

cause a more rapid filtration.) The fiber is then thoroughly washed with boiling 1.25 per cent. sulphuric acid, which will remove the material precipitated by the addition of the alkali, washed free of acid, removed from the linen filter to a crucible, dried, weighed, incinerated and reweighed.

The Sweeney method has a great advantage over the official method by doing away with a filtration and thus saving time. This advantage is preserved in the modification of the Sweeney method.

The preceding table shows the results of all three methods on 5 different samples of feeds.

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STUDIES ON SOIL HUMUS.

By SHERMAN LEAVITT.

Received January 30, 1912.

Humus is recognized as one of the most valuable constituents of a soil and yet little is known as to its composition. Fifty or sixty years ago, chemists thought they had shown humus to have a definite chemical composition with percentages of carbon, hydrogen, nitrogen and oxygen constant. According to their theory, humus was a salt of humic acid (also considered a definite chemical compound) which, upon oxidation, yielded simpler hypothetical organic acids called crenic and apocrenic. Although, as far as the writer knows, they had little or no experimental proof, many of these theories have been held to by some until quite recently.

In spite of all the work which has been done during the past fifty years, but little is known about humus. It is the belief of the writer that most chemists who have worked on the subject within the last fifteen years will agree that it is far from being a definite compound, and, in fact, that it is as variable in composition, if indeed not more so, as the different soils of which it is a component part.

Why does soil *A* accumulate humus matter readily while soil *B*, under similar conditions of treatment, etc., apparently makes no appreciable and permanent improvement?

We are working at this problem along two general lines: First, under field conditions; second, under laboratory control.

This article will be confined mainly to the second class, as definite results from the field cannot be obtained under many years.

In the laboratory, large samples of soils that are under field experimentation are being used. These were procured from car-load lots, thoroughly mixed, so that the samples are quite representative of the types under investigation. These samples represent four distinct type soils in different sections of Tennessee and were chosen for the reason that each one was the poorest soil of that particular type. It was thought of interest to include a Florida Everglade soil, rich in humus, for comparison in the chemical work.

As most of the humus matter in Tennessee soils is

present in the first six inches of soil, the laboratory work on humus has been confined to this layer.

At the beginning of this work it was deemed advisable to remove completely, under the same conditions of extraction, the humus matter from a large quantity of each one of these soils. Under similar conditions of preparation, the humus matter obtained from each one of these soils ought to be at least approximately comparable. Any appreciable difference in the approximate composition of the several samples of humus might have great significance and might point to some quite different behavior of the humification process in the several soils. This may be taken as the key-note of the following investigation:

A number of quantitative chemical methods for the determination of percentage of humus in soils were subjected to examination for their respective values. The investigation earlier reported¹ brought out some valuable points, notably that the humus matter from different soils could be absolutely different both in appearance and in behavior toward reagents. Several of the methods in use for the determination were found unreliable on Tennessee soils for the reason that they failed to show all of the organic matter in the ammonia solutions.

In this later investigation, dealing more specifically with the properties of the several humus samples, a description of the method of procedure in the preparation of the samples of humus will be given. During the work, it was deemed advisable to modify the method of removing clay from the samples, the reasons for which will be given.

Method A.—Five hundred grams of the air-dried soil were extracted with 1 per cent. hydrochloric acid, according to the Official Method, washed free from acid and then extracted three days with 4 per cent. ammonia, allowed to settle and the supernatant liquid drawn off. Fresh 4 per cent. ammonia was added and the process repeated. The soil was extracted three times with successive portions of 4 per cent. ammonia, about two liters of solution being used for each extraction. The last extraction contained very little coloring matter. The extractions were all evaporated to dryness in a large porcelain dish on the hot water bath, baked for some hours, and cooled. The residue was then extracted with about two liters of 4 per cent. ammonia, washed by decantation and filtered. A large proportion of the flocculated clay was retained on the filter paper, which was thoroughly washed with 4 per cent. ammonia. The process of evaporation, baking, extraction, washing and filtering, was repeated a number of times until the filtrate appeared absolutely clear. This was then evaporated to dryness in a large beaker to drive off the excess of ammonia; dissolved in hot, distilled water; filtered and washed into a 500 cc. graduated flask; cooled and 1 cc. of strong ammonia added to prevent fermentation; then made up to the mark. The solution was thoroughly mixed and allowed to stand for two months to give finely divided clay, still in suspension, a chance

