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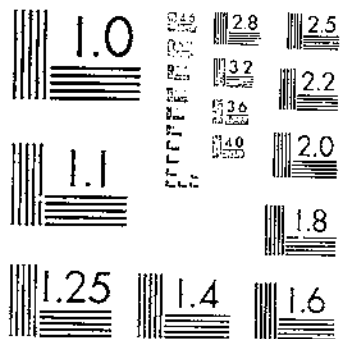
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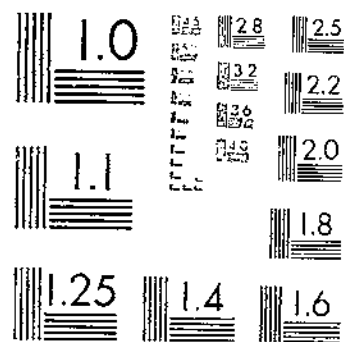
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UNITED STATES DEPARTMENT OF AGRICULTURE  
WASHINGTON, D. C.

THE DECOMPOSITION OF HYDROLYTIC  
PEAT PRODUCTS INCLUDING  
AMMONIATED PEAT

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INTRODUCTION

Numerous studies have been made on the decomposition of various materials by soil microorganisms. Considerable information is available concerning the decomposition of fresh plant material added to the soil as green manure, and it has been found that such material undergoes rapid decomposition. This is presumably because it contains relatively large proportions of readily decomposable substances consisting chiefly of simple and complex carbohydrates, amino acids, certain proteins, etc. Such decompositions are apparently accompanied by an increase of the proportions of ligninlike materials in the residues.

The behavior of peat when incorporated in the soil is quite different from that of fresh plant material. This perhaps may be expected in view of the fact that its composition differs greatly from that of its parent plant materials. A partial decomposition has already occurred, the extent of which is dependent upon a number of factors in the formation, such as type of plant material, climate, water level, etc. In general, the predominating portion of a peat consists of ligninlike material and this may be expected to retard its rate of decomposition. Lignin, as a constituent of plant material, is usually considered to be very resistant to microorganisms and for this reason it is believed to become an increasingly larger fraction of partly decomposed materials. Phillips and his associates (19)<sup>1</sup> have recently shown, however, that lignin may decompose quite rapidly under certain conditions.

<sup>1</sup> Italic numbers in parentheses refer to Literature Cited, p. 31.

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In a previous study of peat profiles (8) it was demonstrated that peat from various sources contains appreciable quantities of carbohydrates, such as cellulose, hemicellulose, etc., which have not disappeared in the formation of the peat, and therefore should be subject to fermentation under proper conditions. As the partial review of the literature, which follows, indicates, such decomposition to any notable degree has not been demonstrated. It seemed highly desirable to make a detailed study of the problem with the object of finding the conditions under which decomposition most readily occurs, if possible. This problem is the more important since peat is now used as a soil conditioner and as a component of fertilizers. A study such as was contemplated might be expected at least to throw light upon the behavior of peat in the soil and furnish a better basis for its evaluation. If any reasonably attainable conditions could be found under which peat will function as an ordinary green manure, the enormous stores of it in nature would become available as a source of supply of soil organic matter.

In the course of the investigation various heat treatments were employed and one of these, autoclaving the peat with ammonium hydroxide, proved of unusual interest. Accordingly, a special study of the product and nature of this reaction was included. During the progress of the research it developed that Davis and Scholl, of the Fertilizer and Fixed Nitrogen Investigations unit of the Bureau, had been studying the product obtained by treatment of peat with liquid ammonia, with a view to the development of an organic carrier of nitrogen. Further study of ammoniated peat for fertilizer purposes is being carried on by them.

The material so produced has interesting physical properties and a very high nitrogen content. Hence it seemed desirable to determine both by chemical methods and by pot tests the availability of the added nitrogen when the material is used as a nitrogenous fertilizer.

#### REVIEW OF LITERATURE

A review of the literature reveals a number of studies of the decomposition of peat which may be summarized briefly.

There is no trace of fermentation of peat either in the presence or absence of nutrient solutions, whereas cellulose, wood, and paper ferment under certain conditions, according to observations made by Schrader (25).

Peat is the seat of retarded biological activity in its natural state, as demonstrated by Demolon and Boisshot (3). They found only slight differences in the carbon dioxide evolution of inoculated and uninoculated samples. The peat responds somewhat to neutralization by lime and also by previous heating to 100° C. for a short time.

Melin, Norrbin, and Odén (18) found that the fermentation of untreated peat inoculated with sludge was very slow but was increased considerably by addition of 0.05 to 1 percent calcium acetate. The gas composition was found to be 62 to 78 percent methane and 30 to 13 percent hydrogen. Only cellulose, hydrocelluloses, pentosans, and hexosans, but not the humic acids or lignins were attacked.

According to Kissling and Fleischer (14, p. 887), decomposition processes are more active in a low-moor than in a high-moor peat, as indicated by the carbon dioxide content of the soil air in each case.

Addition of burned lime to moss peat (12, p. 906) gave an average value over several months of 3.91 grams of carbon dioxide calculated on the basis of 1,000 liters of soil air compared with 1.64 grams for untreated peat. Addition of calcium carbonate, calcium sulphate, potassium chloride, or kainit had less effect than the burned lime.

Schmidt (22) states acid hydrolysis of peat followed by neutralization with calcium carbonate reduces the resistance to bacterial attack.

Wollny (32, p. 289) compared the carbon dioxide evolution from untreated peat with that from peat extracted with ether alcohol. The latter gave approximately twice the quantity of carbon dioxide. Addition of a nutrient solution (32, p. 118) to a sample gave 8.6 volumes of carbon dioxide compared with 6.8 volumes for untreated peat. Another sample (32, p. 253) was boiled with hydrochloric acid, filtered and its decomposition compared with a sample boiled with water only. The values obtained for carbon dioxide were 8.037 volumes and 35.904 volumes, respectively, over a period of 5 days. A lime humate (32, p. 267-268) was prepared by treatment of peat with alkali solution, at room temperature, filtered, and the filtrate treated with calcium chloride. The precipitated material was filtered, washed, and dried for the experiment. Decomposition of the material was compared with humic acid prepared as above but precipitated with hydrochloric acid instead of calcium chloride. The lime humate yielded 16.1 volumes of carbon dioxide, whereas the humic acid gave 8.9 volumes over an 11-day period.

Vandecaveye (27) treated a virgin woody-sedge peat with sterilized and unsterilized manure, wheat straw, superphosphate, sodium nitrate, and lime. The beneficial effect of stable manure was explained as being due to the readily available carbon and nitrogen compounds in the manure which are of greater importance than the microflora. The addition of lime greatly stimulated carbon dioxide production but the addition of superphosphate or sodium nitrate caused no material increase in the activity.

Waksman and Purvis (30) studied the effect of varied moisture content on the decomposition of saw-grass peat. Samples were taken from a cultivated field up to 75 centimeters in depth and were incubated for periods up to 560 days. The carbon dioxide evolved accounted for the greater part of the loss in weight; and the optimum moisture content was found to be 50 to 80 percent. The total dry matter decomposed calculated from the carbon dioxide ( $C \times 1.8$ ) varied from 4.3 to 18.3 percent over the period of 560 days, the actual loss in weight of the peat varying from 8.8 percent to 24.6 percent. Other samples of peat (surface 30-centimeters layer) from a different locality gave values ranging from 4.9 to 45.7 milligrams carbon dioxide recalculated to a basis of 1 gram of dry peat over periods of 54 and 58 days, respectively, with varying moisture contents. Drying and then remoistening peat greatly stimulated the decomposition.

Waksman and Purvis (29) also compared the effect of toluene, ether, and 2 percent hydrochloric acid extractions on the decomposition of saw-grass peat which was increased by all of the treatments and to the greatest extent by ether extraction which gave a value roughly five times the value of untreated peat over a period of 20 days. Addition of nutrients did not increase the carbon dioxide evolution of sphagnum moss peat, but the rate of decomposition was

increased by extraction with 4 percent sodium hydroxide and 2 percent hydrochloric acid to the extent of more than twice the original rate.

Bedford (2) found that nutrients added to sphagnum peat caused relatively small increases in carbon dioxide evolution. Uninoculated samples, in general, gave somewhat lower values for carbon dioxide than inoculated samples, but in some cases the reverse was true.

Powers (20) determined the total loss in weight of sphagnum and saw-grass peats in composting over a period of 4 months. Sphagnum peat with distilled water lost no weight but with nutrients consisting of 3 percent  $\text{CaCO}_3$ , 2 percent  $\text{NH}_4\text{NO}_3$ , and 2 percent  $\text{K}_2\text{HPO}_4$ , a loss of 12 percent was observed. Saw-grass peat with nutrients lost up to 20 percent of its dry weight but "neither inoculation nor drainage gave significant results."

The patent literature abounds with methods for the conversion of peat into a fertilizer by various means, such as heat treatment, neutralization, mixing with sewage or other effluents, addition of salts, or by bacterial inoculation. Included among these are several recent patents (5, 6, 7) for the use of pressure treatment with ammonia at temperatures ranging from  $200^\circ$  to  $300^\circ$  C.

Walton and Gardiner, of this Bureau, have recently been granted a patent (31) for the production of a fertilizer containing a substantial percentage of peat in which the insoluble organic nitrogen is of satisfactory activity. The process comprises a preliminary drying and heating of the peat, followed by incorporation with a hot melt of monopotassium phosphate and phosphoric acid, at a temperature of  $200^\circ$  C., with a subsequent digestion, cooling, and neutralization with ammonia.

Other investigations having a relation to the present study and dealing with the effectiveness of peat as a fertilizer include the following references.

Fertilizer experiments (9) with millet, using raw peat as a source of nitrogen, compared with other sources, showed approximately 10 percent increase in yield of straw over the soil check as compared with 68 percent for cottonseed meal, 71 percent for blood, and 91 percent for ammonium sulphate. Peats, in both limed and unlimed condition, were compared with stable manure in a series of pot experiments with a poor sandy soil (11, p. 172). It was found that 2.6 parts of nitrogen in manure were as efficient as 100 parts of nitrogen in limed low-moor peat. The efficiency of the peat was somewhat less when lime was not used.

Drying a peat at elevated temperatures produced increasing amounts of soluble nitrogen, according to Tacke, as cited by McCandless (17), who found 1 percent of the nitrogen dissolved at  $104^\circ$  F., 6 percent at  $194^\circ$  to  $212^\circ$ , 10 percent at  $1\frac{1}{2}$  atmospheres pressure, and 16 percent at 3 atmospheres pressure.

Lipman and Wank (15) treated peat with sulphuric acid and also with sulphuric acid and steam under 25 pounds pressure, but the product was of practically no value as a source of available nitrogen when used in a soil.

Logvinova (16) composted a high-moor peat with a raw phosphate (phosphorit) and found that 25 percent of the total phosphoric acid was converted to a water-soluble form, whereas low-moor peat did not increase the solubility of the phosphate.

## DECOMPOSITION OF PEAT

## METHODS AND APPARATUS

The course of decomposition of soil organic matter may be followed, with fair accuracy, by measurement of the rate and extent of evolution of carbon dioxide (28, p. 124; 26, p. 294). Estimation of the rates of formation of ammoniacal and nitrate nitrogen are also useful, particularly in determining the changes in the character of the nitrogen in the material undergoing decomposition. These methods were employed in this investigation.

