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ORGANIC COMPOUNDS ASSOCIATED WITH BASE EXCHANGE REACTIONS IN SOILS

By
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ORGANIC COMPOUNDS ASSOCIATED WITH BASE EXCHANGE REACTIONS IN SOILS

By W. T. McGeorge

INTRODUCTION

A distinguishing characteristic of the arid soils of the Southwest is that they contain only very small amounts of organic matter. The organic matter incorporated in the soil during its period of formation, provided such ever existed, has largely disappeared, while the scarcity and nature of recent plant generations have failed to add appreciable amounts. Organic matter, when incorporated in these soils, is especially valuable in improving soil conditions; hence, much time and effort have been spent in studying the chemical and biological factors influencing the decomposition of this fraction of the soil. Its relation to the physical and chemical properties of the soil has attracted considerable attention, as has also the influence upon plant-food availability. With all these, as well as with other widely recognized properties of organic matter, it is not surprising that limited fertility often characterizes arid soils and that they respond markedly to applications of organic materials when brought under irrigation. Hence, any knowledge which may be obtained regarding soil organic matter is of economic interest to the farmers of the Southwest.

The organic matter which enters the soil confines, either naturally or by applying animal manures or by green-manuring, is continuously subjected to chemical and biological reactions which materially alter its composition. It must therefore consist of constituents of plants or animals in all stages of decomposition, of substances in intermediary stages of decomposition, of substances which resist decomposition, and of substances which are synthesized by the biological life in the soil.

While the conditions of aeration govern the speed and nature of the decay, humification, or putrefaction, on the whole the reactions involve an absorption of oxygen and the liberation of carbon dioxide. The more readily decomposible materials, the carbohydrates and proteins, disappear relatively soon after their incorporation in the soil. Other materials or compounds less reactive tend to accumulate and thereby to form a residual complex approximating a more or less constant composition. Thus there is developed a relatively definite ratio in normal soils between the carbon and the nitrogen, organic carbon being remark-

ably constant at 10 to 12 times that of nitrogen. This residual organic material comprises the bulk of what is generally known as humus.

Studies on the mechanism of humus formation leading toward a separation and identification of the constituents of this heterogeneous material have been largely confined to three methods. First, the synthesis of black substances resembling humus from carbohydrates and other organic materials and a comparison of these with natural humus. Second, the decay of plant materials or other organic substances alone or incorporated in soil. Third, the identification of organic materials isolated from soils. While a notable advance has been made using these three methods, we are still but vaguely familiar with this important soil fraction. At present, considerable progress is attending the study of the steps involved and the compounds formed in the decomposition of known parent plant materials, yet much more work is needed before the picture is complete.

The earliest records in soil literature show that there has always been more or less interest in the base-absorbing properties of the organic fraction of the soil. It was only natural then that when the base-exchange property of inorganic soil colloids was discovered the same property should be assumed for organic soil colloids. Any number of investigators have demonstrated the absorbing property of humus, but with rare exceptions, and these are quite recent, their investigations have stopped at this point. The literature is significantly devoid of attempts to identify the nature of the absorption, that is, its chemical equivalency or the nature of the compounds which function in absorption and exchange. This is not surprising when one considers that progress in the study of soil organic matter has always been handicapped by the difficulty involved in the methods of isolation and purification.

Working with a representative collection of some 20 soils, mostly peat and forest types from widely separated sections of the United States, we have recently demonstrated a chemically equivalent base-exchange property for the organic fraction (9) of the soil. We found this exchange capacity to be approximately a linear function of the carbon content of the soil, while no relationship to nitrogen or to the carbon-nitrogen ratio could be established. Our logical conclusion then was that certain definitely defined carbon compounds must therefore play the major role in the exchange property of the organic fraction. Among the more abundant constituents of soil organic matter are the lignins, hemicelluloses, and celluloses. Of these, lignin and lignin-like bodies are the most abundant, that is, they represent the largest single class of constituents, and, as they are colloidal, appeared to be the most likely base exchange agents.

A study of lignin, isolated both from soils and from corn cobs, proved that we were correct in our surmise (9). For the extraction of lignin from the soil, a 2-percent alcoholic solution of sodium hydroxide was used. However, on comparing the exchange capacity of lignin thus obtained with that obtained by extracting the soil with aqueous 2-percent sodium hydroxide, it was found that the exchange capacity of the latter was much greater than that of the former. The solvent action of aqueous sodium hydroxide differs from that of alcoholic sodium hydroxide in that the former, in addition to dissolving lignin, also dissolves hemicelluloses. This indicated either that hemicellulose itself possessed a high exchange capacity, or that a complex ligno-hemicellulose had a greater exchange capacity than lignin alone. Our investigations have therefore been continued along this line, together with other related phases of the problem.

Before inaugurating our work on the base-exchange properties of soil organic matter, we assembled a collection of soils from a number of widely separated sources in this country. These soils have been discussed in our Technical Bulletin 30 (9) and the descriptions will not be repeated here, but they include peats, mucks, and forest types. A number of them were again used in the investigations which make up the subject matter of this bulletin.

EXPERIMENTAL

THE EXCHANGE CAPACITY OF LIGNIN AND LIGNO-HUMIC COMPOUNDS

There has been considerable controversy over the chemical composition of lignin.* This is undoubtedly due to the discovery or observation that it varies greatly with its source or even when isolated from different parts of the same plant. This variation in properties may be largely attributed to the variation in the number of hydroxyl and methoxyl groups present in the molecule. In view of this variation in composition, we could hardly expect the replacement capacity of lignin or the ligno-humic acid complex from soils to be uniform. In order to determine this, 11 soils were selected from the group of 20 which had been used in previous studies and lignin and ligno-humic material extracted from them.

For the extraction of lignin, 500 grams of soil were digested in the cold with 2.5 liters of 2-percent alcoholic sodium hydroxide (prepared

*It is reasonably certain that lignin is a benzene ring compound to which Phillips (10) has recently assigned the formula $C_6H_3O_3(OCH_3)_1(OH)_2$ to that isolated from corn cobs and oat hulls.

by dissolving 50 grams of NaOH in 1 liter of water and adding sufficient 95-percent alcohol to make a volume of 2.5 liters) for 24 hours. The liquor was then poured off, neutralized with HCl and the alcohol distilled off under reduced pressure. Ten cubic centimeters of Con. HCl were then added to the aqueous residue, and the precipitated lignin removed by filtration. It was washed with water until free from chlorides and then dried in the air.

For the aqueous alkaline extract, which we will designate as "ligno-hemicellulose" or "ligno-humate," the same procedure was followed except that 2-percent aqueous NaOH was used instead of an alcoholic solution. The material precipitated from this extract by acidifying with HCl was removed by filtration, washed free of chlorides, and dried in the air.

The replacement capacities of all these separately extracted materials were determined by leaching with normal solutions of either barium acetate or calcium acetate or both. The results are given in Table I. They show a wide variation in the exchange capacity of lignin from different soils, with a maximum of 178 M. E. per 100 grams and a minimum of 38 M. E. On the other hand, the "ligno-humate" material shows a much more constant as well as a much higher capacity. The maximum is 431 M. E. per 100 grams while the minimum is 321 M. E.

During the early part of our investigations, it was noted that lignin of low exchange capacity could be greatly increased in capacity by continuously treating it with an alkaline solution. Later we discovered that dilute acids were much more active in increasing the exchange capacity of lignin, and that the operation could be conducted either by leaching or digesting the lignin with dilute HCl. In view of this, both the basic lignates and "ligno-humates," at the completion of the exchange capacity determinations, were leached with 200 cc. of dilute HCl, the excess HCl removed by leaching with distilled water, and the exchange capacity again determined, using a normal solution of calcium acetate. These data are also given in Table I, and show a notable increase or "build-up" both in the exchange capacity of the lignin and the ligno-humate complex. Increase in the former ranged from 12 M. E. in a willow peat to 120 M. E. in a New Jersey peat, while that in the "ligno-humic" complex ranged from a minimum of 9 M. E. in a Maine peat to a maximum of 56 in a peat bog soil from New Jersey.

It is evident from these data that there is a wide variation in the exchange capacity of the lignin-like bodies in different soils, and also that it is by no means a constant quantity, for in all cases these exchange compounds are able to undergo further alteration, probably a hydrolysis, which increases, or builds up, their exchange capacities.

TABLE I.—REPLACEMENT CAPACITY OF LIGNIN AND LIGNO-HUMATE FROM DIFFERENT SOILS AND EFFECT OF HCl UPON THIS CAPACITY.

Soil No.	Brief description	Rep. Cap. as M. E. per 100 grams			Increase	Rep. Cap. as M. E. per 100 grams			Increase
		Lignin				Ligno-humate			
		Ba	Before HCl Ca	After HCl Ca		Ba	Before HCl Ca	After HCl Ca	
2	Peat bog soil, New Jersey	96	92	213	120	335	365	421	56
3	Hardwood peat, Oregon	92	93	190	97	325	360	378	18
4	Willow peat, Oregon	192	178	190	12	336	360	377	17
5	Forest soil, Douglas fir, Arizona	35	38	54	16	365	409	445	36
6	Forest soil, Eugene spruce, Arizona	....	171	192	21	380	396	438	42
7	Forest soil, aspen, Arizona	37	47	98	51	359	389	408	19
8	Forest soil, yellow pine, Arizona	69	66	81	15	402	411	461	50
9	Carex peat soil, New Jersey	167	162	209	47	373	383	401	18
10	Brown peat soil, Maine	110	104	190	86	....	420	429	9
11	Peat soil, Minnesota	123	148	172	24	326	327	335	8
17	Peat soil, Massachusetts	....	178	203	25	....	....	....	....
	Corn cob lignin	47	36	166	130	....	....	....	....

The great difference in the exchange capacity of the material extracted with alcoholic NaOH (lignin) and that extracted with aqueous NaOH (ligno-humate material) suggests either that lignin exists in soils as several different forms, or that other organic compounds with exchange properties and soluble in aqueous NaOH are present in soils. In view of the fact that lignin is the major constituent of soil organic matter, the data strongly suggest that lignins are present in several altered forms, and that only those of lower replacement capacity are soluble in alcoholic alkaline solutions, while an aqueous alkaline solution is required as a solvent for the forms possessing the higher capacities.