¹ "Soil Humus as Determined by Different Methods," *THIS JOURNAL*, 2, 269.

to settle out. The supernatant solution was pipetted off for analysis and the amount of humus and ash present determined in 10 cc. portions.

All of the preliminary work was carried on with the humus prepared as above until the supply was exhausted. Fearing a possible hydrolysis of some of the organic compounds might have taken place during the many evaporations to dryness and baking of the humus matter, it seemed wise in making up new samples of humus to modify the method of removing clay so as to reduce the chance of hydrolysis to as low a figure as possible.

Since this change was decided upon, the Illinois Experiment Station has published Stewart's doctoral thesis as *Bulletin* 145 of that Station. Among the general conclusions reached, the author says: "The evaporation on the water bath of the ammoniacal solution, in the preparation of the *matiere noire* in quantity for analysis, causes a hydrolysis of the organic phosphorus compounds." This would seem to confirm the fear of possible hydrolysis of some of the organic compounds other than organic phosphorus compounds.

The modified method of removing clay decided upon depends almost entirely on long settling of the solution for the removal of most of the clay, instead of baking on the steam bath, as in Method A. It was also deemed advisable to make all concentrations and evaporations at not over 60° C., final concentrations to be made in a partial vacuum, taking care never to allow the solution to become more concentrated than 700 cc. During the greater part of the evaporation, the volume of the solution was kept at approximately two liters and was not brought below one liter until the final concentration, the excess of ammonia by that time being expelled. Fortunately, this slow evaporation with constant additions of cold fresh solution to the evaporating solution tends to flocculate the clay left in suspension.

Method B.—Twenty-two hundred and seventy grams (approximately 5 pounds) of soil were extracted as under Method A, proportionately larger amounts of acid and 4 per cent. ammonia being used. Reverse filtration through fine mesh linen and the siphon were used as much as possible to avoid handling the great bulk of clay. This solution was transferred to large, deep, tightly-stoppered jars and allowed to stand undisturbed for about three months, until the supernatant liquid was quite clear. The solution was then siphoned off and filtered, first through coarse filter paper and then through S & S special hardened and toughened filter paper No. 575, suction being used toward the end of the operation. The paper, with removed clay, was thoroughly washed with 4 per cent. ammonia to make sure that all organic matter was obtained. The residual clay gave no indication of occluded organic matter on being baked on the bath and extracted with ammonia according to Mooers and Hampton's method.¹ The evaporation and concentration of the filtrate and washings were carried on between 50° and 60° C., as

described in the above paragraph. When the filtrate and washings were concentrated to about 700 cc., they were filtered into a liter graduated flask and the paper thoroughly washed with warm water. The whole solution was now cooled and made up to the mark and 1 cc. of chloroform added as a preservative. The flask was placed aside to stand several months before use, to allow additional finely divided clay an opportunity to deposit. The filtrations at best were mostly slow and troublesome, especially the earlier ones. In order to obtain humus satisfactorily by this method, at least six months were required for the proper preparation of samples.

An investigation of this kind is, for many reasons, extremely difficult. As we have already seen, the preparation of samples for comparison is a tedious process, requiring abundant time and patience. The resulting samples are complex in structure and practically nothing is known of them.

As a preliminary investigation of the subject, a study was made of the effect of different mineral elements, such as calcium and iron, on humus in water solution. Some of the richest soils in Tennessee are of the red type, high in iron and very retentive of humus matter.