The samples of peat or peat product used in the series of experiments were mixed with soil and allowed to decompose for a period of 30 days at room temperature. All the samples were used with the same relative moisture content which was 50 percent of the water-holding capacity, a quantity determined separately for each material.

The apparatus used for the collection and determination of carbon dioxide evolved by the samples is essentially as has been described by

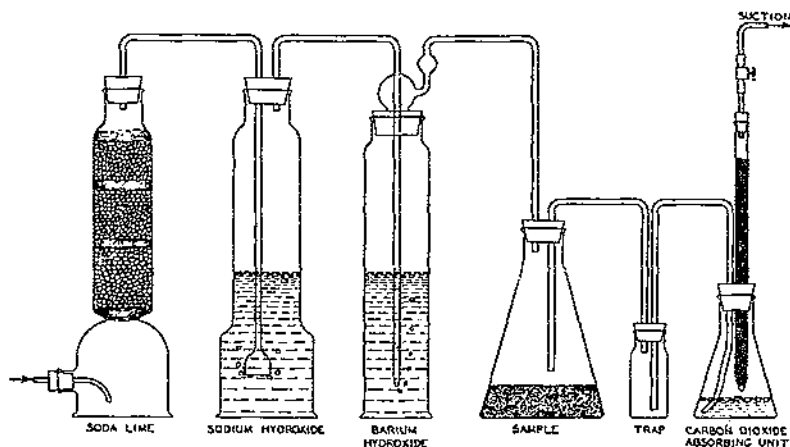


FIGURE 1.—Diagram of apparatus used for the collection and determination of carbon dioxide.

Heck (10). A single unit is shown in figure 1. These units were set up in batteries, abreast, so that a slow current of air, freed from carbon dioxide by the absorbent towers, was drawn over a dozen samples at one time. The samples were placed in 750 cc Erlenmeyer flasks, and the issuing air bubbled through a suitable quantity of 0.5 N sodium hydroxide in a 250 cc flask and thence through a bead tower for complete absorption of the carbon dioxide.

The quantities of carbon dioxide evolved from each sample for any given period were determined by adding to the sodium hydroxide solution an excess of neutral barium chloride solution and titrating the residual sodium hydroxide. All joints and connections in the apparatus were carefully sealed with shellac or paraffin throughout each experiment. The aeration of the flasks containing the samples was continuous for all samples for the periods indicated and the determinations of the carbon dioxide were made periodically.

Nitrogen, in the form of nitrate, was determined in the soil and peat mixtures by the use of the zinc-copper couple reduction method,



essentially as described by Scales (21). The method was varied somewhat, depending on the quantity of nitrate nitrogen present. In cases where very small quantities of ammonia were evolved in the reduction, corresponding to small quantities of nitrate, Nessler's reagent was used to determine ammonia, whereas, for larger quantities, titration was made in boric acid.

A suitable sample for nitrate determination was shaken up with 400 cc of water, using alumina cream as a clarifying agent for the soluble organic matter. The mixture was allowed to stand for a time, after 0.5 to 1 cc of chloroform had been added to prevent bacterial action on the nitrates. A 200 cc aliquot portion of the filtrate was used in the determination after discarding the first 50 to 100 cc passing through the filter paper to avoid any loss of nitrate due to retention by the filter paper. This method was quite satisfactory and appeared to be accurate within limits of 2 to 5 parts per million of nitrate nitrogen, depending on the quantity present and the size of sample used.

Ammoniacal nitrogen in the samples was determined by distillation with magnesia and total nitrogen by the Kjeldahl-Gunning-Arnold method (1). The hydrogen-ion concentration was determined by means of the hydrogen electrode and the results supplemented in certain doubtful cases by the quinhydrone method.

#### PREPARATION OF SAMPLES

Since it was one of the objects of the investigation to find some condition or treatment through which peat might be induced to function in the soil as an organic manure, the various kinds of peat were investigated in the raw condition and after various treatments as indicated below.

#### RAW CONDITION

The samples used consisted of a profile of saw-grass peat from Belle Glade, Fla., previously described (8); sphagnum-moss peat (surface layer) obtained from South Lubec, Maine, through the courtesy of A. P. Dachnowski-Stokes; an imported sphagnum-moss peat obtained from Pennrich & Co.; a heath peat (surface layer) from Beaufort, N.C., previously described (8); fresh saw-grass tops and sweetclover. All the samples were air-dried and the peats were ground to pass a 1-mm mesh sieve. The saw-grass tops and sweetclover were cut up fairly fine instead of being ground. The soil used in the decomposition was the surface horizon of the Chester series, as found in the vicinity of Falls Church, Va., which had also been air-dried and passed through a 2-mm mesh sieve. The sweetclover was mixed with soil in the proportion of 2 to 150 g of soil and the other materials in the proportion of 10 to 150 g of soil, except where otherwise specified.

#### ALCOHOL AND ETHER-ALCOHOL EXTRACTION

The surface layers of Florida saw-grass peat and Maine sphagnum-moss peat were used. Portions of each (12 g) were refluxed for 5 hours with about 200 cc of alcohol, followed by filtering and washing. The residues were dried, reground to pass a 1-mm mesh sieve, and used in the proportion of 10 g of peat to 150 g of soil for the

determination of the rate of decomposition. Ether-alcohol extractions were made similarly on samples of the same peats. Filtrates were discarded in all cases, only the insoluble residues being used for experiment.

#### TREATMENT WITH WATER

Saw-grass peat was heated in a high-pressure autoclave with water for 6 hours at 150° C. One hundred grams of peat were used with 1,700 cc of water in the heating. One gram of the evaporated material was mixed with 50 g of soil for decomposition. In preparing this material an autoclave of cast iron was employed, as was also the case in other heat treatments where larger quantities of material were required than could conveniently be prepared by the use of Carius or sealed combustion tubes.

#### ACID TREATMENT

Ten-gram samples of sphagnum-moss peat, heath peat, and saw-grass peat were treated with 150 cc of 3 percent sulphuric acid. The solutions were boiled for 5 hours then filtered and the filtrate nearly neutralized with CaO. The precipitated CaSO<sub>4</sub> was filtered out and the resulting filtrate recombined with the insoluble peat residue which was then completely neutralized with CaO, evaporated to dryness and reground to pass a 1-mm mesh sieve.

Saw-grass peat was treated with concentrated sulphuric acid in the cold and also at the temperature of the steam bath for approximately 18 hours. Sufficient of the concentrated acid was added to 15-g samples to moisten the entire mass thoroughly. About 7 cc of acid was used in each case. Subsequent to digestion 1 sample of each treatment was neutralized with lime, 1 with ammonium hydroxide, and 1 of each was diluted with water and filtered. The residues in the last case were neutralized with a small quantity of lime. Each sample was then air-dried and amounts corresponding approximately to 10 g of the original material were mixed with 150 g of soil.

Samples of saw-grass peat and sphagnum peat were treated with 40 percent hydrochloric acid at 150° C. and at room temperature. Pyrex combustion tubes of the Carius type were used for the high-temperature work. Samples of saw-grass peat weighing 2 g were placed in pyrex combustion tubes with 30 cc of the fuming acid in each and sealed. A temperature of 150° was maintained by means of an electric furnace for approximately 3 hours. Sphagnum peat was treated similarly except that smaller samples had to be used because of the bulk of the peat and the necessity for as much free circulation of liquid as possible.

In the case of the cold treatment with 40 percent hydrochloric acid, 10 g each of saw-grass peat and sphagnum peat were treated with 200 cc of the acid in a flask and left stoppered overnight. Most of the strong acid was removed under reduced pressure and the remainder evaporated at a temperature not exceeding 50° C. One gram of CaO was added to each sample, a few cubic centimeters of water added, thoroughly mixed, and again evaporated to dryness. Amounts corresponding to 3 g of the original samples were used with 50 g of soil.

Calcium bisulphite solution was used in a manner corresponding roughly to the practice of the paper industry for removing lignin in

the manufacture of wood pulp (13). The solution, as made up, contained approximately 4 percent of free sulphur dioxide and 1 percent of sulphur dioxide combined with lime. Saw-grass peat and sphagnum peat were treated with somewhat varied quantities of calcium bisulphite solution in sealed combustion tubes. The temperature was 130° to 140° C. and the time of heating an average of about 4 hours. The solutions were filtered after heating and the soluble and insoluble matter of each peat was used separately on mixing with soil. One to three grams of material were used with 50 g of soil.

#### TREATMENT WITH BASES

Lime was added to raw peat in the amount of 5 percent CaO and the mixture was mixed with the soil in the proportion of 10 g peat to 150 grams of soil. The same procedure was carried out with the heath peat except that 9 percent of CaO was used because of its more highly acid condition.

A steam distillation in the presence of CaO was carried out with 12-g samples of saw-grass peat and sphagnum peat. One gram of CaO was used with 150 cc of water and the mixtures were distilled for 5 hours after which they were filtered and the filtrates discarded. Ten grams of the insoluble material were used to mix with 150 g of soil.

A 12-g sample of heath peat was boiled with 500 cc water and 10 cc of concentrated  $\text{NH}_4\text{OH}$  for 5 hours. A second addition of ammonia was made after the odor of the first portion had disappeared. The entire mixture was evaporated to dryness and 10 g used with 150 g of soil.

Other samples of saw-grass peat were treated with varying amounts of CaO in a high-pressure autoclave for 3 hours at 150° C. The percentages of CaO used, based on the yields of final products, were 5.6, 11.6, and 25. One hundred and fifty grams of peat were used with 2,500 cc of water in the heating.

A sample of saw-grass peat was heated 3 hours at 150° C. in a sealed pyrex combustion tube with 20 cc of 20 percent NaOH per gram of peat. Concentrated hydrochloric acid was added to the mixture after heating, with subsequent dilution, and filtration. Washing was very difficult and the residue was evaporated to dryness, after which water was added and the residue again filtered and washed. This material contained considerable silica dissolved from the glass used in the heating. Three grams of the material were mixed with 50 g of soil. Solutions of 3 percent and 6 percent NaOH also were used on saw-grass peat and heated in pyrex tubes for periods of 3 hours at 150°. The amount of solution used in each case was 20 cc per gram of peat. The mixtures were filtered after heating and the soluble portions were used in mixing with the soil in the proportion of 1 g to 50 g of soil. It was found that 40.3 percent of the peat was rendered soluble by 3 percent NaOH and 74 percent by 6 percent sodium hydroxide.

Samples of saw-grass peat were heated with  $\text{NH}_4\text{OH}$  at varying temperatures, with varying concentrations and for varying periods of time both in the autoclave and in the pyrex combustion tubes. The treatment used for the samples on which the carbon dioxide evolution in soil was determined, however, was 20 cc of concentrated ammonium hydroxide per gram of peat, heated 6 hours at 150° C. Saw-grass

peat was also treated with ammonium hydroxide and potassium hydroxide.

The amount of peat used was 125 g with 1,250 cc of concentrated ammonium hydroxide, 7 g of potassium hydroxide, and 1,250 cc of water. The final product contained approximately 6 percent potassium hydroxide, or 5 percent expressed as potassium oxide, on the basis of the weight of the final product. This was mixed in the proportion of 1 g of peat material to 50 g of soil.

