gen, than occur in the vegetable proteins. To account for this it was suggested that bacterial action probably causes a more marked splitting off of the basic nitrogen constituents, than of the other groups, at least in the early stages of the decomposition.

On the other hand it is shown in the present paper, that heat causes a breaking up of the organic nitrogen bodies in such a way as to liberate large amounts of ammonia from the antecedents of the non-basic nitrogen bodies—presumbaly the mono-amino acids.

HONOLULU, HAWAII.

THE ORGANIC NITROGEN OF HAWAIIAN SOILS.[1] III. THE NITROGEN OF HUMUS.

BY W. P. KELLEY AND ALICE R. THOMPSON.

Received December 15, 1913.

Introduction.

That part of the organic matter of soils soluble in dilute alkali, and known as humus, is generally considered to exert special influence on fertility. Moreover, it is claimed that the nitrogen contained in humus becomes available more readily than non-humus nitrogen. Dr. Hilgard found,[2] for instance, that during the first four months after extracting the humus from a soil, no nitrification took place, although the non-humus nitrogen in the soil amounted to 0.127%; after the lapse of two years' time an insignificant amount of nitrate was formed, whereas vigorous nitrification took place in the original soil. The fact that no nitrate was formed from the non-humus nitrogen until after several months' time, and then only at a very slow rate, suggests that the alkali-soluble nitrogen existed in different forms from the non-humus nitrogen. It should be borne in mind, however, that other factors than those having to do with the chemical nature of the nitrogen bodies also exert important influence on bacterial action, such factors as the food supply available to the bacteria, and the physical, chemical and biological conditions, all of which probably underwent some change as a result of extracting the humus.

The general interest taken in soil humus justifies some investigation on the nitrogen bodies contained. The so-called humification process has been the subject of much speculation for many years, but it must be admitted that very little definite knowledge exists regarding the chemistry involved in this process. Bacteria undoubtedly bring about manifold chemical changes in the organic matter, causing it to pass through varying degrees of decomposition leading up to the formation of humus, but regarding the transformations the nitrogen bodies undergo in this process little is known.

[1] Contribution from the Hawaii Agricultural Experiment Station.

[2] *Soils*, pp. 358–60.

The experiments discussed below were undertaken with the view of learning something regarding the chemical nature of the nitrogen bodies contained in humus, and with the hope of gaining some light on the chemistry involved in the process. By comparing the different groups of nitrogen compounds in humus with those in the soil as a whole, it is conceivable that some suggestion might be obtained regarding the nature of the bacterial action that has previously taken place. The soils studied in this connection were the same as those employed in the investigations already reported from this laboratory.[1]

Nitrogen Soluble in 1 Per Cent. Hydrochloric Acid.

In order to break up combinations between the humus substances and inorganic matter and increase the solubility of the humus, the samples were treated in the cold with 1% hydrochloric acid until no further calcium and magnesium were dissolved, then filtered and washed free from acid with distilled water. The filtrates were evaporated to small volumes and analyzed. In a previous investigation carried out in this laboratory it was observed that the hydrochloric acid extracts thus obtained[2] contained, in some instances, considerable amounts of organic matter, and as shown by others,[3] considerable amounts of nitrogen may be dissolved in this way. In the following table are recorded the data showing the total nitrogen in the soils studied and the amounts dissolved by hydrochloric acid:

NITROGEN SOLUBLE IN 1% HCl.

Lab. No.	Total in soil. Per cent.	Soluble in HCl. Per cent. of soil.	Soluble in HCl. Per cent. of total N.
347	1.241	0.029	2.34
428	0.770	0.041	5.33
379	0.592	0.019	3.21
406	0.456	0.012	2.63
447	0.354	0.012	3.39
345	0.218	0.007	3.21
343	0.220	0.004	1.82
405	0.195	0.009	4.61
292	0.122	0.004	3.28
			Av. 3.31

Thus it is shown that small amounts of nitrogen were dissolved by 1% hydrochloric acid, and it is noteworthy that on the average these soils contained only about one-half as much nitrogen in the form of ammonia as was dissolved by hydrochloric acid.[4]

[1] THIS JOURNAL; see preceding articles.

[2] U. S. D. A., Hawaii Sta., *Press Bull.* 33.