That this may be true is indicated by the following experiment. One gram of No. 2 soil (185 M. E. per 100 g. total replacement capacity) was weighed into each of three Gooch crucibles. One was leached with a 2-percent alcoholic solution of NaOH until the leachate was practically free from color. The other two were leached with aqueous 2-percent NaOH in a like manner. The replacement capacities of the residual soils were then determined with the following results:

(1) Residue from alcoholic leaching 171 M. E. per 100 grams.
(2) Residue from aqueous leaching 143 M. E. per 100 grams.
(3) Residue from aqueous leaching 138 M. E. per 100 grams.

The total replacement capacity of this soil, after digestion with 15-percent hydrogen peroxide, is 31.8 M. E., which shows that only a small part of the organic complex has been removed by leaching with the above alkaline solutions.

There is also included in Table I data showing the effect of dilute HCl upon the replacement capacity of corn cob lignin. It is especially significant that there is a notable increase in the exchange capacity of this material as well as soil lignin.

In view of the higher replacement capacity of the material soluble in aqueous NaOH, and the larger amount of material readily extracted by this solvent, an additional experiment was conducted under pressure. For a complete extraction of lignin-like bodies, it is necessary to resort to such a method to obtain complete solution.

Fifty grams of soil No. 2 were weighed into a one-liter Erlenmeyer flask, 500 cc. of 2-percent aqueous NaOH were added, a cotton plug inserted in the neck of the flask, and the whole digested in an autoclave for one hour at 10 pounds steam pressure. The whole was then filtered, the filtrate acidified with HCl and the precipitated organic matter removed by filtration. This residue was then dried in the air and its replacement capacity determined. This was found to be 362 M. E. per 100 grams, which agrees very closely with that obtained for the material

prepared without increased pressure, namely, 365 M. E. It is thus shown that while there is an increase in replacement capacity of aqueous alkali-soluble lignin as compared to the alcoholic alkali soluble, the maximum is reached in the former without the aid of the additional solvent effect of increased pressure.

IONIZATION AND HYDROLYSIS OF LIGNATES AND LIGNO-HUMATES

An important characteristic of the inorganic exchange complex, the so-called zeolitic fraction of clay, is its property of ionization and hydrolysis. It is through such reactions that soil properties are so greatly influenced by the clay fraction of the soil. The readiness with which soils absorb water, rate of water movement, degree of aeration, their resistance to the plow, their ability to fix fertilizers, and many other soil properties are almost entirely dependent upon the chemical nature of the exchange complex. It is through ionization and hydrolysis that fixed plant foods become available for plant nutrition; that acid soils show acid reactions; and, that the black-alkali soils are alkaline in reaction and, due to colloidal dispersion, difficult to cultivate.

Another important characteristic of the inorganic exchange complex is its differential energy of absorption for bases. In other words, some cations are more readily absorbed by the complex and others more readily displaced following absorption. Calcium, among the bases most abundant in the soil solution, is very readily absorbed by the complex, and thus we find under normal soil conditions that this base predominates. Under acid or alkaline soil conditions the hydrogen ion and sodium ion, respectively, predominate and it is thus through deviation from normal that they correspondingly influence most soil properties by their different degrees of ionization and hydrolysis. What then of similar properties in the organic exchange complex?

As an initial step in a study of these properties, the hydrogen (acid) lignate and the hydrogen (acid) ligno-humate were quantitatively titrated with 0.1 normal KOH and 0.1 normal $Ba(OH)_2$. The hydrogen-saturated complexes were prepared by washing the lignin and ligno-humate with dilute HCl, after which they were leached with distilled water until the leachates were free of chlorides. One-half gram of hydrogen-saturated ligno-humate, as thus prepared, was weighed into each of three 100-cc. beakers. Ten cubic centimeters of distilled water were added to one, 10 cc. of 0.1 normal KOH was added to the second, and 20 cc. of 0.1 normal KOH added to the third. These were allowed to stand for 24 hours, at the end of which period the reaction (pH) was determined with the hydrogen electrode. An additional measured amount

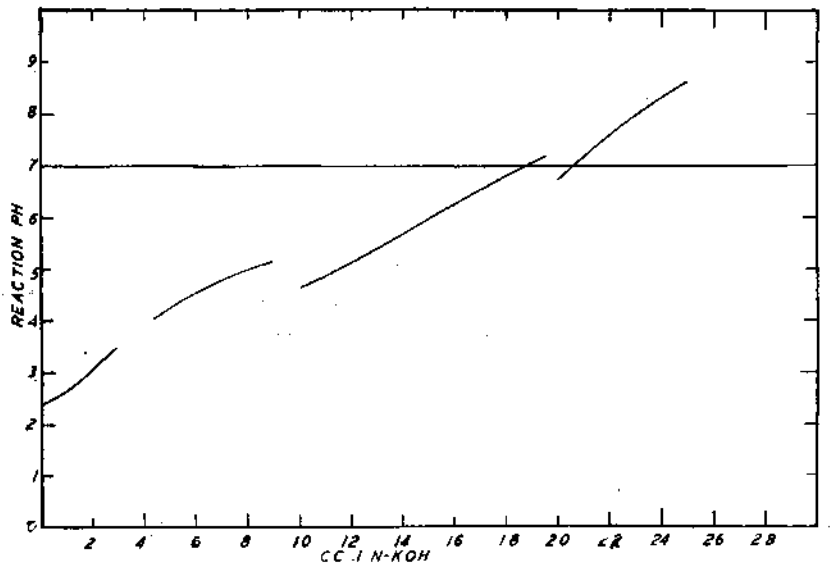

Fig. 1.—Titration curve for ligno-humic acid and .1 normal KOH.

of 0.1 normal KOH, 1 or 2 cc., was then added to each from a burette, allowed to stand with occasional shaking for 24 hours and the reaction again determined. This procedure was repeated daily until 10 cc. or more of 0.1 normal KOH had been added to each. The data are given in Table II and shown graphically in figure 1.

TABLE II.—TITRATION OF LIGNO-HUMIC ACID WITH 0.1 NORMAL KOH.

cc. 0.1 N KOH	Reaction pH	cc. 0.1 N KOH	Reaction pH	cc. 0.1 N KOH	Reaction pH
0	2.40	10	4.66	20	6.75
1	2.51	11	4.90	21	7.17
2	3.05	12	5.13	22	7.60
3	3.55	13	5.35	23	7.95
5	4.23	15	5.95	25	8.60
7	4.75	17	6.50	28	9.30
9	5.15	19	7.05	....	.....
13	5.85	21	7.17	....	.....
		22	8.20	....	.....

The main purpose of this experiment was to determine the absorption capacity of this organic complex at neutrality, pH 7.0. On calculating the amount of absorbed base to a milliequivalent basis, it was found that the base absorption agreed very closely with the exchange capacity as determined with the acetates of barium and calcium.

The titration curve intersects the line drawn horizontally from pH 7.0 at 20.5 cc. of 0.1 normal KOH which is equivalent to 0.0801 gram potassium or a milliequivalency of 410 M. E. per 100 grams. The line is also intersected by one curve at 19.1 cc. 0.1 normal KOH, which is equal to a milliequivalency of 382 per 100 grams.

Both ionization and hydrolysis are quite active in an aqueous suspension of this material. The solubility of the potassium salt is complete at pH 7.0, while the barium salt is comparatively insoluble. The nature of the curves obtained by the above experimental procedure is quite significant and shows the effect of dilution upon hydrolysis and consequent reaction as pH. For example 10 cc. of 0.1 normal KOH added to 0.5 gram ligno-humic acid gave a hydrogen ion concentration of pH 4.65, while with 10 cc. of distilled water and 10 cc. of 0.1 normal KOH the reaction was pH 5.4.

Using the same ligno-humic acid, this experiment was repeated with 0.1 normal $Ba(OH)_2$ as the alkali for neutralization. The experimental procedure, except for the standard alkali used, was exactly as described for the KOH titration. The data obtained are given in Table III, and shown graphically in figure 2, and are quite similar to the results obtained and already described for 0.1 normal KOH.

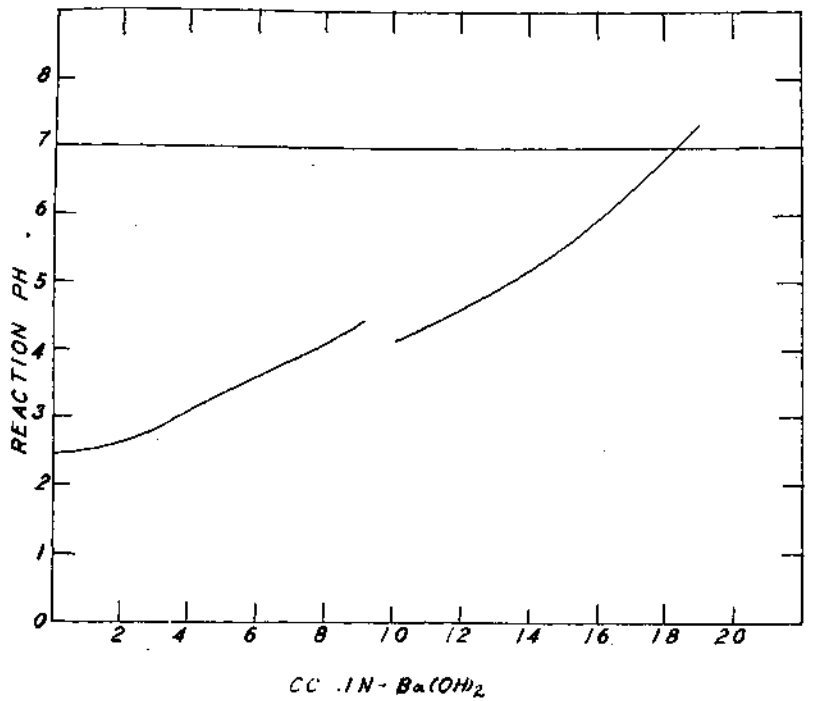

Fig. 2.—Titration curve for ligno-humic acid and .1 normal $Ba(OH)_2$.