A mixture of ammonium hydroxide, potassium oxide, and Tennessee brown-rock phosphate was also autoclaved with saw-grass peat in a manner similar to that described for ammonium hydroxide and potassium oxide. The final product contained 5.9 percent phosphoric acid and 2.9 percent potassium hydroxide expressed as potassium oxide.

Samples of saw-grass peat, sphagnum-moss peat, and heath peat were refluxed with lime water for a period of 125 hours. An amount of calcium oxide was used with 20 g of peat in 425 cc of water such that the final percentage of calcium oxide in the peat was approximately 25. Another set of the samples were refluxed with a solution of 0.15 N potassium hydroxide for a period of 125 hours. The percentage of potassium hydroxide in the final product was approximately 1.8.

RESULTS

The results obtained by attempted fermentation of the samples, prepared as described, are assembled in table 1.

TABLE 1.—The decomposition of raw peat in soil and as affected by various chemical treatments

SECTION 1

UNTREATED (AIR-DRIED PREVIOUS TO USE)

Material used for composts	Description of treatment	CO <sub>2</sub> evolved	pH	Nitrate nitrogen		Ammoniacal nitrogen	
				Before decomposition	After 30 days	Before decomposition	After 30 days
		Mg per g		Parts per million	Parts per million	Parts per million	Parts per million
Chester soil.....	Blank, 150 g of soil.....	3.25	5.5	2	22	45	100
Do.....	Blank, limed (150 g soil plus ½ g CaO).....	3.95	7.4				
Florida saw-grass tops.....	No treatment.....	186		2	2		
Florida sweetclover.....	do.....	642		7	2		
Florida saw-grass peat:							
0-4 inches.....	do.....	10	5.1	31	130	62	244
32 inches.....	do.....	7	5.35	2	51		
63 inches.....	do.....	11	5.45	2	69		
80-88 inches.....	do.....	20	6.8	8	133		
0-4 inches.....	Cultivated in cabbage (previous to collection of samples).....	20	4.85	10	158		
Do.....	Cultivated in cabbage (previous to collection of sample; no soil added).....	9		204	426		
Maine sphagnum-moss peat.....	No treatment.....	13	4.7	2	9		
Imported sphagnum-moss peat.....	do.....	20	4.7	1	9		
North Carolina heath peat.....	do.....	24	4.8	2	37		

<sup>1</sup> 32 days' decomposition.

<sup>2</sup> 60 days' nitrate accumulation.

TABLE 1.—The decomposition of raw peat in soil and as affected by various chemical treatments—Continued

SECTION 2  
TREATMENT WITH ORGANIC SOLVENTS

Material used for composts	Description of treatment	CO <sub>2</sub> evolved	pH	Nitrate nitrogen		Ammoniacal nitrogen	
				Before decomposition	After 30 days	Before decomposition	After 30 days
Florida saw-grass peat.	Extracted with alcohol.	Mg per g 38		Parts per million 21	Parts per million	Parts per million	Parts per million
Do.....	Same sample, decomposition continued for second 30-day period, nutrients added.	4	5.1		170		
Do.....	Extracted with ether alcohol.	30		28			
Do.....	Same sample, decomposition continued for second 30-day period, nutrients added.	4	5.0		193		
Maine sphagnum-moss peat.	Extracted with alcohol.	30		2			
Do.....	Same sample, decomposition continued for second 30-day period, nutrients added.	20	4.85		94		
Do.....	Extracted with ether alcohol.	15		2			
Do.....	Same sample, decomposition continued for second 30-day period, nutrients added.	6	4.6		99		

SECTION 3  
TREATMENT WITH WATER AND ACIDS

Florida saw-grass peat.	Autoclaved with water at 150° C.	133	5.9	54	58	96	0.0261
Do.....	Hydrolyzed with boiling dilute H <sub>2</sub> SO <sub>4</sub> neutralized with CaO.	187	7.65	31	159		
Do.....	Treated with concentrated H <sub>2</sub> SO <sub>4</sub> (cold) neutralized with CaO.	118	6.15	7	145		
Do.....	Treated with concentrated H <sub>2</sub> SO <sub>4</sub> (hot) neutralized with CaO.	111	6.5	6	98		
Do.....	Treated with concentrated H <sub>2</sub> SO <sub>4</sub> (cold) filtered and neutralized with CaO.	36	5.45	3	24		
Do.....	Treated with concentrated H <sub>2</sub> SO <sub>4</sub> (cold) filtered and neutralized with NH <sub>4</sub> OH.	46	5.15	4	27		
Do.....	Treated with concentrated H <sub>2</sub> SO <sub>4</sub> (hot) filtered and neutralized with CaO.	39	5.3	2	37		
Do.....	Treated with 40 percent HCl (cold), some CaO added to residue.	313	7.0	6	15	104	566
Do.....	Treated with 40 percent HCl at 150° C. some CaO added to residue.	185	6.3	6	3	575	940
Do.....	Treated with Ca(HSO <sub>4</sub> ) <sub>2</sub> at 130° to 140° C. insoluble fraction (68 percent).	18	4.8	2	9		

1 32 days' decomposition.

TABLE 1.—The decomposition of raw peat in soil and as affected by various chemical treatments—Continued

SECTION 3—Continued  
TREATMENT WITH WATER AND ACIDS—Continued

Material used for composts	Description of treatment	CO <sub>2</sub> evolved	pH	Nitrate nitrogen		Ammoniacal nitrogen	
				Before decomposition	After 30 days	Before decomposition	After 30 days
Florida saw-grass peat.	Treated with Ca(HSO <sub>3</sub> ) <sub>2</sub> at 130° to 140° C. soluble fraction (32 percent).	Mg per g 103	5.0	Parts per million 29	Parts per million 40		
Maine sphagnum-moss peat.	Hydrolyzed with boiling dilute H <sub>2</sub> SO <sub>4</sub> , neutralized with CaO.	1234	7.95	1	2		
Imported sphagnum-moss peat.	do.	1264	7.95	1	2		
Maine sphagnum-moss peat.	Treated with 40 percent HCl (cold), some CaO added to residue.	362	6.3	2	1	59	112
Do.	Autoclaved with 40 percent HCl (cold) at 150° C., some CaO added to residue.	95	5.8	3	9	168	270
Do.	Autoclaved with Ca(HSO <sub>3</sub> ) <sub>2</sub> at 130° to 140° C., insoluble fraction (48 percent).	384	4.9	2	3		
Do.	Autoclaved with Ca(HSO <sub>3</sub> ) <sub>2</sub> at 130° to 140° C., soluble fraction (52 percent).	232	5.0	5	6		
North Carolina heath peat.	Hydrolyzed with boiling dilute H <sub>2</sub> SO <sub>4</sub> , neutralized with CaO.	1153	7.85	2	87		

SECTION 4  
TREATMENT WITH BASES

Florida saw-grass peat.	Raw peat with 5 percent CaO added.	32	7.3	31	179		
Do.	Steam distilled with CaO and filtered.	60		1			
Do.	Same sample, decomposition continued for second 30-day period, nutrients added.	13	7.4		194		
Do.	Refluxed 125 hours with approximately 25 percent CaO.	215	7.1	24	64	60	113
Do.	Autoclaved with 5.6 percent CaO at 150° C.	221	6.5	45	57	61	191
Do.	Autoclaved with 11.6 percent CaO at 150° C.	343	7.15	43	66	51	134
Do.	Autoclaved with 25 percent CaO at 150° C.	401	7.8	31	88	72	108
Do.	Autoclaved with NH <sub>4</sub> OH at 150° C., soluble fraction (52.8 percent).	492	6.1	65	58	611	804
Do.	Autoclaved with NH <sub>4</sub> OH at 150° C., whole sample.	337	6.1	59	58	341	560
Do.	Autoclaved with NH <sub>4</sub> OH and KOH (6.1 percent KOH).	348	6.3	49	66	239	389
Do.	Autoclaved with NH <sub>4</sub> OH, KOH, and rock phosphate (3.5 percent KOH, 5.9 percent P <sub>2</sub> O <sub>5</sub> ).	220	6.6	43	59	225	403
Do.	Autoclaved with 20 percent NaOH, precipitated with acid, and filtered.	161	5.9	2	9	83	242

<sup>1</sup>32 days' decomposition.

TABLE 1.—*The decomposition of raw peat in soil and as affected by various chemical treatments—Continued*

SECTION 4—Continued  
TREATMENT WITH BASES—Continued

Material used for composts	Description of treatment	CO <sub>2</sub> evolved	pH	Nitrate nitrogen		Ammoniacal nitrogen	
				Before decomposition	After 30 days	Before decomposition	After 30 days
Florida saw-grass peat.	Autoclaved with 3 percent NaOH (20 cc per g of peat); soluble fraction, 40.3 percent.	451	7.3	<i>Parts per million</i>	<i>Parts per million</i> 57	<i>Parts per million</i>	<i>Parts per million</i> 198
Do.....	Autoclaved with 6 percent NaOH (20 cc per g of peat); soluble fraction (74 percent).	488	7.6		47		160
Do.....	Refluxed 125 hours with 9 percent KOH (20 cc per g of peat).	265	7.3	20	57	05	85
Maine sphagnum-moss peat.	Steam distilled with CaO and filtered.	43		1			
Do.....	Same sample, decomposition continued for second 30-day period, nutrients added.	31	7.05		106		
Do.....	Refluxed 125 hours with CaO.	105	7.9	2	8	52	60
Do.....	Refluxed 125 hours with KOH.	215	7.9	2	10	57	42
North Carolina beech peat.	Boiled with dilute NH <sub>4</sub> OH.	94		4			
Do.....	Same sample, decomposition continued for second 30-day period, nutrients added.	25	5.35		209		
Do.....	Raw peat with 9 percent CaO added.	41		3			
Do.....	Same sample, decomposition continued for second 30-day period, nutrients added.	19	7.15		212		
Do.....	Refluxed 125 hours with CaO.	171	7.8	7	35	57	81
Do.....	Refluxed 125 hours with KOH.	175	7.7	7	14	60	49
Sulphite waste liquor.	Autoclaved with NH <sub>4</sub> OH.	311			24	51	474

The data in table 1, section 1, show that peat in the raw condition decomposes very slowly in soil as measured by carbon dioxide evolution, when compared with fresh plant material or when compared with peat that has been treated by certain chemical means (secs. 2, 3, 4). All decomposition periods were for 30 days unless otherwise indicated. Sweetclover yielded 642 mg of carbon dioxide per gram of material as compared with 10 mg for the 0- to 4-inch layer of saw-grass peat over a 30-day period. It was found possible greatly to increase the latter value by treatment with cold 40-percent HCl, autoclaving with lime, and autoclaving with ammonia when values as high as 313 mg, 401 mg, and 337 mg, respectively, were recorded for the same period of time. All the treatments used increased the rate of decomposition. Extraction with organic solvents had in general the least effect, whereas autoclaving at elevated temperatures with ammonium hydroxide or lime had the greatest effect. Duplicate determinations were found to check satisfactorily.

The acidity of the profile of saw-grass peat decreases with depth, and the rate of decomposition shows a tendency toward increasing,

but the actual increase is small and no particular significance can be attached to it in connection with the present data. The heath peat is more acid than the 0- to 4-inch layer of saw-grass peat but gives off 24 mg of carbon dioxide compared with 10 mg for the saw-grass peat. The results on the decomposition of raw peat are in general accord, insofar as they are comparable, with those of Waksman and Purvis (30), who showed that decompositions of the same order of magnitude occur when peats are subjected to aerobic bacterial fermentation, with or without addition of nutrients. The results obtained indicate no appreciable effect from the presence of relatively large quantities of a fertile soil. This is also in agreement with field experience in the use of peat even with addition of fertilizers. (Unpublished data on golf-green plots.)