[3] Emery, THIS JOURNAL, 22, 285–91 (1900); Leavitt, *J. Ind. Eng. Chem.*, 4, 601–41 (1912).

[4] THIS JOURNAL, *loc. cit.*

The Humus Nitrogen.

Dilute ammonia is the solvent usually employed for dissolving humus, but it is apparent that humus solutions to be used in studies on the nitrogen bodies could not be made by the use of this solvent. For this purpose we have employed a 3% solution of sodium hydrate. Forty-gram portions of the air-dried soils, after having been extracted with dilute hydrochloric acid, were shaken with 2000 cc. of the sodium hydrate solution at intervals for one day, then allowed to settle for an additional day, after which, the solutions were siphoned off and aliquot portions used in the studies herein reported.

It is known that a part of the humus can be precipitated from alkali solutions by acids. The relative amounts precipitated, however, vary with the amounts of acid used. Shorey has shown,[1] for instance, that after filtering out the precipitate obtained by acidifying the solution, a still further precipitate was obtained by carefully neutralizing the filtrate, and that the precipitates thus obtained each contained nitrogen. In other words, humus nitrogen is soluble to some extent in water but more so in dilute hydrochloric acid.

In our work we have arbitrarily separated the humus into two portions by making neutral to litmus paper with hydrochloric acid 1000 cc. portions of the humus solutions (corresponding to 20 grams of soil), then acidifying by adding 20 cc. of 1% hydrochloric acid, filtering and washing the precipitate with dilute hydrochloric acid. The precipitates thus obtained were afterwards subjected to acid hydrolysis by boiling with 400 cc. strong hydrochloric acid for a period of ten hours, filtering and washing the residue. The amide and basic nitrogen were determined in the original humus solutions, in the filtrates obtained after filtering out the precipitates formed

THE NITROGEN OF HUMUS.

		Precipitated by dilute HCl.				Precipitated by HCl.		
Lab. No.	Total per cent. of soil.	Hydrolyzable per cent. of soil.	Non-hydrolyzable per cent. of soil.	Not precipitated by dilute HCl. Per cent. of soil.	Total per cent. of soil. N.	Hydrolyzable per cent. of humus N.	Non-hydrolyzable per cent. of humus N.	Not precipitated by HCl. Per cent. of humus N.
347	0.774	0.362	0.125	0.315	62.37	45.14	15.59	39.28
428	0.590	0.289	0.051	0.247	76.62	49.23	8.69	42.08
379	0.439	0.270	0.041	0.129	74.16	61.36	9.32	29.32
406	0.226	0.100	0.027	0.117	49.56	40.98	11.06	47.96
447	0.215	0.094	0.026	0.105	60.79	41.78	11.56	46.67
345	0.147	0.066	0.019	0.070	67.43	42.58	12.26	45.16
343	0.127	0.061	0.012	0.069	57.73	42.96	8.45	48.59
405	0.123	0.044	0.012	0.067	63.08	35.77	9.76	54.47
292	0.058	0.031	0.012	0.015	47.54	53.45	20.69	25.86
				Average	62.15	45.92	11.93	42.15

[1] U. S. D. A., Hawaii Sta., *Rep.* 1906, 51.

by acidifying the solutions and in the solutions obtained by hydrolyzing the precipitates formed.

In the preceding table are recorded the data showing the total nitrogen contained in the original humus solutions, and in the portions obtained by the different separations.

The above data show that the relative amount of humus nitrogen varied from soil to soil, having been found on the average to amount to 62.15% of the total nitrogen. In every instance, except two, more than one-half of the total nitrogen was dissolved by dilute alkali, while in two instances practically three-fourths of it was thus extracted. Likewise the bodies precipitated by dilute hydrochloric acid also contained nitrogen in varying amounts. The nitrogen bodies thus precipitated yielded by far the greater part of their nitrogen to the solution, the insoluble residue having been found to contain on the average 11.93% of the humus nitrogen. By these methods it is seen, therefore, that the nitrogen of humus can be separated into fractional parts.

Amide Nitrogen in Humus.

The amide nitrogen in the original humus solutions was determined as ammonia, after slightly acidifying with hydrochloric acid, by distillation with magnesium oxide. In similar manner the amide nitrogen was determined in the different portions of the humus. The results are shown in the following table:

AMIDE NITROGEN IN HUMUS.