Ionization and hydrolysis are shown to be fairly active with the barium salt as well as with the potassium salt. The effect of dilution, too, is similar. The titration curve intersects the line drawn horizontally from pH 7.0 at 18.5 cc. 0.1 normal $Ba(OH)_2$ which is equivalent to 0.1269 gram barium or a milliequivalency of 370 per 100 grams.

TABLE III.—TITRATION OF LIGNO-HUMIC ACID WITH 0.1 NORMAL $Ba(OH)_2$

cc. 0.1 N $Ba(OH)_2$	Reaction pH	cc. 0.1 N $Ba(OH)_2$	Reaction pH
0	2.40	10	4.13
1	2.51	11	4.45
2	2.63	12	4.55
3	2.78	13	4.90
5	3.35	15	5.50
7	3.80	17	6.30
9	4.35	19	7.35

In our studies the replacement capacity of the lignin from different soils has varied considerably, but has been usually about one-half the absorption capacity of the ligno-humate. So, in titrating the hydrogen-saturated lignin, 0.5 gram was used as in the preceding experiments; however, instead of 10-cc. intervals in the titration, 5 cc. were taken. That is, 0.5 gram of lignin was weighed into each of three beakers, 5 cc. of distilled water was added to one, 5 cc. of standard alkali added to a second and 10 cc. standard alkali added to a third. The reaction of each was

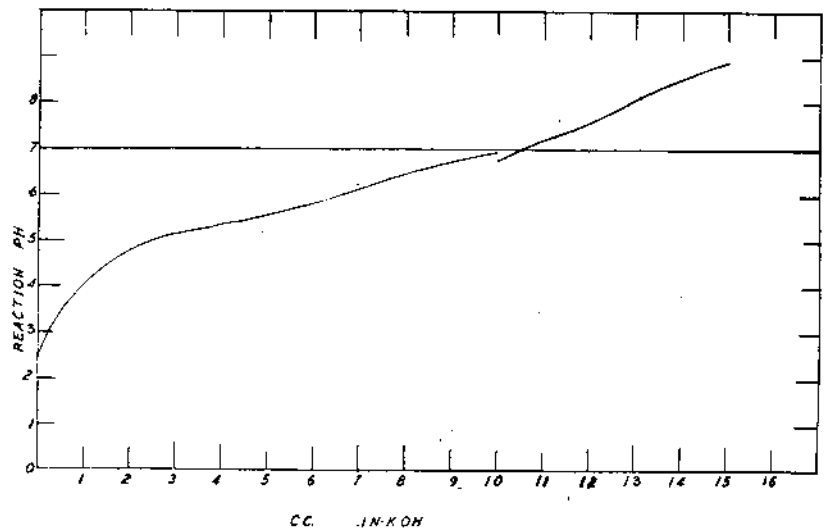

Fig. 3.—Titration curve for lignic acid and .1 normal KOH.

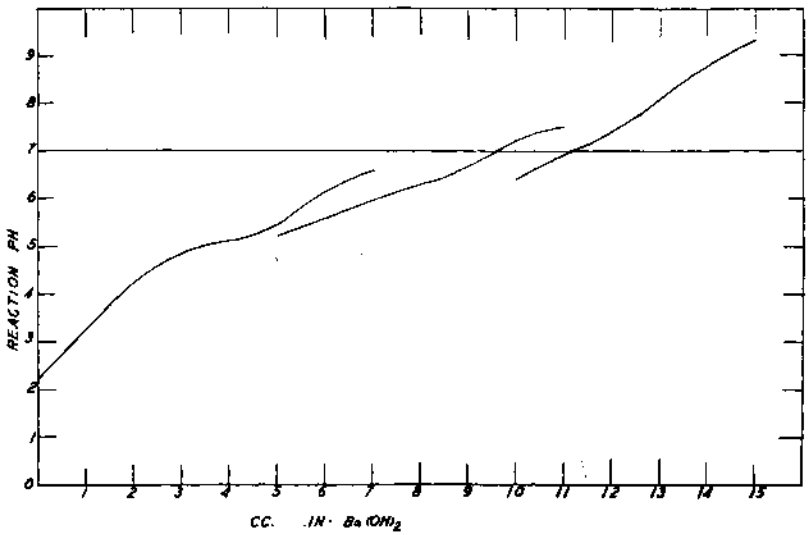

Fig. 4.—Titration curve for lignic acid and .1 normal $Ba(OH)_2$.

determined electrometrically after 24 hours, following which 1 cc. of standard alkali was added to each every 24 hours thereafter until all had received 5 cc. or more. The reaction was determined 24 hours after each addition. These data are given in Tables IV and V and shown graphically in figures 3 and 4.

TABLE IV.—TITRATION OF LIGNIC ACID WITH 0.1 NORMAL KOH.

cc. 0.1 N KOH	Reaction pH	cc. 0.1 N KOH	Reaction pH	cc. 0.1 N KOH	Reaction pH
0	2.42	5	5.45	10	6.75
1	4.05	6	5.80	11	7.20
2	4.80	7	6.15	12	7.55
3	5.15	8	6.45	13	8.10
4	5.30	9	6.65	14	8.50
5	5.55	10	6.90	15	8.85

TABLE V.—TITRATION OF LIGNIC ACID WITH 0.1 NORMAL $Ba(OH)_2$.

cc. 0.1 N $Ba(OH)_2$	Reaction pH	cc. 0.1 N $Ba(OH)_2$	Reaction pH	cc. 0.1 N $Ba(OH)_2$	Reaction pH
0	2.25	5	5.22	10	6.40
1	3.25	6	5.53	11	6.90
2	4.18	7	5.95	12	7.30
3	4.90	8	6.30	13	8.10
4	5.10	9	6.55	14	8.65
5	5.40	10	7.30	15	9.30
6	6.10	11	7.50		
7	6.60	12	8.25		

The nature of the curves obtained in these titrations is very similar to those obtained in the titration of the ligno-humate. Dilution has a greater relative effect on the hydrolysis of the barium salt, which is probably due to the insolubility of the latter, while the potassium salt is relatively soluble. The solubility of the potassium lignate is, however, less than that of potassium ligno-humate. If the results are calculated to milliequivalents of base required to produce neutrality (pH 7.0), the results agree very closely with the base exchange capacity as determined by direct replacement with the acetates of barium and calcium. A volume of 10.5 cc. of 0.1 normal KOH was required to produce neutrality, which is equivalent to 0.041 gram potassium or 209 milliequivalents of potassium per 100 grams lignin. A volume of 9.5 cc. of 0.1 normal $Ba(OH)_2$ was required to produce neutrality, which is equivalent to 0.0651 gram barium, or 190 milliequivalents per 100 grams lignin. The molecular composition of lignin from corn cobs and oat hulls, as determined by Phillips (10) is $C_{36}H_{31}O_9(OCH_3)_4(OH)_3$. Using this molecular weight, and calculating from the amount of base required to produce a reaction of pH 7.0, it was found that one mol of lignin combines with one mol of barium. Making a similar calculation for potassium, the molecular equivalent was found to be slightly less than two mols of potassium to one mol of lignin. The potassium salt is quite soluble, and being the salt of a strong base and a weak acid, it undergoes maximum hydrolysis and therefore complete saturation with base can not be accomplished at pH 7.0. However, we believe we are justified in assuming that the lignin molecule combines with one molecule of barium or two molecules of potassium to produce a saturated compound. This, too, is in agreement with results obtained by Beckmann, Liesche, and Lehmann (1).

Regarding the manner in which the lignin molecule reacts toward bases and functions in base exchange reactions it is easy to demonstrate this property. As already mentioned it is reasonably certain that lignin is a complex phenolic compound and Phillips (10) has rather definitely shown that it is either a homogeneous substance or a mixture of closely related isomers. Furthermore it is definitely established that lignin possesses hydroxyl groups the hydrogen of which can function as acid, or free hydrogens, in the manner which is characteristic of phenolic hydroxyl groups.

The hydrogen of the hydroxyl groups may be replaced or neutralized by monovalent or divalent bases which in turn may be exchanged in whole or in part for other bases present in solutions with which the lignin may come in contact. This appplies only to free lignin.

We have just shown by calculation from the titration of lignin (alcoholic alkaline soluble) that it is dibasic. Yet the work of Phillips (10) has shown the presence of three phenolic hydroxyl groups. The following formulae represent several which he has found for lignin isolated from plant materials.

1. Corn cob lignin $C_{37}H_{33}O_9(OCH_3)_4(OH)_3$ M. W. 796.384.
2. Oat hull lignin $C_{36}H_{31}O_9(OCH_3)_4(OH)_3$ M. W. 782.368.
3. Oat hull lignin $C_{38}H_{25}O_5(OCH_3)_4(OH)_3$ M. W. 784.320.

Using formula 2, except for two hydroxyl groups instead of three, and substituting two potassium ions for the two hydrogen ions, the theoretical ratio of potassium to potassium lignate is 11.0, while by actual titration we found a ratio of 12.2 per soil lignin. In like manner the theoretical ratio for barium lignate is 6.8 while by titration of the soil lignin we obtained 7.68. Both titrations therefore closely approach a dibasic complex and indicate the presence of only two active phenolic hydroxyl groups.

On a milliequivalent basis, the replacement capacity of ligno-humate (aqueous alkaline soluble) is in most cases approximately twice that of lignin. Calculating the basicity of ligno-humate from our titrations we found that this complex is in fact tetrabasic and therefore must possess four phenolic hydroxyl groups. This is shown by again using formula 2 except for four hydroxyl groups instead of three as follows:

$$C_{37}H_{33}O_9(OCH_3)_4(OH)_4$$

If the four hydrogen ions are replaced by four potassium ions the theoretical ratio of potassium to potassium ligno-humate is 6.17 while by titration of ligno-humate with KOH we obtained a ratio of 6.24. In like manner we obtained a ratio of 3.94 for barium ligno-humate by titration with $Ba(OH)_2$ and the theoretical ratio is 3.94. There is a remarkable agreement in both cases.

