INFLUENCE OF TEMPERATURE UPON THE MOBILIZATION OF NITROGEN IN PEAT

By

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In connection with a more extensive work on the mobilization of nitrogen in peat soils of Northern Finland attention was paid to the influence of temperature upon the changes in the nitrogen complex. Although there is not much possibility to control the temperature of peat soils in practice, it seemed, however, desirable to find out whether the microflora inhabiting the soil at higher temperatures could attack the organic nitrogen compounds of peat with better results than the population living there under less favourable conditions. In addition to the changes in nitrogen compounds brought about by microbial activity the burning over of the surface peat can be expected to cause a considerable mineralization of peat nitrogen.

In order to get some information on the biological and chemical mobilization of nitrogen in peat at various temperatures preliminary experiments under laboratory conditions were arranged. The chief results of these experimental series are reported in the present paper.

Experimental procedure

Peat samples. Two samples of peat were used in the experiments: a *Sphagnum*-sedge peat (SCp) and a *Bryales*-sedge peat (BCp). The SCp-sample was taken from a wet treeless oligotrophic bog in Rovaniemi and the BCp-sample from a *Scorpidium*-fen in Alatornio.

In the hollows of the bog the surface vegetation chiefly consisted of *Carex magellanica* and *Menyanthes trifoliata* with a few individuals of *Carex lasiocarpa*, *Carex chordorrhiza* and *Equisetum fluvitiale*. In the surface vegetation of the fen *Scorpidium scorpioides* predominated.

The degree of decomposition was low in both the peat samples corresponding to the grades H_{3-4} in the SC-peat and H_{2-3} in the BC-peat (9).

The samples were air-dried at 15—18°C and ground in a Wiley mill The acidity of SC-peat in water suspension was pH 4.7 and that of the BC-peat 4.8 The weights of volume were 0.26 and 0.21, respectively. The dry matter of the SC-peat contained 2.9 % nitrogen and that of the BC-peat 2.5 %. The chemical composition of these peat samples analyzed by the proximate method of WAKSMAN, modified by SPRINGER (13) was as follows, expressed as a percentage of air-dry matter:

	SCp	BCp
Moisture	9.1	9.3
Ash	4.1	4.7
Loss on ignition	86.8	86.0
Ether soluble material	5.7	3.2
Ethanol-soluble »	2.8	2.0
Water-soluble organic matter	2.6	1.9
HCl-soluble material	22.9	23.8
Hemicelluloses	10.7	12.1
H_2SO_4-soluble material	12.7	22.7
Cellulose	5.9	12.5
Insoluble material	41.5	35.0
»Lignins»	34.2	27.1

The not very marked differences between the chemical compositions of these samples suggest that the SC-peat represents a somewhat higher degree of decomposition than the BC-peat: according to our present knowledge the disappearence of cellulose and the increase in the content of insoluble material are characteristic to the advance of decomposition.

In connection with the analyses of the organic matter also the amount of total nitrogen in various fractions was determined:

	Nitrogen in percentage of dry matter			
	in the peat		in the fraction	
	SCp	BCp	SCp	BCp
Ether-soluble	0.08	0.07	1.3	2.0
Ethanol-soluble	0.08	0.08	2.6	3.6
Water-soluble	0.15	0.10	4.6	4.4
Acid-soluble	1.71	1.81	5.3	4.8
Insoluble	0.88	0.44	1.9	1.1

The SC-peat has a larger amount of its nitrogen in the insoluble lignin-humus fraction than the BC-peat, a fact that agrees well with the probably higher degree of decomposition of the former.

Plan of experiments. In order to compare the ability of psychrophilic, mesophilic and thermophilic microflora to mobilize the peat nitrogen an incubation experiment was arranged:

30 g of air-dry, ground peat was weighed in 1/4 l glass-jars. One half of the samples were limed in order to decrease the acidity to about pH 6. The amounts

of $CaCO_3$ added corresponded to 1.4 % and 1.2 % of the air-dry material in the SC-peat and the BC-peat, respectively. The samples were moistened to 70 % of their water holding capacity, and mixed well. The bottles were loosely covered with cork stoppers and incubated at 5°, 20°, 35°, 50°, or 65° for 100 days.

The chemical mobilization of peat nitrogen by heat was studied by some simple experiments where the dry or moist peat samples were treated at various temperatures. The moist treatment was performed at 75°, 100° and 120°, the time of heating being two hours. The dry samples were heated for three hours at 50°, 75°, 100°, 125°, 150°, or 200°.

