A quinhydrone electrode coupled with a saturated calomel electrode for reference and a Leeds-Northrup

potentiometer were used. In all of the essentials, the procedure recommended by Clark and Collins (1927) was followed. Twenty-five cubic centimeters of distilled water was poured into a 50 cc. Pyrex beaker and 25 grams of well pulverized soil and about 0.02 gram of quinhydrone added. The mixture was stirred with a stirring motor for twenty seconds and placed under the electrodes so that the electrode tips would be in contact with the soil when it settled out of suspension. It was allowed to stand about thirty seconds and then the potentiometer was read as soon as it came to equilibrium. Three determinations were made on each sample and the average taken, except in a few cases where two readings checked close together but the third deviated widely. Then an average of the two was taken and the third discarded. A check upon the apparatus was made by using a buffer solution of known p_H and no readings were used unless the electrode would come within 0.03 p_H or less of the buffer solution. There were a few samples that would not give stable readings at all with quinhydrone, apparently due to some substance that interfered with its reaction. These were determined by the colorimetric method.

Determination of the organic content.—In determining the organic matter the thoroughly air-dried soil was ground in a mortar and passed through a one-half millimeter sieve. Then samples of 0.15-0.20 grams were weighed out to the fourth decimal place, transferred to a 125 cc. Erlenmeyer flask, and 10 cc. of a 0.3% solution of hydrogen peroxide and an equal volume of concentrated sulphuric acid which contained 18.88 grams of chromic acid per liter, run in. The flask was rotated a few times and then allowed to stand until apparently all action had ceased. The contents of the flask were poured into a beaker, the flask being rinsed two or three times and the washings added to the beaker until the volume of the solution was 250-300 cc. The excess chromic acid was titrated with a standardized solution of ferrous ammonium sulphate, which contained 79.89 grams of the salt per liter, using diphenylamine as an indicator. Two determinations on each sample were made and an average of the two taken. From the data thus derived, the organic matter present was calculated.

In order to be certain about the carbon factor of the oxidizing solution, both blank determinations and repeated checks upon dry chemically pure sucrose were made. The results always agreed with the theoretical carbon value to the fourth decimal place. The carbon factor was found to be 0.0007 grams of carbon per cubic centimeter of the solution and consequently the organic factor is 0.0014 grams per cubic centimeter, since organic matter is fifty per cent carbon.

The authors do not claim that this method is absolutely correct, but they do have reason to believe that it is sufficiently accurate for soil work. The question might arise whether or not the oxidizing solution might not be reduced by something else rather than organic matter. Of such materials, iron would head the list, but we found that when it was tested on what appeared to be almost a pure iron

sand that it was not affected at all. Besides, Schollenberger (1927) says that soils which contain any such reducing substances are rare.

FINDINGS

Variations in p_H and Organic Content

The soil p_H varied from.....	4.08 to 7.59
The subsoil p_H varied from.....	3.68 to 7.05
The soil organic content varied from.....	0.34% to 14.00%
The subsoil organic content varied from.....	0.00% to 3.55%

Some General Means

The p_H of the soil.....	5.98
The p_H of the subsoil.....	5.42
Organic matter in the soil.....	2.82 %
Organic matter in the subsoil.....	1.095%

Some Comparisons of the Major Geological Divisions Studied

Mean p_H of the Soils

Plateau Slope of West Tennessee.....	5.26
Highland Rim	5.54
Central Basin	6.25
Eastern Highland Rim.....	6.12
Cumberland Plateau	5.53
Great Valley of East Tennessee.....	6.63

Mean p_H of the Subsoils

Plateau Slope of West Tennessee.....	5.03
Highland Rim	5.14
Central Basin	5.91
Eastern Highland Rim.....	5.45
Cumberland Plateau	5.05
Great Valley of East Tennessee.....	5.61

Mean Organic Matter in the Soil

Plateau Slope of West Tennessee.....	2.26%
Highland Rim	3.44%
Central Basin	3.97%
Eastern Highland Rim.....	2.65%
Cumberland Plateau	2.82%
Great Valley of East Tennessee.....	2.50%

Mean Organic Matter in the Subsoil

Plateau Slope of West Tennessee.....	0.81%
Highland Rim	0.91%
Central Basin	2.16%
Eastern Highland Rim.....	1.07%
Cumberland Plateau	0.71%
Great Valley of East Tennessee.....	1.11%

Some Comparisons of the Bottoms and Divides

Mean p_H of the Soils

Bottoms	5.98
Divides	6.00

Mean p_H of the Subsoils

Bottoms	5.42
Divides	5.41

Mean Organic Matter in the Soils

Bottoms	3.01%
Divides	2.55%

Mean Organic Matter in the Subsoils

Bottoms	1.39%
Divides	0.92%

Correlations.—The coefficients of correlation between the p_H and organic content of both the soil and subsoil were calculated but were found to be so small that they had no significance.

CONCLUSIONS

From the results obtained it seems that the following conclusions may be drawn:

1. That the correlation between the p_H and organic content of soils and subsoils is insignificant.
2. That both soils and subsoils tend to be acid and that the degree of acidity may vary widely.
3. That the subsoils tend to be more acid than the soils from the same regions.
4. That sandy soils tend to be more acid than soils which have a finer structure.
5. That there is no appreciable difference in the acidity of either soils or subsoils of bottoms and uplands.
6. That soils appear to have a higher organic content than subsoils.
7. That the organic content of both soils and subsoils from bottoms tends to exceed that of samples from the uplands.

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