Lab. No.	Determined directly. Per cent. of soil.	Determined in filtrate after precipitation with dilute HCl. Per cent. of soil (*a*).	Determined in precipitate after subjecting to acid hydrolysis. Per cent. of soil (*b*).	Total. *a* and *b*.	Total. Per cent. of total soil N.	Total. Per cent. of total humus N.
347	0.100	0.095	0.073	0.168	13.54	21.70
428	0.073	0.074	0.056	0.130	16.88	22.03
379	0.059	0.056	0.061	0.117	19.76	26.65
406	0.039	0.040	0.020	0.060	13.15	26.55
447	0.033	0.031	0.027	0.058	16.38	26.98
345	0.025	0.022	0.016	0.038	17.43	25.85
343	0.020	0.025	0.018	0.043	19.54	33.86
405	0.026	0.014	0.023	0.037	18.97	42.53
292	0.009	0.008	0.011	0.019	15.57	32.76
				Average	16.80	28.77

The relatively high percentage of amide nitrogen contained in the original humus solutions is noteworthy. It is apparent that the amide compounds are soluble in dilute hydrochloric acid, as shown by the fact that the filtrates contain practically the same amount of amide as the original solutions. On the average the precipitates yielded upon hydrolysis practically the same amounts of amide nitrogen as were contained as such in the

original solutions. The total amide nitrogen when calculated to percentages of the total soil nitrogen varies somewhat, but on the average amounted to 16.80%. When calculated to percentages of the humus nitrogen it will be seen that the amide nitrogen varied inversely with percentages of the humus nitrogen. On the average 28.77% of the humus nitrogen was found to be in the form of amide.

The percentage of amide nitrogen obtained by hydrolyzing these soils as a whole was previously shown to equal[1] 23.91% of the soluble nitrogen, and, while it is true that the absolute amounts of amide nitrogen in the humus amounted to somewhat less than that in the original soils, the percentages in the humus solutions when calculated to percentages of the humus nitrogen were greater.

Basic Nitrogen of Humus.

The basic nitrogen in humus was determined, after removing the amides, by the phosphotungstic acid method, as already outlined. The results are recorded in the following table:

BASIC NITROGEN IN HUMUS.

Lab. No.	Determined in original solutions. Per cent. of soil.	Determined in filtrate after precipitation with HCl (*a*). Per cent. of soil.	Determined in precipitate after subjecting to acid hydrolysis (*b*). Per cent. of soil.	Total (*a* and *b*). Per cent. of soil.	Per cent. of total soil N.	Per cent. of total humus N.
347	0.028	0.024	0.010	0.034	2.74	4.39
428	0.027	0.025	0.010	0.035	4.81	5.93
379	0.017	0.021	0.007	0.028	4.73	6.38
406	0.015	0.014	0.009	0.023	5.05	10.18
447	0.021	0.019	0.006	0.025	7.06	11.63
345	0.003[2]	0.017	0.017	0.034	15.59[3]	23.13[3]
343	0.004[2]	0.017	0.008	0.025	11.36	19.68
405	0.011	0.009	0.008	0.017	8.71	19.54
292	0.014	0.009	0.017	0.026	21.31[3]	44.83[3]
				Average	6.35	11.10

The above data show that basic nitrogen occurred in practically the same amounts in both the original humus solutions and in the filtrates obtained by precipitation with dilute hydrochloric acid, indicating that the basic nitrogen compounds, present as such, are soluble in dilute acid, as was the case with the amides. It is also noteworthy that the precipitates contained less basic nitrogen than the filtrates. The total basic nitrogen, calculated to percentages of the total soil nitrogen, shows a tendency to increase with a decrease in the absolute amount of nitrogen present and when calculated to percentages of the total humus nitrogen the same relationships are borne out, but in a more marked degree.

[1] *Loc. cit.*

[2] Too low, apparently due to error.

[3] Not included in average.

On the average, the amount of basic nitrogen in the humus solutions was somewhat less than was obtained by hydrolyzing the soil as a whole, whereas the percentage of basic nitrogen, when calculated to the basis of the humus nitrogen present, was considerably greater.

Non-basic Nitrogen.