The lignin used in our experiments is therefore dibasic and ligno-humate tetra-basic and we believe that the replacement capacity of the organic fraction is a function of the number of phenolic hydroxyl groups in the lignin complex and will vary accordingly.

In order to obtain more data upon the ionization of the organic exchange complex at different dilutions, the following experiment was conducted: The lignins which were isolated from soils 2, 3, 4, 9, 11, and 17, portions of which were used in obtaining the data shown in Table I, were well mixed so as to be assured of sufficient material with which to work. Likewise, the ligno-humic fractions from soils 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 17 were combined. Both of these were separately leached

with dilute HCl to be assured that the material was free from bases and then washed with distilled water until free from chlorides. These final materials were assumed to be saturated with hydrogen.

From the hydrogen-saturated compounds the base-saturated compounds were prepared by neutralization with hydroxides of the desired bases. For example, potassium lignate and calcium lignate were prepared by titrating the hydrogen lignate, electrometrically, to a pH of 7.0 with 0.1 normal KOH and saturated $Ca(OH)_2$ solution. The respective mixtures were then evaporated to dryness on the hot-water bath. On account of the solubility of the compounds formed by the organic complex with monovalent bases, this is the only method by which the monovalent compounds can be prepared. The divalent bases form relatively insoluble compounds and can therefore be prepared either by titration or by leaching the complex with a neutral salt. In view of the fact that the absorptive capacity for divalent bases agrees very closely, as determined by titration and leaching, it seems fair to assume that both methods are reasonably correct.

The basic compounds thus prepared were weighed into several different volumes of boiled distilled water and the various dilutions (suspensions of the corresponding lignates with water) studied. The proportions approximated very closely the equivalent of 1 gram of dry material to 25, 50, 100, and 400 cc. of water, respectively. These organic compounds contained a small amount of moisture. This was determined and all the dilutions calculated to the basis of water-free material. The dilutions were prepared in Erlenmeyer flasks, tightly stoppered, and shaken daily for 3 weeks in order to permit sufficient time for equilibrium to be established. Conductivity determinations were then made on all dilutions, at 25° C. in a constant-temperature bath. The results are given in Table VI and shown graphically in figures 5 and 6.

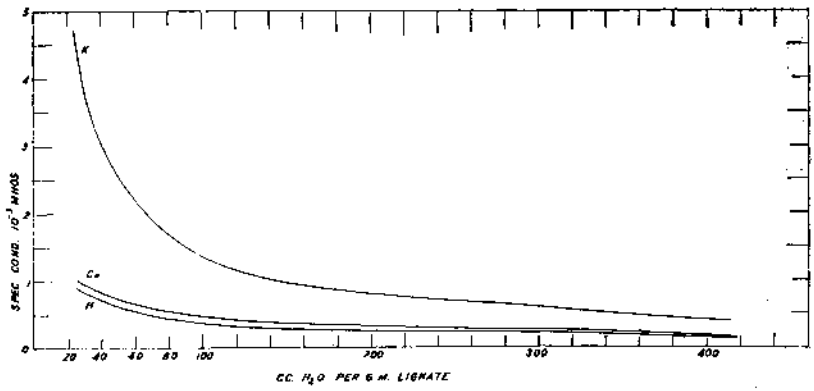

Fig. 5.—Effect of dilution upon the ionization of lignates.

TABLE VI.—IONIZATION OF "LIGNATES" AND "LIGNO-HUMATES" AT VARIOUS DILUTIONS.

	cc. H_2O per gm. lignate	Vol. in cc. per M. E. lignite	Gms. per liter	Mols per liter	Spec. cond. 10^{-3} Mhos.		cc. H_2O per gm. ligno-humate	Gms. per liter	Spec. cond. 10^{-3} Mhos.
Potassium lignate	25.8	11.07	38.75	.045	4.38	Pot. ligno-humate	27.5	36.4	6.22
Potassium lignate	51.6	22.14	19.38	.023	2.43	Pot. ligno-humate	54.9	18.2	3.38
Potassium lignate	103.0	44.28	9.68	.011	1.32	Pot. ligno-humate	110.0	9.1	1.85
Potassium lignate	413.0	177.12	2.42	.003	.39	Pot. ligno-humate	440.0	2.3	.56
Calcium lignate	26.0	10.70	38.54	.047	1.00	Cal. ligno-humate	27.7	36.1	1.03
Calcium lignate	52.0	21.40	19.27	.023	.45	Cal. ligno-humate	55.4	18.0	.55
Calcium lignate	104.0	42.80	9.62	.012	.44	Cal. ligno-humate	111.0	9.0	.31
Calcium lignate	416.0	171.20	2.41	.003	.13	Cal, ligno-humate	443.0	2.2	.12
Hydrogen lignate	25.4	9.92	39.33	.050	.90	Hyd. ligno-humate	28.3	37.5	.99
Hydrogen lignate	50.8	19.84	19.67	.025	.60	Hyd. ligno-humate	56.6	18.7	.63
Hydrogen lignate	102.0	39.68	9.83	.012	.36	Hyd. ligno-humate	113.0	9.4	.38
Hydrogen lignate	407.0	158.72	2.46	.003	.13	Hyd. ligno-humate	453.0	2.3	.15
						Sod. ligno-humate	27.7	36.1	4.96
						Sod. ligno-humate	55.4	18.0	2.79
						Sod. ligno-humate	111.0	9.0	1.51
						Sod. ligno-humate	443.0	2.2	.49
						Bar. ligno-humate	27.3	36.6	.55
						Bar. ligno-humate	54.5	18.3	.24
						Bar. ligno-humate	109.0	9.2	.22
						Bar. ligno-humate	437.0	2.3	.08

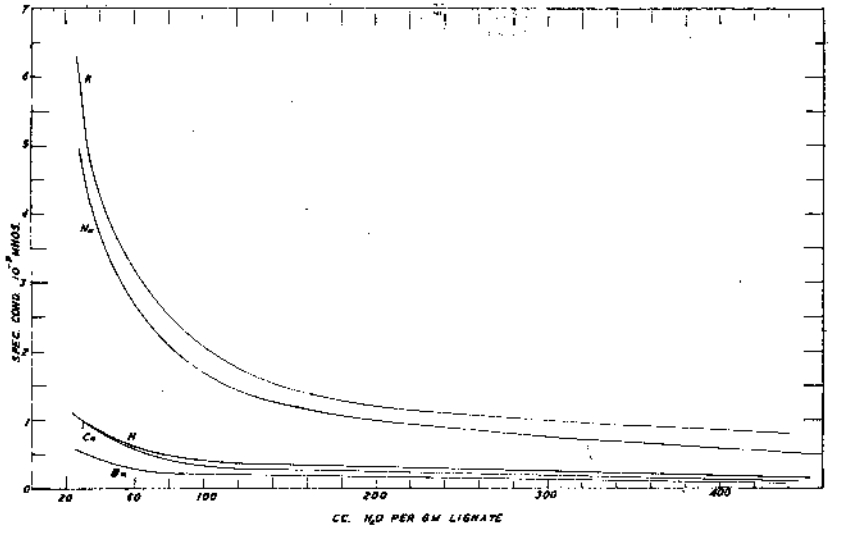

Fig. 6.—Effect of dilution upon the ionization of ligno-humates.

These experiments show that lignin-like materials in soils possess hydrolysis and ionization properties similar to the inorganic zeolites of the clay fraction. Both are weak acids and their monovalent salts will therefore hydrolyze readily to form hydroxides. The amount of hydrolysis is a function of dilution. The black color of the soil solution or soil extract of a black alkali soil is, therefore, evidence of the presence of the sodium salt of lignic acid, usually hydrolyzed, and *may* not be due to the solvent effect of sodium hydroxide, formed by the hydrolysis of sodium zeolite, upon organic matter. An un-ionized solution of sodium lignate also has a black color.

COMMON-ION EFFECT

Previous investigations conducted in this laboratory (4) have shown that sodium carbonate is not present in most so-called "black alkali" soils. Alkalinity in soils is a function of dilution and therefore of the hydroxyl ion formed by the hydrolysis of the sodium salt of the exchange complex. The soil solution of a black alkali soil at or approximating the wilting point, the static moisture, will rarely contain sodium carbonate or hydroxyl ions. With dilution, as in a 1:5 water extract, for example, there will be an increase in hydroxyl ions from the hydrolysis of sodium zeolite, which by ordinary methods used in soil analyses would be calculated as sodium carbonate. If an excess of sodium chloride or any other soluble sodium salt is added, introducing the common ion, sodium, the

ionization of the sodium zeolite will be forced back. If the concentration of sodium chloride is high enough all hydrolysis of sodium zeolite will be prevented and the soil-water-NaCl mixture will show no color with phenolphthalein. If, instead of sodium zeolite, sodium carbonate is used in such an experiment the sodium chloride will have little or no effect upon the ionization of sodium carbonate. In studying the properties of the organic exchange complex of soils, it is of interest to know that we have found a similar property for the lignin salts of the monovalent bases. An aqueous solution of the potassium salt of ligno-humic acid was prepared, which gave a pink color with phenolphthalein. On adding an excess of potassium chloride to this solution, ionization was forced back and the pink color of the phenolphthalein completely disappeared. There is thus proof that the hydrolysis of potassium lignate is prevented by the presence of a sufficient concentration of the common ion, potassium. We have again, therefore, demonstrated another important property which is similar for the zeolite and humate base-exchange compounds in soils.