The residual peat material after extraction with alcohol, and with ether-alcohol (table 1, sec. 2), shows a somewhat increased activity in evolution of carbon dioxide. This increase is not of great magnitude and is apparently temporary since continuation of the experiment for a second 30-day period, with addition of mineral nutrients, produced practically no additional evolution of carbon dioxide. Shive's nutrient solution was employed, which consists of 0.018 gram-molecular weight of potassium dihydrogen phosphate, 0.0052 gram-molecular weight of calcium nitrate, and 0.015 gram-molecular weight of magnesium sulphate per liter of water. These results are also in accord with those of Waksman and Purvis (30) and probably indicate that the slow rate of decomposition is owing to lack of available organic matter. Similar lack of effect of addition of nutrients was also found when peat in the raw condition was treated with lime and when steam distilled in the presence of lime.

The data presented in section 3 of table 1 offer several points of special interest. When peat is heated in an autoclave with water at 150° C., a marked increase in evolution of carbon dioxide takes place when the evaporated product is fermented with soil. A somewhat greater activity is shown by saw-grass and heath peat when digested with hot dilute sulphuric acid, with subsequent neutralization by lime, and a very markedly greater activity is shown by sphagnum peat.

When the saw-grass and sphagnum peats were treated with 40-percent hydrochloric acid in the cold, a like increase in the activity of the neutralized residue was observed, and again this was more marked for the sphagnum than for the saw-grass peat. Indeed, the rate of decomposition was the highest in this case for any of the acid treatments. For this reason the content of the reducing sugars in the samples was determined. For the saw-grass peat the value was 7.4 and for the sphagnum peat 11.9 percent. The quantity for the saw-grass peat corresponds roughly to the hemicellulose content, as reported in previous analyses (8), but is very much lower than was found for the sphagnum peat. It is obvious that acid hydrolysis, whether by water or by acids, is responsible for the conversion of peat material to fermentable form. However, the quantity of reducing sugars produced is neither quantitatively nor relatively sufficient to account for the large evolution of carbon dioxide and the differences shown by boiling sulphuric and cold concentrated hydrochloric acids. Whether the results are due to increased availability of cellulose or of protein matter is not apparent, though the alteration of the nitrogenous material seems to indicate the latter possibility.



When the peat samples are treated with either cold or hot concentrated sulphuric acid or heated at 150° C. with 40-percent hydrochloric acid, a marked decrease in fermentable activity is noted as compared with treatment by boiling dilute acid or cold treatment with 40-percent hydrochloric acid. This is more marked in the case of the hydrochloric acid. The fermentable material remaining is for the most part soluble, since the insoluble portion is still more inactive and for the sulphuric acid residue, at least, approaches the inactivity of the raw peat. The apparent cause of this difference is the alteration of the decomposable material similar to the "humification" of sugars by acids.

Since calcium bisulphite is used extensively in the paper industry to effect a separation of cellulose from lignin, it seemed probable that a like procedure with peat might be effective in making the cellulosic material available for bacterial action. The results in section 3 of table 1 indicate that the expected results were obtained. They also bring into sharp relief the marked difference in composition of the saw-grass peat and the sphagnum peat reported in a previous publication (8). In the sphagnum peat the ligno-humic complex is approximately 20 percent, while in the saw-grass peat it averages approximately 50 percent. It is also of interest to note that in the saw-grass peat the portion rendered soluble is active, while the insoluble portion, after treatment with bisulphite, is quite inactive. In the case of the sphagnum peat the insoluble fraction is more active than the soluble portion, both being relatively very extensively decomposed.

In table 1, section 4, the data concern the effect of treatment of peat with bases. The addition of calcium oxide to the peat in quantities insufficient to leave an excess of free calcium hydroxide had but small effect on the rate of decomposition. Steam distillation with subsequent filtration increased the rate of decomposition to a somewhat greater extent but still not markedly. The addition of Shive's nutrient solution was not effective in altering the rate. The results indicate that steam distillation removes no toxic material and that the failure of the peat fermentation is not due to a lack of inorganic food materials. When the peat is refluxed for long periods in the presence of calcium hydroxide, very marked hydrolysis is produced as indicated by the rate of fermentation. The effect so obtained was even greater than when the peat is heated with water at 150° C. (table 1, sec. 3). Autoclaving the peat with calcium hydroxide still further increased its rate of decomposition and, indeed, to a maximum greater than the best acid hydrolysis secured. The process of autoclaving with lime produced but small amounts of carbon dioxide from the peat, as is shown by the fact that even when 25 percent calcium oxide was used the carbon dioxide present in the dry product was but 3.5 percent.

In this case the pH value of the product was 11.4. Nevertheless, but little free hydroxide was present, since at the end of the fermentation period the pH value of the peat and soil mixture was 7.8 and the carbon dioxide was 0.08 percent, which corresponds to approximately 4 percent of the weight of the peat. It is therefore clear that no appreciable error in the estimation of the rate of decomposition is due to either retention or evolution of carbon dioxide by the added lime.

The various samples of peat were also refluxed for 125 hours with 9 percent potassium hydroxide solution with the result that the rate of decomposition of dry material produced was fairly rapid and approximately the same as by similar treatment with calcium hydroxide.

When saw-grass peat was heated with a 20 percent solution of sodium hydroxide, the residual material, after precipitation with acid and washing, had a rate of decomposition somewhat less than the product resulting from refluxing with lime water. Since soluble sodium salts were removed by the washing process, it may be assumed that the more easily decomposable material was lost. The peat was therefore treated with 3 and 6 percent solutions of sodium hydroxide and heated at 150° C. for 3 hours. This product was then leached with water and the soluble material obtained by evaporation. The rate of decomposition of this material was very rapid and in the 6 percent treatment involved the greater part of the peat since 74.0 percent was rendered soluble by this treatment.

The treatment of peat with ammonium hydroxide at the boiling temperature had but relatively little effect upon its rate of decomposition but when the peat was heated in a sealed tube, at 150° C., with an excess of ammonium hydroxide the dried residue showed an activity in soil in excess of any other material produced except that treated with 25 percent of calcium oxide. The portion of this material soluble in water had a rate of decomposition of the same order as the soluble portion obtained by treatment with 6 percent sodium hydroxide.

Examination of this sample showed it to contain 8.44 percent of nitrogen while the original sample contained but 3.88 percent. The percentage of nitrogen in the soluble portion was 11.51 percent. Nevertheless, only about 26 percent of this nitrogen was present in the form of ammonium salts, as shown by distillation with magnesium oxide. A special study of this material and combinations of it with other materials was therefore made. The details are given on page 17 et seq.

The fermentation rate of two of these products is included in table 1. These are the reaction products obtained by autoclaving peat with potassium hydroxide and ammonia and with these and rock phosphate. Also included in section 4 of the table is the result on the rate of decomposition of waste sulphite extract. This raw material is extremely resistant to bacterial decay. When digested with ammonium hydroxide it develops an activity comparable to that of peat treated with ammonia. This is particularly interesting as pointing to a possible utilization of this waste product.

In the series of treatments with bases the same general relations found with acid treatment are repeated. The increased activity is the result of hydrolysis. To what extent the fermentation affects the ligninlike, cellulosic, or nitrogenous material has not been ascertained. In general the soluble material is more active and the increased activity might therefore be ascribed to the decomposition of the salts of acidic decomposition products of the peat. Whether this is the case with the materials produced in the presence of calcium hydroxide is not clear, since the hydrolytic products are relatively insoluble. A minor consideration in this connection is the possibility that a portion of the carbon dioxide evolution results from a stimulation of

activity on the part of the soil organic matter<sup>2</sup> by reason of the addition of rapidly decomposing organic matter. This seems of little significance in comparison with the activity of the plant material (saw-grass tops) forming a part of the source of the saw-grass peat and with sweetclover when these react in the soil under like conditions. Figure 2 gives a graphic illustration of the relative rates of decomposition of some of these materials.

Table 1 also presents the pH values of the mixtures of peat and soil after the various carbon dioxide evolution periods. There seems to be no causal relation between these values and rates of evolution of carbon dioxide. Also, in table 1, are included those determinations which were made of the nitrogen present as nitrates or as ammonia before and after each period of fermentation. In general, it may be seen that in the case of raw peats or when the treatment used had little effect on the rate of decomposition there was a tendency toward

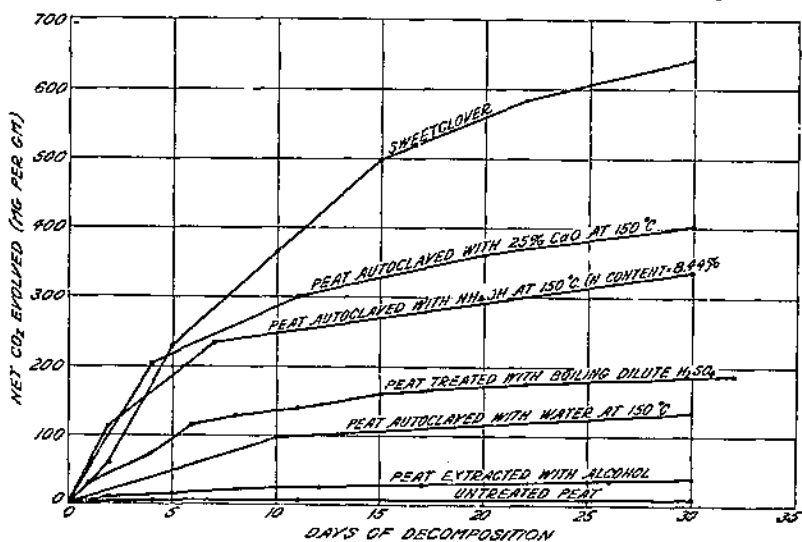


FIGURE 2.—Effect of various treatments on the rates of decomposition of peat as compared with the rate for sweetclover.

increase of nitrates. In the cases where the rate of decomposition is relatively rapid the results are not consistent. In a few cases there is a considerable increase; in the greater number of cases there is either no increase or it is very small. Moreover, there occurred an increase in nitrate content of the soil blanks. These facts make any definite conclusions impossible. It is also impossible to draw any definite inferences from the alteration of the ammonia content. In general, however, the treatments which resulted in relatively rapid decomposition also resulted in an increase of ammonia content before decomposition and a further increase as the decomposition proceeded.

The effect of various basic treatments of peat on the reaction of the resulting products, as determined by the hydrogen electrode, is given in table 2. The samples indicated in the table were taken from the same samples treated as previously described, and no further descrip-

<sup>2</sup> The soil contained 2.4 percent organic matter by the hydrogen-peroxide method.

tion is necessary. It will be seen that when saw-grass peat is autoclaved with ammonium hydroxide present, even with 5.1 percent potassium hydroxide and an excess of ammonium hydroxide, the product is still slightly on the acid side with a pH of 6.8 for the latter.