It is obviously not permissible to consider the difference between the total nitrogen in humus, on the one hand and the amounts of amide and the basic nitrogen that occurred in the original humus solutions, on the other, as non-basic nitrogen, for the reason that these solutions cannot be considered to have been completely hydrolyzed. It is well known, for example, that various proteins are somewhat soluble in alkalies without the proteins undergoing any particular hydrolysis, as is shown by the fact that they can be precipitated in a more or less unaltered condition from such solutions. The nitrogen compounds in the filtrates obtained from precipitation with dilute hydrochloric acid, however, and also those split off in the hydrolysis of the humus precipitate, may reasonably be considered to be made up of amide, basic and non-basic nitrogen bodies. We have, therefore, calculated the amounts of non-basic nitrogen in these portions of humus. The results are shown in the following table:

NON-BASIC NITROGEN IN HUMUS.

Lab. No.	In the filtrates after precipitation with HCl. Per cent. of soil.	In the precipitates after subjecting to acid hydrolysis. Per cent. of soil.	Total. Per cent. of soil.	Per cent. of total soil N.	Per cent. of total humus N.
347	0.196	0.249	0.445	35.86	57.49
428	0.148	0.213	0.361	46.88	61.18
379	0.052	0.203	0.255	43.07	58.08
406	0.063	0.071	0.134	29.38	58.84
447	0.055	0.061	0.116	32.77	53.94
345	0.031	0.033	0.064	29.35	43.54
343	0.027	0.035	0.062	28.18	48.82
405	0.046	0.011	0.057	29.23	45.17
			Average	34.34	53.38

These data are of interest as showing the relatively large amounts of non-basic nitrogen in humus. It is especially noteworthy that on the average about 25% of the humus nitrogen occurred in the filtrates as non-basic nitrogen compounds, or 52.59% when calculated to percentage of the nitrogen soluble in dilute hydrochloric acid. Considering the solutions obtained upon hydrolyzing the humus precipitated by dilute hydrochloric acid, a still greater amount of non-basic nitrogen was found. On the average 64.84% of this nitrogen occurred in non-basic forms, which, when calculated to percentages of the total humus nitrogen, equals 31.98%. By combining these two portions it was found that 53.38% of the humus nitrogen was made up of non-basic nitrogen compounds. By referring

to the data shown in the previous paper[1] it will be seen that the relative amounts of non-basic nitrogen in humus are somewhat less than the amounts obtained by hydrolyzing the soil as a whole.

Considering the different groups of nitrogen compounds obtained from humus, the preceding data show that in absolute amounts less amide, basic and non-basic nitrogen were contained in the humus than were split off upon hydrolysis of the soil as a whole. But on the other hand the humus nitrogen bodies, as such, contained relatively more amide and basic nitrogen and less non-basic nitrogen than the soil nitrogen as a whole. In other words, the nitrogen of soils soluble in 3% sodium hydrate is combined in bodies differing somewhat from the nitrogen bodies not soluble in the solvent.

While it cannot be definitely stated that no hydrolysis took place as a result of the treatments employed in the extraction of the humus and in the solutions subsequently, it seems probable that a considerable part of the humus nitrogen had already undergone some hydrolytic change in the soil. As previously stated, it is certain that the protein complex must become split up into simpler components before its nitrogen becomes available to plants. These components are now known to consist principally of acid amides and amino acids. The humification process, resulting in a considerable simplification of the protein complex with the probable cleavage of the amide, diamino and monoamino acids, therefore, is to be looked upon as a step towards the production of available nitrogen.

HONOLULU, H. I.

[FROM THE DEPARTMENT OF ANIMAL HUSBANDRY, UNIVERSITY OF ILLINOIS.]

A PRELIMINARY STUDY OF THE CHANGES OCCURRING IN MEATS DURING THE PROCESS OF DRYING BY HEAT AND IN VACUO.[2]

BY L. H. DAVIS AND A. D. EMMETT.

Received December 16, 1913.

It is a well known fact that some food products, when heated to 100–105°, give a lower percentage of dry substance, than when dried *in vacuo* at room temperature (20°), or lower.[1] Especially is this difference apparent for substances which contain certain sugars, oils, or fatty acids. On the other hand, there is a tendency for some of the fats to oxidize, when heated to 100–105°, and thus indirectly the dry substance of such materials is increased.

Of the two methods of drying, the use of heat at 100–105°, with or with-

[1] *Loc. cit.*

[2] The results presented in this paper formed part of the thesis which was submitted by Lloyd H. Davis to the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Master of Arts in Chemistry.