Further investigation of the common-ion effect has been pursued by means of certain equilibrium studies in which four humate salts, in contact with their several salt solutions of varying concentration, have been used. A salt exists in solution as active and inactive fractions. The active fraction consists of the ions into which the salt is dissociated. It is to the ions that chemical reactions are all attributed. The inorganic exchange compounds, the zeolites, have been shown to exhibit reactive properties according to their degree of ionization. Breazeale (3) has shown that ionization of such compounds in soils is largely controlled or limited by the nature and concentration of electrolytes in the soil solution. For example, the ionization of the sodium in a sodium zeolite soil was so completely forced back by a sodium chloride solution of 4-percent strength that no base replacement could be obtained using a solution of a calcium salt equivalent in concentration to a saturated gypsum solution. In a like manner the ionization of a potassium zeolite was forced back to the same degree by a 2-percent solution of potassium chloride.

We have conducted similar studies with the humates and somewhat similar results were obtained. The humate compounds used were prepared as follows from the peat soil No. 2: Five hundred grams were heated with 5 liters of water for 1 hour under 10 pounds steam pressure. The whole was then allowed to settle and was filtered. The filtrate was acidified with HCl and the precipitated organic matter (humate) removed by filtration. From this hydrogen humate the sodium, potassium, magnesium, and calcium salts were prepared by methods already described, namely, the two former by neutralizing with hydroxides, and

the two latter, the divalent bases, by leaching the hydrogen humate with the acetates of magnesium or calcium. These basic humates were allowed to dry in the air, and as thus prepared, used in the experiments described.

Breazeale (3) conducted his common-ion studies by leaching the respective zeolites with the salt solutions, all the inorganic zeolites being sufficiently insoluble for such a procedure. The humates of the monovalent bases are very soluble, which precludes the utilization of such a method in conducting a similar study on the organic exchange complex. In view of this, we adopted the alternative procedure of allowing the humates to remain in contact with the respective salt solutions for a period of 24 hours with frequent shaking.

Experiment 1.—In this experiment, 2 grams of sodium humate were treated in the above manner with 200 cc. of the solution shown in Table VII. In one case the concentration of calcium ion was kept constant, while in the other the concentration of sodium was kept constant. Calcium was determined by analyzing the solution at the end of the period of contact.

TABLE VII.—BASE REPLACEMENT IN A SODIUM LIGNO-HUMATE AS AFFECTED BY A COMMON ION IN SOLUTION.

Number	Percent NaCl in solution	Gm. Ca as $CaCl_2$ 200 cc. solution	Gm. Ca in solution not absorbed	Gm. Ca absorbed by the humate
1	.0	.1350	.0540	.0800
2	.4	.1350	.0434	.0916
3	.8	.1350	.0450	.0900
4	1.2	.1350	.0490	.0856
5	1.6	.1350	.0510	.0840
6	2.4	.1350	.0584	.0766
7	5.0	.1350	.0645	.0705
8	7.5	.1350	.0645	.0705
9	10.0	.1350	.0690	.0660
10	2.5	.0675	.0345	.0255
11	2.5	.1350	.0675	.0675
12	2.5	1.0350	.9600	.0750

The concentration of calcium where used as a constant is but slightly greater than that in a saturated solution of gypsum. The great affinity of the humate molecule for calcium in the presence of sodium is therefore clearly demonstrated. While there is a consistent decrease in calcium absorbed with increase in sodium chloride, it is still, even in the presence of a 10-percent sodium chloride solution, being absorbed to more than 50 percent of its saturation capacity. Therefore, while the

common-ion sodium decreases the ionization of the sodium humate, it does not completely prevent replacement of sodium ions by calcium ions. This is significant when compared with the effect of a common ion on the inorganic zeolite, in which a 4-percent sodium chloride solution completely stops replacement of sodium ions by calcium. However, this may be due partially to the different method which we were forced to use because of the high solubility of the sodium humate salt.

Experiment 2.—In this experiment 2 grams of potassium humate were treated in a similar manner with 200 cc. of the solutions indicated in Table VIII.

TABLE VIII.—BASE REPLACEMENT IN A POTASSIUM LIGNOHUMATE AS AFFECTED BY A COMMON ION IN SOLUTION.

Number	Percent KCl in solution	Ca as $CaCl_2$ in 200 cc. solution	Gm. Ca in solution not absorbed	Gm. Ca absorbed by the humate
1	.0	.1350	.0285	.1065
2	.5	.1350	.0285	.1065
3	2.5	.1350	.0496	.0854
4	5.0	.1350	.0615	.0735
5	7.5	.1350	.0645	.0705
6	10.0	.1350	.0675	.0675

The effect of the common-ion potassium upon ionization and replacement by calcium is very similar to the case of sodium. There was a gradual and consistent decrease in calcium absorbed by the humate with increase in concentration of KCL, but even at 10-percent KCl the calcium ion is still being absorbed to more than 50 percent of the saturation capacity of the humate.

Experiment 3.—In this experiment 2 grams of calcium humate were treated in a similar manner with 200 cc. of the solution indicated in Table IX.

In the first part of the table, data are given to show the replacement capacity of potassium ion in the presence of increasing amounts of calcium ion. It is evident from these data that replacement with potassium is completely stopped in the presence of a 2.5-percent solution of $CaCl_2$. Data are also given in this table showing the slight ionization of the calcium humate in solution. In the lower part of the table, data are given showing the saturation of calcium humate in the presence of varying amounts of calcium and magnesium salts in solution. The results obtained in this experiment are about what one would expect from the properties of the two bases. Calcium appears to have the greater affinity. In the presence of 25 milliequivalents of Ca, 205 milliequivalents

TABLE IX.—BASE REPLACEMENT IN A CALCIUM HUMATE AS AFFECTED BY A COMMON ION IN SOLUTION.

Number	Percent $CaCl_2$ in solution	Percent KCL in solution	Gm. Ca in solution	Gm. Ca absorbed by humate		
1	0.0	0.0	.0016	.1132		
2	0.0	.4	.0124	.1020		
3	1.0	.4	.0024	.1120		
4	2.5	.4	.0000	.1148		
5	5.0	.4	.0000	.1148		
	Gm. Ca per 200 cc. solution	Gm. Mg per 200 cc. solution	Gm. Mg absorbed by humate	Gm. Ca absorbed by humate	M. E. Mg absorbed	M. E. Ca absorbed
6	.5(25)	.0	.0000	.1152	0.00	5.76
7	.5(25)	.5(41)*	.0186	.0842	1.52	4.21
8	.5(25)	1.0(82.2)	.0271	.0700	2.26	3.50
9	.5(25)	2.5(205)	.0374	.0528	3.12	2.64
10	.0	.5(41.1)	.0428	.0438	3.57	2.19
11	.5(25)	.5(41.1)	.0198	.0822	1.65	4.11
12	1.0(50)	.5(41.1)	.0122	.0948	1.02	4.74

*Calculated to milliequivalents.

of Mg replace only slightly more than 50 percent of the Ca ions. On the other hand, maintaining the Mg at 41 milliequivalents, 50 milliequivalents of Ca (in addition to the Ca present in the humate) only allowed the entry of 1.02 M. E. Mg. into the humate complex, the total capacity of which was 5.76 M. E.

Experiment 4.—In this experiment 2 grams of magnesium humate were treated in a similar manner with 200 cc. of the solutions indicated in Table X.

The magnesium humate shows a greater solubility of magnesium, from the ionization of its humate salt, than calcium, in view of which it is not surprising to note that replacement of magnesium by potassium is not completely stopped. On the other hand, the amount of magnesium displaced by potassium remains practically constant above a 1-percent solution of $MgCl_2$. It should be mentioned in this connection that magnesium humate shows some solubility in distilled water as measured by the color of the solution, while the calcium humate may be shaken with water without appearance of color. The equilibrium obtained by varying the concentration of magnesium and calcium in contact with magnesium humate again serves to demonstrate the greater affinity of the humate for calcium as compared to magnesium. In contact with a solution containing 41 M. E. magnesium, the amount of calcium absorbed by increasing the calcium content of the solution increased until the magnesium humate had been changed to one containing 4.8 M. E. Ca and 1.1 M. E. Mg by a solution containing 125 M. E. Ca. On the other hand, in the presence of 25 M. E. Ca in the solution and 205 M. E. Mg, the magnesium humate came to equilibrium at 2.1 M. E. Ca and 4.0 M. E. Mg.

HEMICELLULOSES

As already stated, one of the principal differences between the solvent action of alcoholic NaOH and aqueous NaOH lies in the additional solubility of hemicelluloses in the latter and its insolubility in the former. The logical question in view of this is the role of hemicelluloses in the greater exchange capacity of the aqueous NaOH soluble material. Since xylan is one of the most abundant hemicelluloses present in plant materials, the chief parent substances of soil organic matter, the exchange property of this compound was studied as follows:

Xylan was prepared by the following method: One kilogram wheat straw was digested in the cold with 2-percent aqueous NH_4OH to dissolve the albuminoids. The ammonia extract was then pressed out of the material with the aid of suction on a porcelain filter, repeating the process three times. This extracted material was then digested with

TABLE X.—BASE REPLACEMENT IN MAGNESIUM HUMATE AS AFFECTED BY A COMMON ION IN SOLUTION.

Number	Percent $MgCl_2$ in solution	KCl gms. per 200 cc.	Milligrams Mg. in solution	Milligrams of Mg absorbed by humate		
1	0	.0	.0031	.0724		
2	0	.4	.0162	.0579		
3	1	.4	.0038	.0717		
4	2.5	.4	.0062	.0693		
5	5	.4	.0038	.0717		
	Gm. Mg per 200 cc.	Gm. Ca per 200 cc.	Gm. Ca absorbed by humate	Gm. Mg absorbed by humate	M. E. Ca absorbed	M. E. Mg absorbed
6	.5(41.1)*	.0	.0000	.0717	.0	5.9
7	.5(41.1)	.5(25)*	.0726	.0305	3.6	2.5
8	.5(41.1)	1.0(50)	.0856	.0206	4.3	1.7
9	.5(41.1)	2.5(125)	.0970	.0128	4.8	1.1
10	0.0	.5(25)	.1028	.0096	5.1	0.8
11	.5(41.1)	.5(25)	.0694	.0306	3.5	2.5
12	1.0(82.2)	.5(25)	.0584	.0398	2.9	3.2
13	2.5(205)	.5(25)	.0420	.0490	2.1	4.0

*Calculated as milliequivalents.

warm 5-percent aqueous NaOH. After 24 hours the extract was pressed out and the digestion repeated for another 24 hours. After allowing the small amount of sediment present to settle out, the clear supernatant extract was mixed with an equal volume of 95-percent alcohol. The precipitated xylan was filtered on a cloth, washed with alcohol until the washings were colorless, and then treated in the presence of alcohol with HCl, sufficient HCl being added to make the solution just slightly acid. The xylan was then washed with alcohol until free from acid, then with ether and dried.