For this reason it seemed advisable to study the effect of iron in its different states of oxidation, as *ic* and *ous* iron on the removal of humus matter from water solution. Humus prepared from both good and poor soils was used. Some interesting results were obtained which, however, will need further confirmation. As a matter of interest, these results have been inserted and will be discussed briefly. The writer, however, does not wish to lay stress on the results or the conclusions drawn until they are borne out by more extensive work.

TABLE I.

Character of soil.	Laboratory number.	Humus in soil.	Humus by ferric iron.	Humus by ferrous iron.	Humus by calcium chloride.
		Per cent.	Per cent.	Per cent.	Per cent.
Good.....	916	1.46	60.39	65.06	41.10
Good.....	819	1.29	66.67	64.34	45.74
Good.....	1206	5.11	61.65	73.19	42.67
Good.....	1267	1.66	65.82	57.14	49.74
Poor.....	1266	0.39	69.63	83.22	53.57
Poor.....	844	0.52	48.07	39.65	42.31
Poor.....	867	0.87	22.96	44.82	18.40
Poor.....	1096	0.93	46.61	85.92	64.22
Poor.....	1101	0.90	28.15	66.81	40.76

In connection with the above work, it is interesting to note that the analysis of the humus ash of a Florida soil, which had 9.56% of humus, showed an ash content of 21.4 per cent. ferric oxide.

Ferrous iron precipitated more humus matter than ferric iron from the same humus samples, in two-thirds of the soils experimented with. Out of nine soils, four of which were classified as good, having from 1.30 per cent. to over 5.00 per cent. of humus, and five soils ranked as poor, having less than 1.00 per cent. of humus, with one exception ferric iron precipitated 20 per cent. more from the humus of the good soils than from the humus of the poor soils.

Calcium, in the form of chloride, was found to pre-

¹ *J. Am. Chem. Soc.*, 30, No. 5 (1908).

precipitate less humus matter from good soils than either form of iron.

In all of the above cases, organic matter was left in solution. This could be removed as a copper salt more or less completely, when the solution was slightly acid and after the removal of any interfering element, such as excess of iron. This result is quite similar to the writer's finding in the first paper on the subject,¹ where it was noted that a precipitate of organic matter with copper was always obtained after a precipitation of humus matter with hydrochloric acid. It would seem possible that hydrochloric acid and ferric iron precipitate approximately the same substances.

This result is very similar to the one obtained in this laboratory.

Pentosans were obtained, by the Official Method, from all samples of humus examined in this laboratory. This result is also fully in accord with the findings of Schreiner and Shorey,² who obtained pentosans in all ten soils examined by them. Our results varied from 1.74 per cent. in the case of the Florida soil (all percentages on the basis of humus and not on original soil) to 3.72 per cent. on the Gallatin soil; in terms of pentoses, the figures would be 1.99 per cent. to 4.22 per cent., respectively.

In the preparation of the samples of humus under method B, the 1 per cent. hydrochloric acid extracts

TABLE II.
Most of the results given are averages of from three to five determinations.
Percentages on original soil.

Location of soil.	Humus in original soil.	Nitrogen in original soil.	Nitrogen in 1% hydrochloric acid extract.	Total nitrogen dissolved by 1% acid.	Weight of humus used for determination, ash not included.	Weight of ash not counted as humus.	Proteins or like proteins pptd. by (NH ₄) ₂ SO ₄ .	Starch-like bodies calculated to starch.	Furfural determination calculated to	
									Per cent. pentoses.	Per cent. pentosans.
Cookeville, Tenn.	0.93	0.0730	0.0020	2.74	0.369	0.065	70.4	10.40	3.83	3.37
Crossville, Tenn.	0.90	0.0737	0.0014	1.90	0.238	0.013	33.6	8.37	4.14	3.64
Jackson, Tenn.	0.39	0.0560	{ Nitrogen present; partly lost.	Over 2.00	0.112	0.012	75.0	10.80	Present ²	Present ²
Gallatin, Tenn.	1.66	0.1350		3.11	0.392	0.016	57.9	10.60	4.22	3.72
Florida Everglades, Fla. . .	9.56	1.750	0.0345	1.97	2.392	0.067	61.4	4.47	1.99	1.74

In all the samples examined, strong evidence was found of a carbohydrate body in amounts varying from 4.5 per cent. to 10.8 per cent., calculated as starch. This body is very similar to starch, although it gives no reaction with iodine.