TABLE 2.—Effect of various treatments on the reaction of peat

Type	Treatment	pH
Florida saw-grass peat	None	6.30
Do	Autoclaved with water	5.10
Do	Autoclaved with $\text{NH}_4\text{OH}$	6.15
Do	Autoclaved with $\text{NH}_4\text{OH}+5.1$ percent $\text{KOH}$	6.80
Do	Autoclaved with $\text{NH}_4\text{OH}+3.5$ percent $\text{KOH}+17.4$ percent rock phosphate	6.85
Do	Autoclaved with 5.6 percent $\text{CaO}$	6.70
Do	Autoclaved with 11.6 percent $\text{CaO}$	7.80
Do	Autoclaved with 25 percent $\text{CaO}$	11.40
Do	Refluxed 125 hours with 25 percent $\text{CaO}$	10.40
Do	Refluxed 125 hours with 9 percent $\text{KOH}$	8.20
North Carolina heath peat	None	4.00
Do	Refluxed 125 hours with 25 percent $\text{CaO}$	9.15
Do	Refluxed 125 hours with 9 percent $\text{KOH}$	8.00
Maine sphagnum-moss peat	None	4.00
Do	Refluxed 125 hours with 25 percent $\text{CaO}$	8.35
Do	Refluxed 125 hours with 9 percent $\text{KOH}$	6.60

Similarly, the same peat autoclaved with 5.6 percent calcium oxide has a pH of 6.7 and does not become basic, with a pH of 7.8 until 11.6 percent lime has been used in the autoclaving. The use of 25 percent calcium oxide results in a product having a pH of 11.4. This sample contains 3.5 percent carbon dioxide which, calculated to the carbonate, is equivalent to 7.95 percent. Refluxing for a period of 125 hours with the same quantity of lime has approximately the same effect on the final pH as does autoclaving 3 hours at  $150^\circ\text{C}$ . The extent to which peat will take up lime has been shown previously by Schneider and Schellenberg (24), who found over 20 percent of calcium salts soluble in 5 N HCl after autoclaving a sample of peat with milk of lime from 2 to 4 hours at  $180^\circ$ .

The heath and sphagnum-moss peats apparently have a greater capacity for lime than has the saw-grass peat. This is as should be expected, since they are more acid. Their respective values for pH are 9.15 and 9.35 when refluxed with 25 percent calcium oxide for 125 hours.

### AMMONIATED PEAT

#### PREPARATION OF MATERIAL

Certain features of the reaction between peat and ammonium hydroxide and of the behavior of the product were of such interest as to warrant a detailed study. The nitrogen content of the residual product was from twofold to tenfold over that of the raw peat. The increased nitrogen was found to be contained for the most part in the portion of the peat rendered soluble by the reaction. The residue was capable of active and extensive decomposition in the soil. The increased nitrogen content was not, for the most part, present in the residue as ammonium salts since it was not removed by distillation with magnesium oxide. The dried residue was a black, brittle solid, readily converted to a powder. These properties of the material indicate that peat might be converted into a nitrogenous organic

fertilizer and indeed, by proper admixture of inorganic salts, into a complete fertilizer. If these objectives can be attained at reasonable cost, increased utilization of our vast resources in peat would result.

The incorporation of ammonia with organic matter as a means of producing fertilizers is not novel.

Dragunov (4) studied the extraction of humic acid from peat by sodium and ammonium hydroxides of different strengths. By the use of 10 percent ammonia at 90° C., 31.2 percent of humic acid was obtained which contained 6.31 percent nitrogen.

Certain patents have recently been granted relative to the production of fertilizers from peat and other plant materials resulting from action of ammonia at high temperatures and pressures. Carbohydrates of plant origin (wood sugar, cellulose, etc.) (7) may be heated with ammonia under pressure at 300° C., and it is claimed that products are obtained which contain up to 20 percent nitrogen. When lignin is heated under these conditions the product contains 10 percent nitrogen. The time required is about 30 minutes.

According to a patent granted to Ehrenberg and Heimann (5) materials such as coal and peat are converted to fertilizers by pressure oxidation at a temperature of 200° to 250° C., using oxygen and ammonia. A statement is made that the body of chemically bound ammonia is equivalent to the free organic acids present or produced by the oxidation and that up to 6 percent nitrogen may be obtained in the form of ammonia. A later patent (6) describes a process whereby the nitrogen content of treated peat may reach 15 percent. Peat is first subjected to a partial "wet carbonization" followed by a pressure oxidation with ammonia, as described above, aided by positive catalyzers, such as alkali, alkaline earth, or heavy metal salts. Oxides, hydroxides, and carbonate are said to be negative catalyzers.

#### QUANTITY OF NITROGEN ABSORBED

The quantity of nitrogen absorbed by peat and certain related materials, under varied conditions, is given in tables 3 to 7. The materials (usually 2 grams) were placed in pyrex combustion tubes of the Carius type, together with the proper quantity of ammonium hydroxide solution. The sealed tubes were placed in an electrically heated Carius furnace, brought slowly to the required temperature, and held, under pyrometric control, for the periods indicated. At the end of the heating period the tubes were cooled and opened. The contents were evaporated to dryness on a steam bath except when the material was filtered through a Pasteur-Chamberland filter, and the filtrate and insoluble portions dried separately. In these cases the insoluble residue could be given a second or third treatment.

The effect of heating with aqueous ammonia for 3-hour periods at 150° C. was determined with sphagnum-moss peat, heath peat, saw-grass peat, lignin from corncobs, sulphite waste liquor from wood pulp, and on organic matter from Marshall silt loam soil. The lignin used was furnished by Max Phillips, of this Bureau, and the sulphite waste liquor by H. K. Benson, of the University of Washington. The lignin and sulphite waste were given but one digestion with ammonium hydroxide. The insoluble residue in these was so small as to make further digestion impractical. In the case of the organic matter from the Marshall soil and of the heath and saw-grass peats, the insoluble residue was heated a second time. In the case of the sphagnum-moss

peat the material was heated a third time since the appearance of the mass after the first heat treatments was such as to indicate incomplete reaction, it being still somewhat fibrous.

The results of these treatments are given in table 3, wherein the absorption of considerable quantities of nitrogen is shown by all the materials treated. The largest total nitrogen, as well as the largest content of nitrogen in both the soluble and insoluble material, is shown by the saw-grass peat, but the largest relative increase compared with the nitrogen content of the raw peat is shown by the sphagnum-moss peat. The smallest content of nitrogen is shown by the sample of lignin. The ammoniacal nitrogen of the soluble fractions<sup>3</sup> amounts to approximately 30 percent of the total nitrogen present in this fraction. Only traces of ammoniacal nitrogen are found in the insoluble portion. The absolute quantities of absorbed nitrogen shown by the lignin and the ligninlike waste liquor residues indicate that apparently the most effective absorbent fraction in peat is not its lignin content, also that this fraction of peat does function in this manner. The organic matter from the Marshall soil reacts in a manner similar to peat. No definite relation exists between the nitrogen content of the original materials and the amount of increased absorption.

TABLE 3.—The effect of  $NH_4OH$  at  $150^\circ C.$  on various organic materials

Material	Soluble material	Total nitrogen		Ammoniacal nitrogen, soluble fraction	Total nitrogen of whole sample	Nitrogen added by reaction	Increase in nitrogen content over original content
		Soluble fraction	Insoluble fraction				
Maine sphagnum-moss peat, <sup>1</sup> 0.60 percent N	52.2	9.39	2.05	3.08	0.38	5.73	963
North Carolina beath peat, 1.97 percent N	45.4	9.96	5.11	2.58	7.56	5.59	284
Florida saw-grass peat, 3.88 percent N	52.8	11.83	5.40	3.24	8.74	4.87	126
Lignin from corncobs, 0.94 percent N	86.2	3.55	1.84	1.30	3.31	2.37	252
Sulphite waste liquor, <sup>2</sup> 0.66 percent N	( <sup>3</sup> )	5.12	-----	1.86	5.12	5.06	844
Organic matter from Marshall soil, 2.77 percent extracted by $NH_4OH$ containing 7.1 percent ash	-----	10.75	-----	3.28	-----	-----	-----

<sup>1</sup> 3 treatments with  $NH_4OH$ .

<sup>2</sup> 1 treatment with  $NH_4OH$ .

<sup>3</sup> Almost entirely soluble.

These results are in general accord with those obtained by Davis and Scholl on treatment of peat with liquid ammonia, as privately communicated, although the peats treated by them were not the same and there were wide differences in the temperatures employed and in the time of treatment.

#### EFFECT OF CONCENTRATION OF AMMONIUM HYDROXIDE

The effect of increasing the concentration of the ammonium hydroxide upon the absorption of nitrogen is indicated in the results given in table 4. A constant quantity of solution was used, 20 cc per gram of air-dry peat; the concentration of the solution was varied from 0.6 to 26.9 percent ammonia. The conditions of heating were constant, being  $150^\circ C.$  for 3 hours.

<sup>3</sup> The fraction rendered soluble in ammonium hydroxide by the reaction is, however, only partly soluble in water after evaporation to dryness.

TABLE 4.—Effect of varying concentrations of ammonia on the reaction with saw-grass peat at 150° C. for 3 hours

Concentration of NH <sub>3</sub> (20 cc solution per g of peat)	Total nitrogen	Ammoni- cal nitro- gen	Concentration of NH <sub>3</sub> (20 cc solution per g of peat)	Total nitrogen	Ammoni- cal nitro- gen
Percent NH <sub>3</sub>	Percent	Percent	Percent NH <sub>3</sub>	Percent	Percent
0.0	3.88	0.01	6.2	7.72	1.97
.6	6.23	1.12	9.5	7.53	1.42
1.2	6.74	1.26	12.7	8.03	1.53
3.1	7.26	1.41	19.6	8.28	1.56
4.3	7.51	1.64	26.9	8.27	1.50

<sup>1</sup> Original material with no treatment.

The total nitrogen content increased with a fair degree of regularity corresponding to increases in concentration of ammonia. It is to be expected, therefore, that liquid ammonia would increase the nitrogen content further. The results of Davis and Scholl indicate that this is true, although different types of peat were used.

The values for ammoniacal nitrogen (distilled with magnesia) fluctuate somewhat but are sufficiently constant in table 4 (as well as in tables 5, 6, and 7) to indicate that a fairly definite and constant quantity of acid was neutralized regardless of the variable conditions imposed on the reaction.

#### EFFECT OF VOLUME OF AMMONIUM HYDROXIDE

Table 5 shows the effect of varying quantities of concentrated ammonium hydroxide (26.9 percent ammonia) on saw-grass peat at 150° C. The insoluble residues after heating for a period of 3 hours were treated for a second period of 3 hours at the same temperature, as indicated in the table, in order to determine the effect of removing the preliminary products of solution.

TABLE 5.—Effect of quantity of solution on reaction of ammonia with saw-grass peat at 150° C.

Quantity of concentrated NH <sub>4</sub> OH solu- tion per gram of air-dry peat	Soluble matter <sup>1</sup>			Insoluble matter	Total material after re- action	Total nitrogen			Ammoni- cal nitro- gen	
	First treatment 3 hours at 150° C.	Second treatment 3 hours at 150° C.	Total			Soluble fractions combined	Insoluble fractions	Whole sample		Soluble fractions combined
	Percent	Percent	Percent			Percent	Percent	Percent		Percent
6 cc.....	38.8	8.1	46.9	48.0	91.9	11.85	5.31	8.05	3.52	
10 cc.....	41.2	8.6	49.8	48.7	90.6	12.16	5.24	8.81	3.46	
20 cc.....	44.8	8.0	52.8	48.7	101.5	11.83	5.40	8.74	3.24	

<sup>1</sup> All percentages based on oven-dry material.