One gram of this xylan was weighed into each of four 100-cc. beakers, 22 cc. of normal barium acetate added, and the whole stirred occasionally for 24 hours in order for the xylan to become completely wetted. These were then washed into Gooch crucibles, using suction. Two were leached with 100 cc. of normal barium acetate (A) and two with 100 cc. of dilute HCl (B), followed by 100 cc. of normal barium acetate. They were then washed free of excess barium acetate and the absorbed barium determined. The amounts of absorbed barium were as follows:

A 11.8 M. E. Ba per 100 grams.
A 11.8 M. E. Ba per 100 grams.
B 8.3 M. E. Ba per 100 grams.
B 8.3 M. E. Ba per 100 grams.

They were then leached with 200 cc. of normal calcium acetate and washed free of excess of this salt. The absorbed calcium was determined by displacing it with 200 cc. of normal ammonium chloride. The amounts of absorbed calcium were as follows:

A 13.0 M. E. per 100 grams.
A 10.0 M. E. per 100 grams.
B 9.0 M. E. per 100 grams.
B 9.5 M. E. per 100 grams.

It is thus shown that there is strong evidence under the above conditions of a small exchange capacity for xylan, but this is not built up by treatment with HCl, as in the exchange capacity of lignin, nor is it of sufficient magnitude to account for the greater exchange capacity of ligno-humate as compared to the lignin. It is, however, interesting to consider the role of the decomposition products of these more complex carbohydrate bodies.

In our previous studies (9) on the exchange property of organic matter, some attention was given to synthetic humus, namely, the black material formed by treating carbohydrates with acids. We found that such a synthetic product prepared from sucrose was quite similar to soil

humus in exchanging its absorbed base for another base in a solution with which it may come in contact. In view of this we ventured the suggestion that there is much basis for assuming a marked degree of similarity between the synthetic and natural products.

It is significant, and should be mentioned here in connection with our work on the exchange properties of lignin and synthetic humates, that Beckley (2) has shown that carbohydrates may yield first furfuraldehyde or methyl-hydroxy-furfuraldehyde, which as a condensation product is analogous to humus and has been identified as a product of the rotting of straw in the soil. Schrauth (14) suggests the formation of a fundamental unit of the lignin molecule by condensation of three molecules of methyl-hydroxy-furfuraldehyde. Then again, Marcusson (8) suggests that the carbohydrate in the plant residues may be converted into furfuraldehyde and this through a paradifurane ring to a benzenoid grouping.

These few references are presented in order to show that carbohydrates may often yield furfural derivatives when decomposed under certain conditions of environment, and may even proceed through condensation or some similar reaction to lignin-like bodies. Gortner and Bliss (5) have shown that when furfural is boiled with HCl it is converted into a black insoluble mass. This suggests that the synthetic humus which is formed from carbohydrates and acids is formed in turn from furfural condensation products. Other materials than carbohydrates may be converted into synthetic humus-like material, as was shown by Hoppe-Seyler (7), who prepared it by treating phenols and quinone with alkalis.

Lignin, as we have previously stated, varies in the number of hydroxyl and methoxyl groups which it possesses. A comparison of synthetic and natural humus by Robertson, Irvine, and Dobson (12) showed that a natural humus contained 1.7 to 2.4 percent methoxyl groups, while the synthetic humus contained 6.47 percent. Natural humus material usually contains more furfural bodies than artificial humus which should probably alter quantitatively the properties in which we are interested.

From the above there is noted a rather convincing array of evidence that carbohydrates are closely linked with lignin formation in soils and, therefore, with the base-exchange property of the organic fraction of soils, although directly in themselves they are not greatly involved. In view of this, may not other carbohydrates less soluble and less reactive, such as the hemicelluloses and celluloses, enter into similar reactions? Rose and Lisse (13) have shown a direct inverse relation between the cellulose and lignin content of decaying wood.

Since celluloses and hemicelluloses were known to compose two of

the larger chemical groups of plant constituents (parent humus material), and were known to yield black substances on decomposition in soils it was early assumed that they played a dominant role in the formation of soil humus. Later investigations showed that these same groups were extremely resistant to decomposition in soils which cast some doubt upon the above assumptions. There soon followed, however, the discovery that an ample supply of available nitrogen was highly essential for the life processes of organisms active in cellulose decomposition, and that this element is often a limiting factor. Thus, while decomposition of these groups was shown to be relatively slow, the correctness of the early assumptions regarding its relation to humus formation was demonstrated. Waksman (16) has shown that under optimum conditions cellulose will decompose fairly rapidly and yield humus-like material. The same may be said to apply to hemicelluloses.

In view of our success in demonstrating an exchange capacity for synthetic humus from sucrose, similar experiments were conducted using xylan and cellulose as raw material. One hundred grams of xylan were placed in an evaporating dish with sufficient 10-percent HCl to form a thick paste. The mixture was warmed on the hot-water bath, stirring occasionally until the whole had been transformed into a thick black mass. Hot water was then added and the whole filtered and washed. This material was then dried in the air.

In a similar manner, 25 grams of filter paper were digested with HCl on the hot-water bath until it had darkened perceptibly. This did not form a black mass, as did the xylan and sucrose, but was dark brown at the time digestion was discontinued. This mass was then diluted with water, filtered, and washed.

The replacement capacity of these synthetic products was then determined in the usual manner with the following results:

Synthetic humus from xylan, 189 M. E. rep. cap. per 100 gms.*
Synthetic humus from cellulose 40 M. E. rep. cap. per 100 gms.

This experiment shows quite conclusively that both xylan and cellulose will be converted into humus-like bodies, with base exchange properties, by digestion with HCl on the hot-water bath. The cellulose is more resistant to the reactions involved. In spite of the fact that mineral acids are largely absent, and that sugars undergo very rapid decomposition in soils, the reaction trend noted above cannot be denied. But on the same basis, we might say that biological reactions in soils, as conducted under controlled laboratory conditions do not necessarily hold true for field conditions.

*Original replacement capacity of xylan 11.5 M. E. For cellulose it was not determined.

DYE ABSORPTION

Basic dyes have often been used in studying the absorptive property of soil celloids, basic fucshine being quite satisfactory for this purpose. In view of this, the absorptive properties of xylan, lignin, and the ligno-humate were examined with this reagent.

About 1 gram of each of these materials was mixed in a beaker with an excess of a 0.5-percent aqueous solution of basic fucshine. They were then washed into a Gooch crucible and all leached with water and alcohol until the leachings were entirely free of color. They were then leached with normal ammonium chloride. In all three cases this salt displaced absorbed color. The xylan showed the least absorption. This gives strong evidence that the dye is chemically absorbed by these materials.

EXCHANGE PROPERTIES OF UNDECOMPOSED ORGANIC MATERIALS

Waksman (17), in his study of the relation between soil organic matter and parent plant material, has obtained quite illuminating data regarding the nature of the group of organic materials which composed soil organic matter. With the exception of protein, which is largely built up in soils by soil micro-organisms, lignin is the only major constituent which is present in larger percentage in the so-called humus than in the parent plant material. Lignin is extremely resistant to the chemical and biological reactions which take place in soils. Celluloses and hemicelluloses also are quite resistant to these reactions. In view of this it occurred to us that these organic compounds, or even some inorganic compounds similar to zeolites which may be present in plants possess exchange or absorpttive properties before becoming incorporated in the soil. Considerable time has therefore been devoted to a study of base exchange in natural, undecomposed plant material.

A large quantity of alfalfa tops was obtained, dried thoroughly, ground after drying in the air, and its base exchange properties studied. As in all our previous work where materials of high base exchange capacity have been studied, only 1 gram of material was used and leachings were made with normal solutions of barium and calcium acetates. Using the above salt solutions, barium acetate first, an absorption of 50 M. E. of Ba per 100 gms. was found, which on displacement with calcium acetate solution, an absorption of 58 M. E. Ca was noted. There is, therefore, evidence of a chemically equivalent exchange property in ground alfalfa.

In our previous work (9) we have shown that by digesting soils with 15-percent H_2O_2 it is possible to determine approximately to what extent the absorption is due to organic material and how much to inor-

ganic matter. In other words, we may closely approximate the exchange capacity of organic matter in soils, with this reagent. It seems quite fair to assume that this should hold true for parent plant material as well as for soils. On the basis of this assumption the effect of the H_2O_2 reagent upon the exchange capacity of ground alfalfa was studied.

One gram of ground alfalfa was weighed into each of eight 100-cc. beakers and treated as follows:

A. To the first two, 25 cc. of normal barium acetate solution was added and allowed to stand, with occasional stirring, for 24 hours.

B. To the second two, 15 cc. of H_2O and 15 cc. of 30-percent H_2O_2 were added, covered with watch glasses and placed on the hot-water bath for 3 hours. They were then filtered through a Gooch crucible, returned to the beakers and again digested with 15-percent H_2O_2, filtered again and returned to the beakers and 25 cc. of normal barium acetate added.

C. To the third set of duplicates, the same treatment as in B was employed, except that the alfalfa was digested three times with H_2O_2 instead of twice as in B.

D. These two were digested once with H_2O_2, after adding 1 gram of soil to catalyse the reaction. This step was suggested by the investigations of Robinson (11), in which he found that for fairly pure organic materials, destruction was most active and only complete in the presence of soil or other similar material.