Dilute, boiling, hydrochloric acid, according to the Sachsee method, hydrolyzed it to reducing sugars which were determined by Allihn's method, and for convenience calculated to starch. On treating the humus with diastase, with subsequent acid hydrolysis, we obtained practically the same results as by the direct acid hydrolysis. The original solutions of humus gave no reactions with Allihn's solution either before or after inversion with cold hydrochloric acid.

From the acid hydrolysis solution on a sample of humus obtained from a Florida Everglades soil, a crystallizable sugar was obtained which reduced Allihn's solution. Some of the mother liquor had no optical rotation and was easily fermentable. The solution, after fermentation, gave reactions for ethyl alcohol and acetic acid, and also continued to reduce Allihn's solution.

This crystallizable sugar, on account of its ease of fermentation, we classify as a hexose sugar, although it has not as yet been completely identified. Schreiner and Shorey³ have recently obtained a pentose sugar by hydrolysis of a gummy mass precipitated by alcohol from a caustic soda extract of a soil high in pento-

of the original soils were saved as completely as could conveniently be done. These were evaporated to dryness and, with some difficulty, determinations of nitrogen were made upon the total large residues. The determination on the Jackson soil was partly lost. It is interesting to note that in every case an appreciable amount of nitrogen was obtained in the 1 per cent. hydrochloric acid extract of the original soil. This, the writer believes, is contrary to the generally accepted opinion that there is no nitrogen in the 1 per cent. acid extract. This nitrogen is probably due to amino acids,² which are somewhat soluble in dilute mineral acids.

We must keep in mind the fact that these nitrogen determinations, as given in Table II, are all too low as a result of the inevitable loss in handling the large bulks of soil and extract. In the Tennessee soils under examination, a variation of from 1.9 per cent. to 3.1 per cent. of the total nitrogen in the soil was found to be soluble in 1 per cent. hydrochloric acid. This quite appreciable portion of the whole nitrogen is probably present as amino acids. It is not included as humus nitrogen.

In this paper the writer has tried to emphasize the following facts:

INVESTIGATION.

a. Two methods were used for the removal of clay in the preparation of large amounts of humus:

¹ *Experiment Station Record*, 23, No. 1, 11.

² The writer is indebted to Professor W. R. Orndorff for this suggestion.

¹ "Soil Humus as Determined by Different Methods," *THIS JOURNAL*, 2, 269.

² Had enough solution for only a qualitative analysis.

³ *Experiment Station Record*, 23, No. 1, 11.

1. Mooers and Hampton's method.
2. Mechanical separation, without evaporation, to dryness.
- b. Preliminary indications were obtained of the relative behavior of ferric iron, ferrous iron and calcium in the retention of humus from water solution.
- c. Protein or like-proteins were present in humus examined.
- d. A starch-like body was present which can be hydrolyzed by acids and also acted upon by diastase with subsequent acid hydrolysis. Both of these processes gave reducing sugars, in comparable amounts, in all samples of humus examined.
- e. One of these reducing sugars was obtained in a crystalline form but has not, as yet, been fully identified. This was obtained from the humus of a Florida soil.
- f. Pentosans were present in appreciable amounts in all samples of humus examined.

g. Nitrogen, probably present as amino acids, was found in the 1 per cent. hydrochloric acid extract in all soils examined by the Official Method for the determination of humus.

The work was done at the Agricultural Experiment Station of the University of Tennessee, Knoxville, during the years 1909 and 1910.