The use of larger quantities of solution per gram of peat resulted in a greater percentage of peat being dissolved by the first treatment with ammonium hydroxide. The quantity dissolved by the second treatment was, however, practically the same in each case. It is interesting to note that the percentages of final insoluble residues also increase with increase in the volume of the ammonium hydroxide. It must be assumed that there is a greater loss of material by formation of volatile products when smaller quantities of liquid are present in the reaction tube, which loss decreases the total residue. The extent of this loss is shown by the summation of soluble and insoluble fractions

and amounts to as much as 8.1 percent in the case of the smallest quantity of solution.

The total nitrogen content of the insoluble fraction and of the combined soluble fractions is practically constant for all three conditions. The total nitrogen content of the samples likewise shows no definite trend and may be considered as constant over the range of variation in quantity of ammoniacal solution used.

The net effect, therefore, of varying the volume of solution under the conditions of the study, seems to be, primarily, of a corresponding variation of the yield of final product. The quantitative character of the product with respect to total and ammoniacal nitrogen is essentially constant.

#### EFFECT OF TIME AND TEMPERATURE OF HEATING

The effect of time of heating with concentrated ammonium hydroxide was determined by varying the time from 1 to 36 hours. The temperature employed was 150° C. and was held constant. The results given in table 6 indicate that the solubility increases with time up to a period of 3 hours then remains fairly constant until a period of 18 hours is reached, when another increase is apparent. The insoluble fraction, on the other hand, progressively decreases from 1 hour heating to 36 hours heating. The difference between the sum of the soluble and insoluble matter and 100 percent may be accounted for by assuming that prolonged heating causes an increasing formation of volatile substances which are lost on drying the reaction mixture. The gain in weight up to 2 hours heating may be explained on the basis of addition products with ammonia, but with longer heat the loss by volatilization exceeds the gain resulting from the formation of addition products.

TABLE 6.—Effect of time of heating on reaction of concentrated ammonia with saw-grass peat at 150° C.

Period of heating (hours)	Soluble matter	Insoluble matter	Total	Total nitrogen, soluble fraction	Ammoniacal nitrogen, soluble fraction	Total nitrogen	
						Insoluble fraction	Whole sample
	Percent	Percent	Percent	Percent	Percent	Percent	Percent
1	35.6	67.7	103.2	11.21	3.12	4.34	0.71
2	38.2	63.0	101.2	12.72	3.46	4.96	7.89
3	44.8	54.3	99.1	12.08	3.44	5.11	8.27
6	44.8	54.1	98.9	12.79	3.71	5.19	8.03
9	44.2	53.8	98.0	12.33	3.67	4.06	8.26
18	48.3	51.1	99.4	12.61	3.77	5.28	8.84
36	48.1	48.7	96.8	12.61	3.62	5.52	9.05

There is no significant trend in the values for total nitrogen nor for ammoniacal nitrogen in the soluble fraction after a period of 1 hour's heating. There is a gradual increase, however, in the insoluble nitrogen as heating is continued with a corresponding increase in the total nitrogen of the entire sample.

The effect of 3 hours' heating with 20 cc of ammonium hydroxide per gram of peat at varying temperatures from 100° to 225° C. is shown in table 7. As the temperature is increased the total nitrogen increases fairly regularly. The ammoniacal nitrogen tends to increase up to a temperature of 150°, after which there is a decrease with increasing temperature, possibly because the higher temperatures either tend to decompose the ammonium salts formed or do not permit them to form.



TABLE 7.—Effect of varying temperatures on the reaction of ammonia with saw-grass peat at 150° C., 3 hours

[20 cc of concentrated ammonia per gram of peat]

Temperature (°C.)	Total nitrogen	Ammoniacal nitrogen	Temperature (°C.)	Total nitrogen	Ammoniacal nitrogen
	Percent	Percent		Percent	Percent
100	7.14	1.22	157	8.80	1.05
125	7.78	1.18	200	8.83	.87
150	8.27	1.56	225	9.04	.99

1:1 concentration of ammonia.

## POT EXPERIMENTS WITH TREATED SAW-GRASS PEAT AS A FERTILIZER

It seemed desirable to determine the degree to which plants would be able to utilize the elements essential to their nutrition in the treated saw-grass peat. Accordingly, the peat was used as autoclaved at 150° C. with ammonium hydroxide and potassium hydroxide; with ammonium hydroxide, potassium hydroxide, and rock phosphate, 5.6 percent calcium oxide and 11.6 percent calcium oxide. Raw peat was also used.

Quartz sand in gallon pots was used for the experiment and millet plants were grown. The experiment was divided into three parts, namely, a series in which nitrogen was either lacking or was a variable, a series in which phosphate was a determining element, and a series in which potash was the variable.

The basic fertilization per pot in the nitrogen series was as follows: 0.18 g K as KCl, 0.12 g Ca as CaCl<sub>2</sub>, 0.05 g Mg as MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.0035 g Fe as ferric tartrate, 0.0035 g Mn as MnSO<sub>4</sub>·2H<sub>2</sub>O, and 0.15 g P<sub>2</sub>O<sub>5</sub> as CaH<sub>4</sub>(PO<sub>3</sub>)<sub>2</sub>·1 H<sub>2</sub>O.

Sodium nitrate was used as a source of nitrogen as compared with nitrogen from dried blood and treated saw-grass peat. The check pots contained quantities of sodium nitrate varying from none to an amount equivalent to 0.16 g of nitrogen per pot. Dried blood, containing 13.89 percent N, was used in an amount equivalent to 0.10 g of nitrogen per pot. The treated saw-grass peat was similarly used in varying amounts, as indicated in table 8.

TABLE 8.—Data on pot experiments with millet grown in sand, peat and other fertilizing materials being used

NITROGEN EXPERIMENT		
Treatment	Average air-dry weights of plants †	pH of soil (colorimetric)
	Grams	
0 nitrogen.....	0.06	6.5
0.04 g N as NaNO <sub>3</sub> .....	2.05	6.7
0.08 g N as NaNO <sub>3</sub> .....	2.84	7.4
0.16 g N as NaNO <sub>3</sub> .....	3.18	6.5
0.10 g N as dried blood.....	2.85	5.5
0.16 g N as peat autoclaved with NH <sub>4</sub> OH.....	2.19	6.5
0.32 g N as peat autoclaved with NH <sub>4</sub> OH.....	3.80	6.5
0.16 g N as peat autoclaved with NH <sub>4</sub> OH+KOH.....	1.92	6.6
0.16 g N as peat autoclaved with NH <sub>4</sub> OH+KOH+rock phosphate.....	2.12	6.3
0.16 g N as peat autoclaved with 5.6 percent CaO.....	1.07	6.8
0.16 g N as peat autoclaved with 11.6 percent CaO.....	1.32	7.6
0.16 g N as raw untreated peat.....	.70	6.0

† Roots not included.

TABLE 8.—Data on pot experiments with millet grown in sand, peat and other fertilizing materials being used—Continued

PHOSPHATE EXPERIMENT <sup>1</sup>		
Treatment	Average air-dry weights of plants <sup>1</sup>	pH of soil (colorimetric)
0 P <sub>2</sub> O <sub>5</sub> .....	0.10	5.5
0.05 g P <sub>2</sub> O <sub>5</sub> as CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O.....	4.44	5.0
0.10 g P <sub>2</sub> O <sub>5</sub> as CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O.....	4.52	5.3
0.05 g P <sub>2</sub> O <sub>5</sub> as peat autoclaved with NH <sub>4</sub> OH+KOH+rock phosphate.....	.81	5.3
0.10 g P <sub>2</sub> O <sub>5</sub> as peat autoclaved with NH <sub>4</sub> OH+KOH+rock phosphate.....	2.52	5.5
0.05 g P <sub>2</sub> O <sub>5</sub> as raw phosphate rock.....	.15	5.3

POTASH EXPERIMENT <sup>2</sup>		
Treatment	Average air-dry weights of plants <sup>1</sup>	pH of soil (colorimetric)
0 K <sub>2</sub> O.....	0.06	6.2
0.08 g K <sub>2</sub> O as K <sub>2</sub> SO <sub>4</sub> .....	3.02	4.7
0.16 g K <sub>2</sub> O as K <sub>2</sub> SO <sub>4</sub> .....	4.49	4.8
0.08 g K <sub>2</sub> O as peat autoclaved with NH <sub>4</sub> OH+KOH.....	3.27	6.5
0.16 g K <sub>2</sub> O as peat autoclaved with NH <sub>4</sub> OH+KOH+rock phosphate.....	3.35	6.5

<sup>1</sup> Roots not included.<sup>2</sup> 0.16 g N added to basic fertilization, half as ammonium sulphate and half as calcium nitrate.

All treatments of pots were made in duplicate. The mineral nutrients were added in solution and the organic materials (ground to pass 100 mesh or finer) were mixed with the sand to which 1 percent of water had been added to facilitate mixing. The total water content was adjusted to a suitable quantity and was held constant by daily additions of distilled water according to the loss in weight of each pot. All the pots were inoculated with a few cubic centimeters of a soil suspension. Ten millet plants were grown per pot after thinning down from a planting of approximately 50 to 60 seeds.

The plants were harvested when it became evident that growth had reached an approximate maximum under the given conditions, as indicated by a ripening or drying up of the lower leaves and lower portions of the stems. A sample of the sand was taken from near the center of each pot after harvesting to determine the hydrogen-ion concentration. The results of the experiment are recorded in table 8.

The growth of millet receiving no nitrogen was negligible. There was a response to additions of sodium nitrate to the extent of 3.18 g of air-dry matter when 0.16 g of nitrogen was added in this form. During the course of the experiment the pots containing the two largest quantities of NaNO<sub>3</sub> developed a condition of chlorosis, presumably due to lack of iron which, if unchecked, would materially have affected the growth. Sufficient ferric sulphate was added to neutralize the effect of sodium on the acidity of the medium. Recovery of the plants affected was almost immediate and no further difficulty was experienced in this respect.

Dried blood showed an availability of its nitrogen of approximately 80 percent since 0.10 g of nitrogen in this form gave a growth equivalent to 0.08 g of nitrogen in the form of NaNO<sub>3</sub>, which is assumed to have been entirely available under the conditions. Peat autoclaved with ammonia furnishing 3.16 g of nitrogen gave a growth slightly better than 0.04 g of nitrogen in the form of sodium nitrate. Its availability may therefore be considered to be about 25 percent. Were comparison to be made between the yield ob-

tained with 0.16 g of nitrogen in the form of nitrate and that obtained from 0.16 g in the form of autoclaved peat, the indicated percentage availability would be 69. This comparison is faulty in that it involves a comparison of a peat application not in excess with a sodium nitrate application which is presumably in excess and moreover the plants receiving particular sodium nitrate application were affected by chlorosis. However, in the use of 0.32 g of nitrogen in the form of ammonia, a growth was obtained greater than by 0.16 g of nitrogen as sodium nitrate. The availability in this case cannot be directly calculated since there is no pot having sodium nitrate giving an equivalent growth. It is significant to note, however, the superiority over the pot having 0.16 g of nitrogen as sodium nitrate.

Peat autoclaved with ammonium hydroxide and potassium hydroxide, and with ammonium hydroxide, potassium hydroxide, and rock phosphate, gave growths which were practically equivalent to that obtained with peat autoclaved with ammonia alone. The samples treated with calcium hydroxide were much less effective, but gave a better yield than raw peat. The effectiveness of the nitrogen in the latter is very low.