The four duplicate sets were then transferred to Gooch crucibles and each leached with 150 cc. of normal barium acetate, then washed with distilled water until free from excess of this salt, and the absorbed barium determined with the following results:

A. Rep. cap. of original material, 58 M. E. per 100 gms.
B. Rep. cap. after two digestions with H_2O_2, 35 M. E. per 100 gms.
C. Rep. cap. after three digestions with H_2O_2, 34 M. E. per 100 gms.
D. Rep. cap. after digestion with soil and H_2O_2, 37 M. E. per 100 gms.

These data show that the replacement capacity of alfalfa is in large part not destroyed by H_2O_2. Yet the work of Robinson (11), just cited, has shown that with the exception of the several forms of carbon, such as charcoal, coal, etc., all the organic materials which he studied were almost completely destroyed by digestion with 15-percent H_2O_2 in the manner employed in the above experiment. There is no other conclusion if we are to accept previously published investigations except to assume that natural plant materials not only contain organic complexes

which possess base exchange properties, but also that inorganic compounds of similar property are also present.

A partial analysis of the ground alfalfa used in these experiments is given in the following table:

	Percent of dry matter	Percent of ash
Ash	12.18	.....
Silica SiO_2	1.49	12.25
Aluminum, AL	0.16	1.29

In the above data we have shown the elements silicon and aluminum which go to make up the nucleus of the inorganic exchange complex. While we cannot deny that these may exist in fresh plant material as zeolite-like bodies, it is impossible to conceive of such a small amount being responsible for the large replacement capacity not destroyed by hydrogen peroxide.

In order to answer this question we determined the carbon content of the alfalfa before and after digestion with hydrogen peroxide. The results obtained were as follows:

Percent carbon in alfalfa	38.7
Percent carbon in alfalfa after digestion with H_2O_2	21.6
Percent carbon in alfalfa after leaching with hot water	32.8

These data show that raw plant material is not easily decomposed by hydrogen peroxide, as is soil organic matter, and indicate additionally that the exchange capacity of the alfalfa residue, after digestion with hydrogen peroxide, is due to undecomposed lignin bodies.

The next question is, what effect does humification or decay of plant material have upon its base exchange properties? This was studied by conducting the following experiment:

1. Two hundred grams of ground alfalfa were weighed into a galvanized pan, moistened to saturation with water, and placed in a dark cupboard for spontaneous decomposition. Moisture was added from time to time to maintain saturation. No attempt was made to prevent ingress of fly larvae, and at the end of the period of fermentation the material was literally alive with larvae.

2. Two hundred grams of ground alfalfa were treated exactly as in (1), except that during the entire period of decomposition the material was protected from flies by being covered with cheesecloth.

In both cases the period of decomposition was 3 weeks. At the end of this time the samples were dried in the air (No. 1 was placed in the oven at 110° C. for a few minutes to kill the larvae), ground through

a mill, and the base exchange capacity of this material determined by the methods already described. These data are given in the following tables:

	No. 1	No. 2
Weight of original material in grams	200	200
Weight of material after period of decay	115	135

	Original alfalfa	Decomposed product No. 1	Decomposed product No. 2
Base exchange capacity, M. E. per 100 gms	58	205	163
Base exchange capacity, after digestion with H_2O_2, M. E. per 100 grams	35	79	59

These data were calculated back to the original basis of 200 grams, and the following relation was shown:

	Decomposed product No. 1	Decomposed product No. 2
Base exchange capacity, original basis	118 M. E.	110 M. E.
Base exchange capacity, after digestion with H_2O_2, original basis	45 M. E.	40 M. E.

It is thus shown that decomposition or humification reactions greatly increase the exchange capacity of organic matter, probably through a destruction of the simple carbohydrates and the proteins, resulting in a concentration of larger amounts of lignin-like bodies in the humified residue.

An additional experiment was conducted in which the alkali-soluble materials were extracted from alfalfa meal by three separate methods. 1. Alfalfa meal was digested with a cold 2-percent alcoholic solution of NaOH by the same method used in extracting lignin from soils. 2. Alfalfa meal was digested with a cold 2-percent aqueous solution of NaOH by the same methods also described under the soil studies in the early part of this bulletin. 3. Alfalfa meal was digested with 2-percent aqueous NaOH, as in 2, except that the digestion was conducted under a pressure of 10 pounds of steam for 1 hour. The materials extracted by these methods were separated from solution by precipitation, dried, and their exchange capacity determined with the following results:

1. Residue from alcoholic extraction, 99.8 M. E. per 100 gms.
2. Residue from aqueous extraction, 106.8 M. E. per 100 gms.
3. Residue from pressure extraction, 142.2 M. E. per 100 gms.

These data prove a number of things. Humification has greatly increased the organic exchange capacity. It is also shown that the compounds which impart to the organic matter its exchange properties are least attacked by the agents of humification, both the chemical and biological, and that the organic exchange property of alfalfa meal is largely due to lignin and lignin-like bodies.

RELATION OF LIGNIN TO ORGANIC EXCHANGE CAPACITY OF SOILS

During the study of the organic exchange complex, our data and observations have pointed very strongly to lignin and its closely related bodies as being the major organic constituents of soils and parent plant materials possessing base exchange properties. The complex carbohydrates, if at all related, are primarily involved by reason of their decomposition into lignin-like materials. In view of this, which appears the only logical conclusion from our investigations to date, a number of representative soils were selected from the group which we have been studying, and lignin, cellulose, and hemicellulose determined in these. These data, together with the total replacement capacities and the replacement capacities of the organic fraction of these soils, are given in Table XI. Alfalfa meal was also included in the samples analyzed. Total replacement capacity was determined by the saturation capacity for calcium from neutral calcium acetate. The organic replacement capacity was determined as that part of the total replacement capacity destroyed by digestion with 15-percent H_2O_2. Lignin and cellulose were determined by the methods outlined by Waksman (15), while the hemicellulose was determined by distillation with 12-percent HCl, as outlined in "Methods of Analysis A. O. A. C." The results are given in Table XI.

TABLE XI.—RELATION BETWEEN PERCENT CELLULOSE, HEMICELLULOSE, AND LIGNIN AND THE REPLACEMENT CAPACITY OF SOILS.

Sample	*M. E. total rep. cap.	M. E. organic rep. cap.	Percent lignin	Percent hemicellulose	Percent cellulose
Alfalfa	58	23	5.26	10.67	13.23
Soil No. 2	186	154	49.62	1.00	1.38
Soil No. 6	34	18	1.80	.28	Trace
Soil No. 13	54	23	5.21	1.09	.49
Soil No. 17	158	133	41.97	4.04	5.04
Soil No. 19	127	109	37.97	1.19	.64

*M. E.—Milliequivalent replacement capacity per 100 grams.

One of the first observations made during our study of the base exchange properties of organic matter in soils was that there appeared to be a linear relationship between the total replacement capacity and the carbon content of highly organic soils. Also, that the loss in replacement capacity which they suffered on digestion with 15-percent H_2O_2 was a linear function of the carbon lost. So, in selecting the soils for

lignin, cellulose and hemicellulose determinations, they were selected relative to representative points on the linear curve.

It will be noted from Table XI that we again meet this same linear relationship. This time between the lignin content of the soil and its organic replacement capacity. It is of especial interest that this holds true for lignin in alfalfa and the replacement capacity of this material. The data are shown graphically in figure 7.

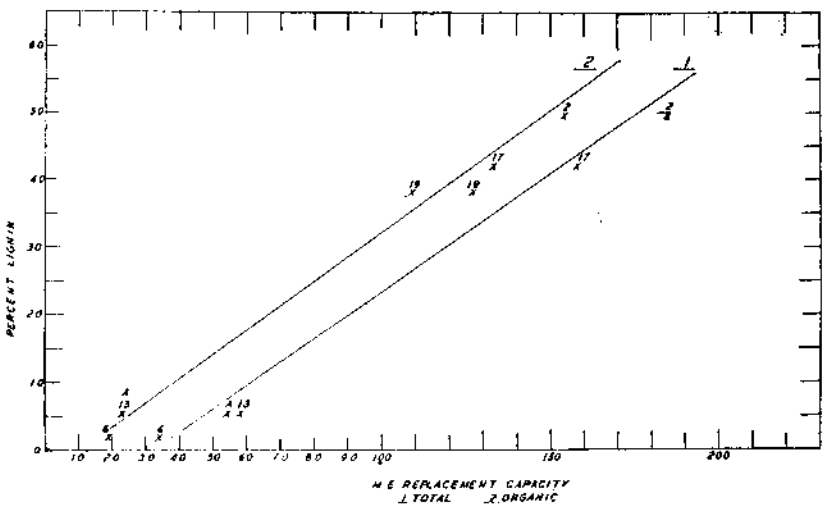

Fig. 7.—Relation between the percent lignin in soils and organic matter and replacement capacity.

Turning to the cellulose and hemicellulose content of these soils and the alfalfa, we find no relationship existing between these constituents as determined, and replacement capacity. This tends to emphasize the role and properties of lignin-like bodies in soils and raw plant materials which have been evident throughout this work.

DISCUSSION

The subject matter of this bulletin deals with so many different phases of the exchange reaction of organic matter that it seems necessary to clarify the whole with a brief general discussion of our investigations.

In our previous publication (9), the following outstanding observations were made: (1) a linear relationship exists between the exchange capacity of organic soil types and their carbon content; (2) a similar relationship exists between the organic matter in soils which is destroyed

by digestion with H_2O_2, and the loss in replacement capacity from this reaction; (3) the discovery of a base exchange property for lignin and lignin-like bodies in soils, which is just as great, if not greater, than the exchange capacity of bentonite clays, and (4) that all reactions in the above take place in chemically equivalent proportions.