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AN EXAMINATION OF CITY STREET SWEEPINGS.¹

By J. J. SKINNER AND J. H. BEATTIE.

Received April 19, 1912.

The value of street sweepings is a matter that is of interest to officials of all the large cities. The débris which is collected from the streets of cities is commonly used as fertilizing material, being sold to near-by gardeners, truckers, and farmers, its rather low cost making it particularly attractive. The main object of the city official is to dispose of the material; in some cases it is burned and in others it is hauled to a dumping ground and used as filling material.

There is some variation in the character of the material collected from the streets of different cities, depending on the nature of the industries, the kind of paving material used, and the character of traffic on its streets, yet on the whole the collections from sweepings are very similar and consist chiefly of manure from animals, leaves, dirt, and trash, such as paper, fruit skins, particles of coal, etc. It is possible that the sweepings contain finer particles of the paving substance and some oily material dropped from vehicles. This is especially true at the present time, when the use of power vehicles for pleasure and business is so extensive. The effect of the sweepings on crops, especially when used continually year after year on the same fields, is one of much interest and has caused considerable speculation.

This article deals with an investigation of the street sweepings of one of the larger cities. The material has been studied from the point of view of its organic and inorganic constituents and through

cultural tests, where its effects on plant growth was observed.

CHEMICAL EXAMINATION FOR MINERAL SALTS.

Three samples of the sweepings were examined: sample No. 1 consisted of the débris secured by hand sweeping with a brush, sample No. 2 was that secured by sweeping with a machine, and sample No. 3 was the decomposed débris from a dump pile which had been accumulating for some length of time. There was no apparent physical difference between Samples No. 1 and No. 2, both being composed mostly of the raw horse manure. Sample No. 3 consisted principally of well-decomposed horse manure. The chemical analysis of the three samples is given in Table I, the results being stated in per cents. of dry material. The analyses were made by Mr. J. G. Smith, of the Laboratory of Physical and Chemical Investigations:

TABLE I.—ANALYSES OF STREET SWEEPINGS.

Number and description.	Nitrogen (N). Per cent.	Potash (K ₂ O). Per cent.	Phosphate (P ₂ O ₅). Per cent.
1 Hand sweepings.....	1.34	0.71	1.03
2 Machine sweepings.....	0.86	0.55	0.55
3 Decomposed sweepings.....	0.60	0.56	0.60

This table shows each of the samples to contain appreciable amounts of nitrogen, potash, and phosphate, sample No. 1 being somewhat higher in each of these fertilizing constituents. Stable manure as determined from an average of a large number of samples² contains about 1.6 per cent. of nitrogen, 1.5 per cent. of potash, and about 1.00 per cent. of phosphoric acid, the figures being based on dry material. Comparing these amounts with that contained in ordinary horse manure from the stable, it will be seen that the content of nitrogen, potash and phosphate is higher in the latter. The lower result might be expected, as the sweepings are not all horse manure, but contain considerable foreign material, aside from the fact that they are frequently subjected to leaching by rain.

EFFECT ON GROWTH.

The efficiency of street sweepings and other manures of this nature as fertilizing material should not be judged merely by the percentage of mineral salts which they contain. The organic material itself has an important bearing on the question, as it may be of such a nature or contain constituents which cause it to have either a beneficial or harmful effect on soils.

Experiments were undertaken to test the effect of sweepings on crops, by growing plants in soil to which they had been added. In these experiments an especially constructed paraffine wire pot,² possessing certain advantages over the ordinary clay pot, was used.

To test the effect of sweepings on soil, wheat was grown in the paraffine wire pots for one month. The soil used in the test was a clay loam. The soil was divided into four portions. To three of these was added a sample of one of the three types of sweepings, while to the fourth good stable manure was added

¹ From the Laboratory of Soil Fertility Investigations by permission of the Secretary of Agriculture.

² Storer, F. H., "Agriculture in Some of its Relation with Chemistry."

² For description of method, see *Circular 18*, Bureau of Soils.