The phosphate experiment was carried out similarly to the nitrogen experiment except that the basic fertilization was changed to permit the use of phosphate in the form of calcium acid phosphate ( $\text{CaH}_4(\text{PO}_3)_2 \cdot \text{H}_2\text{O}$ ) as the variable. Nitrogen was added in amounts of 0.16 g, half of which was in the form of ammonium sulphate and half in the form of calcium nitrate. The amounts of phosphate calculated as phosphorus pentoxide varied in the check series from none to 0.10 g.

Peat autoclaved with ammonia, potash, and rock phosphate in an amount equivalent to 0.05 g of phosphorus pentoxide gave a growth of 0.81 g, as compared with 0.15 g for untreated rock phosphate and 4.44 g for the superphosphate. A growth of 2.52 g was obtained by the use of 0.10 g of phosphorus pentoxide in the form of the autoclaved peat. These results show that the availability of the phosphate in rock phosphate under the given conditions was materially increased by the autoclaving process, since the pots containing raw rock phosphate as a source of phosphorus were practically no better than the blanks. It is recognized, however, that a single test is not conclusive.

In the potash experiment it was found that the potassium in the form of KOH used in autoclaving was essentially all available in comparison with the potassium of  $\text{K}_2\text{SO}_4$  used in the check series.

The relative appearance of some of the plants is shown in figure 3.

A second experiment was carried out in poor sandy soil, using saw-grass peat autoclaved with ammonium hydroxide, potassium sulphate, and rock phosphate as a fertilizer in comparison with a fertilizer of the same percentage composition consisting of nitrogen in equal amounts in the form of ammonium sulphate and sodium nitrate, potash in the form of potassium sulphate, and phosphorus in the form of calcium acid phosphate. The constituents expressed as nitrogen, phosphorus pentoxide, and potassium oxide were, in both cases, approximately in the proportions 4:12:4. The soil used was the Norfolk loamy fine sand. The fertilization treatments were made with the following materials: (1)  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaNO}_3$ ,  $\text{K}_2\text{SO}_4$ ,

and  $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ; (2) saw-grass peat autoclaved with  $\text{NH}_4\text{OH}$ ,  $\text{K}_2\text{SO}_4$ , and rock phosphate; (3) saw-grass peat autoclaved with  $\text{NH}_4\text{OH}$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ; and (4)  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaNO}_3$ ,  $\text{K}_2\text{SO}_4$ , rock phosphate and raw saw-grass peat.

The weights of each material used in the experiments were such as to be as nearly equivalent to the analysis of 4 percent nitrogen, 12 percent phosphorus pentoxide, and 4 percent potassium oxide as possible.

Applications were made in gallon pots at the rate of 500, 1,000, 1,500, and 2,000 pounds per acre. Five pots were used in each specific treatment, including one set having no treatment. The materials were mixed with the soil in a moist condition. Millet was

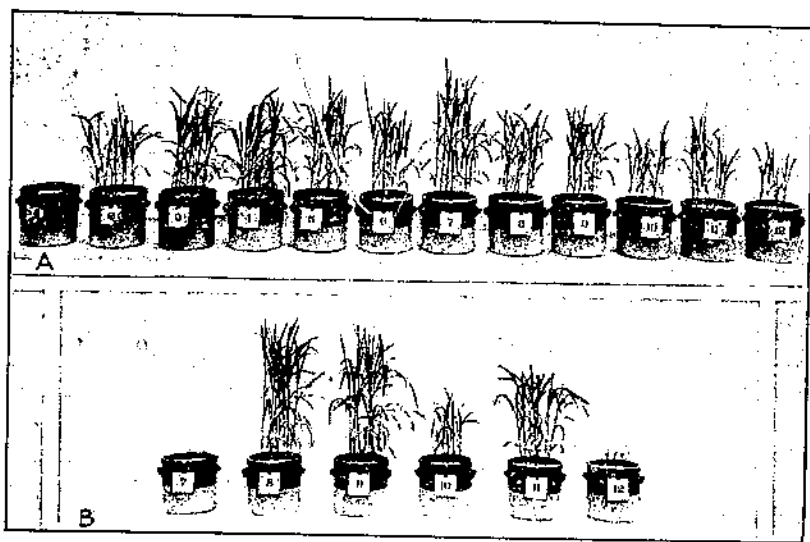


FIGURE 3.—A, Growth of millet in quartz sand using raw and treated saw-grass peat as a source of nitrogen compared with sodium nitrate: 1, No N; 2, 0.04 g of N as  $\text{NaNO}_3$ ; 3, 0.08 g of N as  $\text{NaNO}_3$ ; 4, 0.16 g N as  $\text{NaNO}_3$ ; 5, 0.16 g of N as dried blood; 6, 0.16 g of N as peat autoclaved with  $\text{NH}_4\text{OH}$ ; 7, 0.32 g of N as peat autoclaved with  $\text{NH}_4\text{OH}$ ,  $\text{KOH}$ , and rock phosphate; 8, 0.16 g of N as peat autoclaved with  $\text{NH}_4\text{OH}$  and  $\text{KOH}$ ; 9, 0.16 g of N as peat autoclaved with 5.6 percent  $\text{CaO}$ ; 10, 0.16 g of N as peat autoclaved with 11.6 percent  $\text{CaO}$ ; 11, 0.16 g of N as peat autoclaved with 5.6 percent  $\text{CaO}$  and with rock phosphate; 12, 0.16 g of N as raw peat. B, Growth of millet in quartz sand using treated saw-grass peat as a source of phosphate in comparison with calcium monophosphate and with rock phosphate: 7, No phosphate; 8, 0.05 g of  $\text{P}_2\text{O}_5$  as  $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ; 9, 0.10 g of  $\text{P}_2\text{O}_5$  as  $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ; 10, 0.05 g of  $\text{P}_2\text{O}_5$  as peat autoclaved with  $\text{NH}_4\text{OH}$ ,  $\text{KOH}$ , and rock phosphate; 11, 0.10 g of  $\text{P}_2\text{O}_5$  as peat autoclaved with  $\text{NH}_4\text{OH}$ ,  $\text{KOH}$ , and rock phosphate; 12, 0.05 g of  $\text{P}_2\text{O}_5$  as rock phosphate.

grown as in the first experiment and the moisture content of each pot was kept such that the soil was in an optimum condition, or as nearly so as possible.

The results of this experiment are shown in table 9. A maximum growth was obtained by as low as a 1,000-pound per acre application of the 4:12:4 fertilizer consisting of ammonium sulphate, sodium nitrate, superphosphate and potassium sulphate, which hereafter will be referred to as the standard of comparison. The yield from the 2,000-pound application of this material is slightly less than from the 1,000-pound and the 1,500-pound applications. That the soil itself was poor is shown by yield of the checks which was an average of only 0.25 g per pot of 10 plants.

TABLE 9.—Data on pot experiments with millet grown in Norfolk loamy sand, peat and other fertilizing materials<sup>1</sup> being used

Treatment	Application	Average oven-dry weight of plants <sup>2</sup>	pH of soil (colourimetric)
	Pounds per acre	Grams	
None.....		0.25	4.60
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , NaNO <sub>3</sub> , Ca <sub>2</sub> H <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> .H <sub>2</sub> O; and K <sub>2</sub> SO <sub>4</sub> .....	500	1.08	4.55
	1,000	3.48	4.60
	1,500	3.47	4.55
	2,000	3.00	4.55
Peat autoclaved with NH <sub>4</sub> OH, rock phosphate, and K <sub>2</sub> SO <sub>4</sub> .....	500	.62	4.05
	1,000	1.12	4.70
	1,500	1.02	4.60
	2,000	2.70	4.70
Peat autoclaved with NH <sub>4</sub> OH, CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> .H <sub>2</sub> O, and K <sub>2</sub> SO <sub>4</sub> <sup>3</sup> .....	500	.05	4.50
	1,000	1.04	4.50
	1,500	3.06	4.50
	2,000	3.57	4.45
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , NaNO <sub>3</sub> , raw peat, rock phosphate, and K <sub>2</sub> SO <sub>4</sub> .....	500	2.02	4.55
	1,000	1.68	4.50
	1,500	2.72	4.50
	2,000	3.50	4.55

<sup>1</sup> Fertilizers contained 4 percent nitrogen, 12 percent phosphorus, and 4 percent potassium oxide as nearly as possible.

<sup>2</sup> Roots not included.

<sup>3</sup> Contained 6.1 percent N.

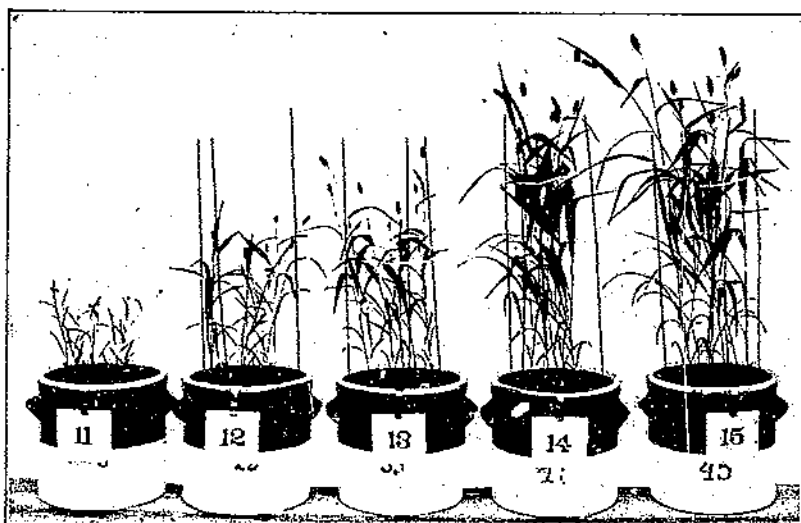


FIGURE 4.—Growth of millet on poor sandy soil as affected by fertilization with treated saw-grass peat: 11, No fertilizer; 12, peat autoclaved with NH<sub>4</sub>OH, rock phosphate, and K<sub>2</sub>SO<sub>4</sub> (4:12:4 composition), 500 pounds per acre; 13, same as 12, 1,000 pounds per acre; 14, same as 12, 1,500 pounds per acre; 15, same as 12, 2,000 pounds per acre.

A 2,000-pound application of the peat autoclaved with ammonium hydroxide, potassium sulphate, and rock phosphate gave a growth of 2.70 g. The value is greater than the 500-pound application of the standard but less than the 1,000-pound application. The effectiveness of this fertilizer is therefore between 25 and 50 percent, compared with the standard.