In attempting to evaluate the role which lignin plays in the exchange property of organic matter, one must recognize that more or less uncertainty exists regarding the chemical composition of lignin, at least that its composition is variable and depends upon the source. Also, there is considerable evidence that it may exist as an organic complex combined with one or more similar organic compounds. This is suggested by the fact that we found a very high exchange capacity for synthetic humus prepared from several carbohydrates, namely, sucrose, xylan, and cellulose. By the reactions employed, they may yield lignin-like compounds by a condensation of complex furfuraldehyde molecules. If lignin is built up in this manner by decomposition reactions in soils it must necessarily follow that the exchange capacities of the organic fraction will be extremely variable. The separation of lignin from 11 different soils proved this to be true, as shown by a variation of from 38 to 178 M. E. per 100 grams of lignin. Further evidence of this variable composition of lignin was shown by the fact that on treatment with HCl, the base exchange capacity was greatly increased. In one case this increase amounted to 120 M. E. per 100 grams. This same property was observed for lignin from corn cobs and alfalfa, as well as for soil lignin.

The amount of lignin dissolved from soils by alcoholic NaOH represents only a very small percent of that actually present. Solubility in aqueous NaOH is much greater, and this is still further increased if solution is aided by steam pressure. It was surprising to note that the exchange capacity of lignin extracted by aqueous NaOH solution was several times that extracted by alcoholic NaOH. In the former case, to cite one example, 409 M. E. were found as compared to 38 in the latter, or a difference of 371 M. E. While we recognize that aqueous NaOH has more complete solvent properties than alcoholic NaOH and dissolves the hemicelluloses as well as the lignin, we failed to find sufficient exchange capacity in the latter, as represented by xylan, to account for this difference. Two explanations of this phenomenon suggested themselves. First, it is possible that lignin exists in soils as a complex insoluble in alcoholic NaOH, but soluble or broken down into its component parts by aqueous NaOH. Second, it is possible that by a reaction with the aqueous NaOH, possibly hydrolysis, the solubility of lignin-like bodies, as well as the exchange capacity of lignin, may be increased. The

latter is suggested by the fact that the increase in replacement capacity of the aqueous soluble lignin is not so great as that of the alcohol-soluble lignin when subsequently treated with HCl. All our evidence indicates that the replacement capacity of lignin increases as the organic fraction passes through the successive stages of decomposition in soils. Attention is called to the 36 M. E. exchange capacity for corn cob lignin, of 100 M. E. for alfalfa lignin, and a range in variation of from 38 M. E. to 178 M. E. for soil lignin. The lower-capacity lignins from soils appear to represent the less altered forms of lignin.

As an example let us refer to the composition of the lignin and ligno-humate fractions from fresh alfalfa and from soils. The replacement capacity of lignin from the former (alcoholic NaOH soluble) is 100 M. E. while the capacity of ligno-humate (aqueous NaOH soluble) is 107 M. E. There is practically no difference between these two figures. On the other hand as already stated the difference between lignin and ligno-humate from soils is very great. In one soil this amounted to 371 M. E. (38 M. E. for the lignin and 409 M. E. for the ligno-humate).

Additional evidence which we have obtained further points to this exchange property as being a true chemical reaction. Like the zeolite of bentonite clays and soil colloids, and the synthetic inorganic exchange compounds, they exhibit the property of ionization, of hydrolysis, the common-ion effect, and will absorb basic fuchsine dye in a form replaceable by the base of a neutral salt solution. Of equal importance, we found a linear relationship existing between the lignin content of the organic matter, as quantitatively determined, and the exchange capacity.

Throughout the investigations described in the preceding discussion we became more and more convinced that, since lignin and lignin-like bodies were present in all plants, raw plant materials should possess the property of base exchange. Following this line of reasoning and using alfalfa, the principal soil-building crop of the Southwest, we found that this was actually true. And, further, we found that its exchange capacity was highly resistant to the biological and chemical reactions involved in the decomposition of organic matter, and was therefore higher for the material after fermentation than for the fresh material.

We were surprised to find, on digesting the raw plant material with H_2O_2, that a large part of the exchange capacity was not destroyed. While there is always present in plants appreciable amounts of the inorganic elements, such as silica, alumina, and the bases which go to make up the inorganic zeolite molecule, no one thus far has ventured the suggestion that they may be combined, in plants, to form zeolite-like compounds. While we are unable at this writing to affirm or deny this, from our own investigations we have shown that the organic exchange

compounds in fresh plant material are not readily destroyed by digestion with H_2O_2.

As we have already shown, the variation in exchange capacity, both in lignin and ligno-humate, is a function of the phenolic hydroxyl groups in the molecule. There is much to lead us to believe that for each phenolic hydroxyl group an exchange capacity of 100 M. E. is imparted to the complex provided the active bond of the group is free to react. In other words the lignin complex exists in nature largely combined with carbohydrates and this linkage takes place through the phenolic hydroxyl groups which function in base exchange reactions. When combined with carbohydrate the complex does not ionize and cannot therefore function in base exchange reactions. As the carbohydrates are removed by chemical and biological reactions, such as we have demonstrated in our experiments, the phenolic hydroxyl groups are rendered free to act and the exchange capacity of the complex increases accordingly.

The exchange capacity is lowest in raw organic materials. Judging by the small amount of lignin extracted from soils and plant materials by alcoholic NaOH and the greater solubility in aqueous NaOH, where complete solubility is obtained only at relatively high temperature and pressure, we are led to believe that lignin is not similarly combined in all cases. The nature of this linkage has been studied by Phillips and others. To quote Phillips (10), "Data obtained on the fractional extraction of the lignin from corn cobs indicate that the lignin is dissimilarily combined with carbohydrates. The assumption that all of the lignin is combined with the carbohydrates either as an ester or an ether is unwarranted as far as the lignin from corn cobs is concerned. It is believed that both types of linkage are present, which explanation would account for the fact that only a part of the lignin may be removed from corn cobs by alcoholic sodium hydroxide solution even after exhaustive extraction." Our experiments indicate that either a small amount of free lignin does exist in raw plant material as shown by the exchange capacity of ground alfalfa or that in the lignin-carbohydrate complex some free phenolic hydroxyl groups are present and active in base exchange.

The difference between the exchange capacity of lignin and ligno-humate from soils indicates that either the lignin complex exists in two different forms, a dibasic and a tetrabasic, or that it is unequally combined with carbohydrates. In the one case solubility is complete in alcoholic NaOH while in the other a more exhaustive treatment, digestion with aqueous NaOH, is necessary to obtain solubility or to split off the combined carbohydrate. Phillips (10) in commenting upon the difference in solubility of corn cob lignin says: " * * * part of it is loosely

bound, possibly in the form of an ester, and the remainder is more firmly held, probably in the form of an ether-like combination."

We feel our observation that green manure adds greatly to the base exchange capacity of soils is of considerable economic value to agronomic practice. In addition, we feel that this property of raw plant material opens up a new phase of plant physiology which, while slightly foreign to the subject of this bulletin, should be briefly mentioned here. If raw plant materials possess the property of base exchange, and we have proved this to be true, may not this property exert an influence on the nature and ratio of bases present in the sap of plant cells, as well as that fixed in forms for storage within the plant? If the presence of compounds capable of base exchange reactions in the cell wall of the plant could be demonstrated, one could easily visualize the important relationships which these would hold to cell wall permeability, as well as to many other physiological processes.

While there are, besides the lignins and hemicelluloses, several compounds present in plants which offer potential possibilities, we have not studied these as yet. Notable among these are the highly collodial pectin bodies, the lipoids, and the proteins. Thus far all of our evidence indicates that proteins are not involved, yet Gortner and Hoffman (6) have demonstrated a binding power of proteins for alkalis and acids at rather definitely defined hydrogen-ion concentrations. On the other hand, we believe that a possibility exists of lipoids and pectins possessing such base exchange properties. Work upon these and other phases of the problem is being continued in our laboratory.

SUMMARY

1. The exchange capacity of the lignin present in soils is not a constant quantity but varies in different soils.

2. The same is true for "ligno-humates" although the range of variation is not so great.

3. The aqueous-alkali-soluble "ligno-humate" has a much higher exchange capacity than the alcoholic-alkali-soluble lignin. The average for the former, in ten soils, is 382 M. E. and the latter 116 M. E. per 100 grams.

4. Leaching the lignin and "ligno-humate" with hydrochloric acid increases the exchange capacity, probably by hydrolysis.

5. The quantity of lignin extracted from soils by alcoholic alkali represents a comparatively small percent of that actually present. Maximum solubility may be obtained by digesting with aqueous alkali at increased pressures.

6. Titration of lignic acid (hydrogen-saturated lignin) and ligno-humic acid (hydrogen-saturated "ligno-humate") with potassium hydroxide and barium hydroxide indicates that the lignin molecule is dibasic, and "ligno-humate" tetrabasic.

7. The absorption of the base of an acetate by lignin is equal to that required as hydroxide to neutralize the hydrogen-saturated salt.

8. Ionization of the acid and basic salts of lignin and "ligno-humates" was determined by measuring the conductivity of their respective solutions at several dilutions.

9. The sodium and potassium organic complexes show rather high ionization, while those of calcium, barium, and hydrogen are very low.

10. The effect of a common ion on ionization and base exchange in organic matter was studied.

11. The influence of a common ion upon replacement by another base is appreciable but, except for calcium, it is less outstanding than in inorganic zeolites.

12. Xylan exhibits, to a slight degree, the property of base replacement, but this is not of sufficient magnitude to account for the greater exchange capacity of the "ligno-humate" as compared with lignin.

13. Synthetic humus, prepared from xylan or cellulose, like that prepared from sucrose, yielded materials with rather high base-exchange capacities.

14. Xylan, lignin, and "ligno-humate" absorbed color from basic fuchsine solution, and this color was replaceable by the base of a neutral salt solution.

15. Green manure (ground dry alfalfa) shows an appreciable base exchange capacity, a large part of which is not easily destroyed by digestion with H_2O_2.

16. The base exchange capacity of ground alfalfa was increased fourfold by spontaneous decomposition.

17. Just as in the case of soils, the extraction of ground alfalfa with alcoholic or aqueous sodium hydroxide yields a lignin of high base exchange capacity.

18. The lignin content of organic matter and highly organic soils is a linear function of the base exchange capacity, while there is no relationship between hemicellulose or cellulose and the exchange capacity.

19. All our investigations show that the exchange capacity of the organic fraction increases as the organic matter passes through successive stages of decomposition in the soil.

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