Analytical methods. A 10 % solution of potassium chloride was used in the extraction of NH_4-nitrogen. The air-dried 5 g-samples were first shaken for ½ hour in 100 ml of the solution and, after filtration, washed twice with 25 ml of the liquid. The ammonia in the extract was determined by distillation with MgO.

Nitrate-nitrogen was estimated in $CaSO_4$-extracts by the modified method of Berge (1) using a photoelectric colorimeter. The presence of nitrite-nitrogen was observed only ocularly: the intensity of the red colour in the $CaSO_4$-extracts produced by the Griess reagents was compared with that of standard solutions.

The acid-insoluble nitrogen supposed to represent the nitrogen in the lignin-humus complex was determined as total nitrogen in the insoluble residue of the hydrolysis brought about by treating the air-dry sample with 80 % sulfuric acid for 2½ hours and boiling it in diluted acid under reflux condensor for 5 hours.

The pH-values were determined in water suspensions using a quinhydrone-electrode, or from fresh material with a glass electrode.

Results

In the incubation experiment no inoculation of active decomposers was employed. Thus the biological changes in the composition of peat samples during the incubation at various temperatures were brought about by representatives of common microorganisms that could adapt themselves to grow under these different conditions. Losses of peat dry matter at the end of the incubation period were:

	in the SC-peat		in the BC-peat	
incubated	without lime	with lime	without lime	with lime
at 5°	1.5 %	1.5 %	7 %	5 %
20°	8 %	3 %	10 %	8 %
35°	7 %	7 %	10 %	10 %
50°	13 %	17 %	13 %	13 %
65°	18 %	18 %	17 %	20 %

In view of the fact that the decomposition period was more than three months, the destruction of organic matter has not been very marked except in the range of thermophilic microflora. This, of course, is due to the high resistance of the carbon compounds even in these very slightly humified samples, or to the shortage of some essential nutrial elements as phosphorus or potassium. It is of particular interest to note that the acidity was not a limiting factor, since the effect of liming was negligible.

The acidity of the incubated samples was determined both from the fresh material and from the water-suspensions (1 : 4) of the dried samples. In the fresh samples the pH-values were as follows:

	SCp		BCp	
	untreated	limed	untreated	limed
incubated at 5°	4.56	6.08	4.75	6.53
20°	3.93	4.86	4.70	5.38
35°	4.79	5.85	4.95	5.95
50°	4.80	5.72	5.03	6.10
65°	3.20	5.58	4.79	6.30

The corresponding values for the dried samples in the untreated series were at a somewhat higher level:

	SCp		BCp	
incubated	untreated	limed	untreated	limed
at 5°	5.00	5.96	4.96	6.19
20°	4.48	5.18	5.12	5.77
35°	5.18	5.92	5.34	5.95
50°	5.22	5.65	5.45	6.01
65°	3.99	5.68	5.27	6.00

Particularly disturbing are the low pH-values obtained for the samples incubated at 20°. Yet, this unexpected result can be explained partly at least, on the basis of the accumulation of nitrate-nitrogen in these samples. The acidity of the SC-peat incubated at 65° may have its origin in the same phenomenon, but probably also other factors are involved.

The amounts of various forms of mineral nitrogen in the incubated and original samples are reported in Table 1. The fact must be taken into consideration that these data represent the net results of mineralization and biological immobilization of nitrogen. Thus, the large amounts of mineral nitrogen in the samples incubated at the higher temperatures do not merely indicate an intensive destruction of organic nitrogen compounds but also a less efficient biological absorption of nitrogen under these conditions as compared to that occuring at lower temperatures. This is due to the fact that microorganisms live, die, and decompose much more rapidly at higher temperatures, on account of which the nitrogen is changed more rapidly within the microbial cycle (15). Also the different composition of microbial population at higher and at lower temperatures is a significant factor. The fungal flora that is known to utilize a relative large amount of nitrogen in the synthesis of new cell substance is absent in the range of thermophilic population or only scarcely represented (5, 16).