The pots having applications of the mixture of ammonium sulphate, sodium nitrate, raw peat, rock phosphate, and potassium sulphate

indicated that the phosphorus<sup>4</sup> in the rock phosphate under the acid condition of the medium was sufficiently available for a 2,000-pound

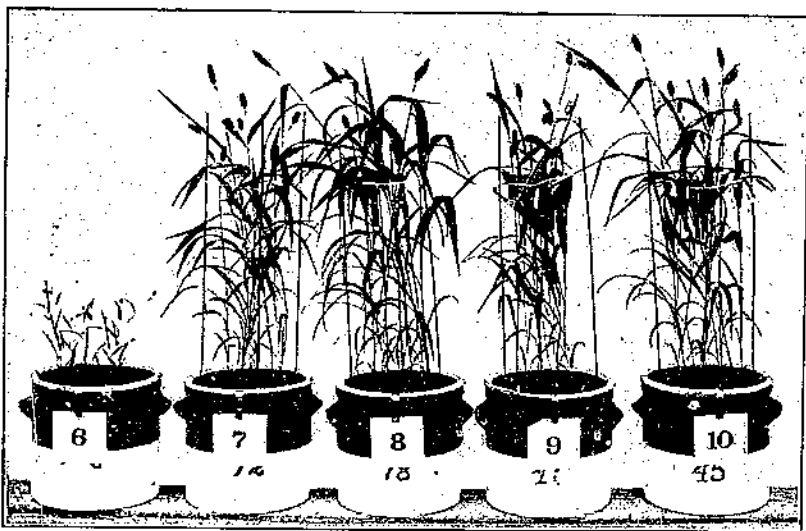


FIGURE 5.—Growth of millet on poor sandy soil enriched with a complete mineral fertilizer as compared with fertilization by treated saw-grass peat: 6, No fertilizer; 7, mineral fertilizer (4:12:4) 500 pounds per acre; 8, same as 7, 1,000 pounds per acre; 9, peat autoclaved with  $\text{NH}_4\text{OH}$ , rock phosphate, and  $\text{K}_2\text{SO}_4$  (4:12:4) 1,500 pounds per acre; 10, same as 9, 2,000 pounds per acre.

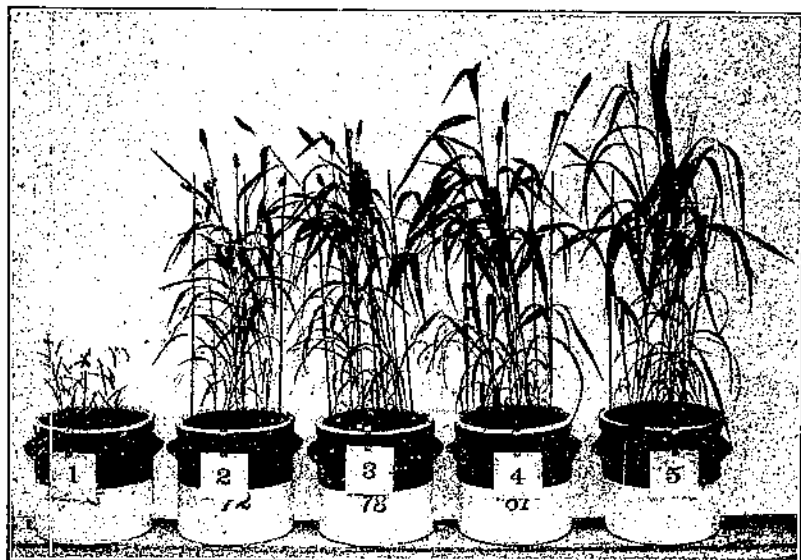


FIGURE 6.—Growth of millet on poor sandy soil as affected by mineral fertilization: 1, No fertilizer; 2,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NaNO}_3$ ,  $\text{CaH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  and  $\text{K}_2\text{SO}_4$  (4:12:4 composition) 500 pounds per acre; 3, same as 2, 1,000 pounds per acre; 4, same as 2, 1,500 pounds per acre; 5, same as 2, 2,000 pounds per acre.

application to give a growth corresponding to the 1,000-pound application of the standard. It may be said, therefore, with reasonable

<sup>4</sup> The phosphoric acid content of the peat itself is neglected since this value is approximately only 0.1 to 0.2 percent of the raw peat used.

certainty, that under these conditions nitrogen is the limiting factor in the peat autoclaved with ammonium hydroxide, rock phosphate, and potassium sulphate.

The peat which was autoclaved with the soluble phosphate,  $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , instead of the rock phosphate, was included to determine the difference in the behavior of these two forms of phosphate, other factors being as nearly equal as possible. However, a comparison cannot be made since this material contained 6.1 percent of nitrogen as compared with the approximate 4 percent in the other materials, the increased nitrogen content resulting from the reaction between ammonia and the acidity of the monophosphate which was not taken into consideration in the preparation. The effectiveness of this fertilizer is 50 percent of the standard, having a yield from the 2,000-pound application equivalent to the 1,000-pound application of the standard.

The relative effects of these treatments are also shown in figures 4, 5, and 6. It is realized that the two series of pot experiments are not adequate for final conclusions as to the value of this material. They show the degree of availability under two sets of special conditions. The work is being continued in the Soil Fertility Division of the Bureau of Chemistry and Soils.

#### DISCUSSION

The decomposition of raw peat in the soil, as indicated by the carbon dioxide evolution, is extremely limited in extent whether or not the inoculation by soil be supplemented by nutrients. When the peat is subjected to treatment before mixing with soil the evolution of carbon dioxide varies between wide limits and according to the type of treatment. Extraction of the peat by alcohol, or alcohol ether, increases its rate of decomposition but slightly, while autoclaving the peat at  $150^\circ \text{C}$ . for 3 hours with ammonium hydroxide or calcium oxide greatly stimulates the rate of decomposition. The extreme limits for a 30-day period are 7 mg of carbon dioxide for a sample of raw saw-grass peat and 401 mg for a sample of the same type of peat digested with 25 percent of its weight of calcium oxide.

It is possible to arrive at an estimate of the quantity of peat actually decomposed in these changes. The sample of saw-grass peat used in these experiments contains approximately 55.2 percent<sup>6</sup> of carbon (8, table 5). The evolution of 7 mg of carbon dioxide per gram of peat corresponds to  $\frac{0.007 \times 12}{0.552 \times 44} \times 100$  or 0.3 percent, while for 401 mg the decomposition becomes 17.6 percent. This calculation assumes no decomposition of the peat to have occurred during the treatment, but table 6 indicates that some decomposition does occur. Also, it has been shown by Schneider and Schellenberg (23) that a peat treated with sodium hydroxide for 2 hours yields 40 percent of a humic acid containing 33.1 percent carbon as compared with 54.5 percent of carbon in the original peat and 52 percent in the insoluble residue.

In general, autoclaving with bases is very effective as a means of promoting decomposition of peat in the soil, and, indeed, in the cases of ammonium hydroxide and of lime produces an evolution of carbon

<sup>6</sup> This value corresponds to 51.70 percent on the ash-free basis, as given in the reference for the 32-inch layer.

dioxide approximately two thirds that from sweetclover. The treatment with cold 40 percent hydrochloric acid is also remarkably effective.

There are certain indications that the soluble hydrolytic products are more readily decomposed than those that are insoluble. This is not true in all cases since there is relatively little soluble matter in the material produced by hydrochloric acid and by lime, while these are quite readily decomposed, and in the sulphite treatment of the sphagnum-moss peat the insoluble product is more active than that which dissolves. In this last case the greater activity of the insoluble residue is attributed to its higher cellulose content.

It may be assumed that any treatment which will increase the rate of decomposition of peat in the soil will increase its value as a fertilizer component. The nitrogen of the peat which, in its raw condition, is almost wholly unavailable, may be expected to become available as the decomposition proceeds. The inorganic ash components should also be liberated and at the same time those benefits will be derived which are ordinarily ascribed to the presence of humus in the soil.

When peat is treated with either aqueous or anhydrous ammonia at elevated temperatures, and under pressure, changes are produced which are of special interest. Although, as has been pointed out, the greater portion of the nitrogen so added is not present as ammonium salts, there is, nevertheless, ample evidence that nearly all of it is present in a form immediately or ultimately available to plants. The product is not only desirable by reason of its chemical composition and behavior in the soil, but it has physical characteristics which make it attractive as a means of distributing fertilizing material within the soil.

The reaction of ammonia with peat seems to be general for all varieties of peat and there appears to be no relation between the nitrogen content of the raw material and the maximum increased content of the product.

From the available data it appears that the maximum nitrogen content of the product is greater with high-nitrogen peats, though whether any notable portion of this original nitrogen is made available is not yet determined. The character of the nitrogenous compounds in the ammoniacal peat also remains to be determined. Nevertheless, the data assembled indicate that ammoniated peat gives fair promise of furnishing a highly useful fertilizer material. Whether such conversion of peat will repay the cost of manufacture is a question beyond the scope of this investigation but is being given attention by the Fixed Nitrogen Research Laboratory in the work to which reference has already been made.

The data so far obtained by the writers make it appear that there is no evidence of decomposition of peat under anaerobic conditions subsequent to its formation (8, p. 24) nor from the present data dealing with aerobic conditions is there evidence of material chemical alteration. It would seem probable, therefore, that any beneficial results from the use of raw peat in agriculture must be ascribed to alteration in the physical condition of the soil or to the water-holding and base-exchange capacities of the material rather than to any direct utilization of the peat itself, as a source of plant food.

The availability of the nitrogen in ammonia-treated saw-grass peat was found to be from 25 to 50 percent from the results of 2 pot



experiments, 1 in quartz sand and the other in a poor sandy soil. The percentage of added nitrogen over the original nitrogen in this particular peat is slightly over 100 or, in other words, the nitrogen content has been doubled. There is reason to believe that the added nitrogen is far more effective in the nutrition of growing plants than the fraction of the nitrogen originally present which has undergone the same or similar treatment, since the samples which were autoclaved with lime, while showing a superiority over raw peat, did not show as high nitrogen availability as did the ammonia-treated peat. It is reasonable to assume, therefore, that with a peat in which the added nitrogen was present to the extent of nearly 10 times the original content, as was the case with a sample of sphagnum-moss peat, much more favorable results would have been obtained with respect to the percentage availability of the nitrogen, although the quantity of total nitrogen would have been only 6.38 percent for the sphagnum-moss peat in comparison with 8.74 in the case of saw-grass peat (table 3).

#### SUMMARY

A study has been made of the decomposition of peat when mixed with soil as measured primarily by carbon dioxide evolution. The samples of peat were used in the raw condition and as the products of various types of chemical treatments, including extraction by solvents and reactions with water, acids, and bases at ordinary and at elevated temperatures under pressure. The raw peats decomposed very slowly, whereas peat treated at ordinary temperature with 40 percent hydrochloric acid or at 150° C. under pressure with lime or ammonia decomposed quite rapidly, the maximum rate being approximately two thirds of the rate of sweetclover under the same conditions.

Peat is capable of reacting with ammonia in such a way that relatively large quantities of nitrogen are added, yet only a fraction of the added nitrogen is ammoniacal in form. This reaction was studied at temperatures varying from 50° to 225° C. and for periods of time varying from 1 to 36 hours. The percentages of added nitrogen ranged from 2.83 to 5.78 on the basis of the dry product. There is apparently no relationship between the nitrogen originally present and the additional nitrogen taken up in the treatment. Lignin, sulphite-waste liquor from the paper industry, and soil organic matter were also found to respond to the ammonia treatment by showing increased percentages of nitrogen.

Fertilizer pot tests with millet in quartz sand are believed to indicate that the possibilities of preparing a satisfactory nitrogenous fertilizer from peat by the action of ammonia are excellent. The immediate availability of the total nitrogen in treated samples of saw-grass peat was found to be between 25 and 50 percent, as compared with inorganic nitrogen. The availability of the phosphorus in rock phosphate is apparently increased by the autoclaving process when the rock phosphate is added previous to the treatment with ammonia. The data on fertility are incomplete, and the work must be continued in order to make definite conclusions possible.

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