In the untreated series of SC-peat the amounts of ammonia and total mineral nitrogen show an increase with a rising temperature, whereas the nitrate formation has its maximum at 20°. In the limed series a minimum quantity of ammonia nitrogen

Table 1. Mineral nitrogen in the incubated samples (Expressed as ppm of dry matter)

Incubated at	NH_4-N		NO_2-N		NO_3-N		Total mineral N	
	0	$CaCO_3$	0	$CaCO_3$	0	$CaCO_3$	0	$CaCO_3$
SC-peat								
Original	330		5		30		370	
5°	690	670	5	5	30	70	720	750
20°	780	220	8	2	230	480	1020	700
35°	1410	1050	5	trace	70	100	1490	1150
50°	2250	2460	trace	0	—	—	—	—
65°	5960	4860	trace	0	200	160	6160	5020
BC-peat								
Original	390		trace		50		440	
5°	650	550	5	5	30	30	680	590
20°	480	290	2	5	60	190	540	480
35°	740	590	2	5	40	40	780	630
50°	2660	1750	trace	trace	—	—	—	—
65°	3810	2080	0	trace	170	110	3980	2190

is found at 20° where also the maximum of nitrate-nitrogen lies. This relation may form the cause for the high acidity of these samples. The nitrate-nitrogen content is high also in the samples incubated at 65°, thus offering an explanation for their low pH-values. No accumulation of nitrite-nitrogen could be found.

An equal relationship between the incubation temperature and the mobilization of nitrogen can be found also in the BC-peat. However, the rate of the accumulation of mineral nitrogen has been lower than in the SC-peat. This is particularly true of the samples incubated at 20° and 35°. Probably, the higher cellulose and hemicellulose contents of the BC-peat has been responsible for a more intensive biological immobilization of nitrogen as compared with that which took place in the SC-peat. The lower content of total mineral nitrogen in both the limed series may also have its cause in a more intensive synthesis of new cell substance. The possibility of denitrification must also be taken into consideration, as well as the loss of ammonia by volatilization. The latter mechanism, however, seems to be less important, since the volatilization of ammonia from a medium more acid than pH 6.5 occurs at a very slow rate (14). In addition to these the possible fixation of ammonia as a structural part of humic acids may deserve some attention.

In general, the optimum temperature for nitrification has been found to be between 20° and 30°C, while the minimum and maximum temperatures are about 4° and 40°C, respectively (2, 8). As to the lower temperatures, the results of these experiments agree with the earlier conceptions, but the fairly high content of nitrate-nitrogen in the samples incubated at 65° is unexpected. Before further investigations has been made it is unnecessary to pay more attention to the mechanism of nitrate-formation at high temperatures. Perhaps also the accumulation of ammonia at 50° and at 65° is partly a purely chemical phenomenon.

Table 2. Nitrogen fractions in the incubated samples

Incubated at	Tot. N %		Mineral N		Insoluble N		Soluble org. N	
			per cent of tot. N					
	0	$CaCO_3$	0	$CaCO_3$	0	$CaCO_3$	0	$CaCO_3$
SC-peat								
Original	2.9		1.3		33		66	
5°	2.9	2.9	2.5	2.6	32	31	65	67
20°	2.9	2.9	3.5	2.4	34	31	62	66
35°	3.0	3.0	5.0	3.8	35	33	60	63
50°	3.1	3.2	(7.3)	(7.7)	34	30		
65°	3.2	3.3	19.5	15.4	37	37	44	48
BC-peat								
Original	2.5		1.5		34		64	
5°	2.7	2.7	2.5	2.2	33	32	64	65
20°	2.8	2.8	1.9	1.7	33	31	65	67
35°	2.8	2.9	2.8	2.2	29	32	68	66
50°	2.9	2.9	(9.1)	(6.0)	33	32		
65°	3.0	3.1	13.4	7.1	34	33	53	60

In the samples incubated at 50° and 65° the mineral nitrogen represents a considerable proportion of the total nitrogen (Table 2) It means that under favourable conditions from one tenth to one fifth of the peat nitrogen can be rendered available fairly easily. But also at the lower temperatures, even at 5°, the mineralization of organic nitrogen has not been quite negligible. The part of total nitrogen that exists in insoluble form or in the fraction of the lignin-humic complex is nearly equal in all the samples. The largest amount of nitrogen occurs in hydrolyzable compounds.

Most of the available information in regard to the influence of heat upon soil properties is obtained in connection with soil sterilization experiments. In general it is stated that steaming or dry heating increase the amount of ammonia, but the nitrate-nitrogen content does not change or it may even drop (4, 7, 10, 11, 12). Similar results were obtained also in the present experiments. The data in tables 3 and 4 show a marked increase in the ammonia content of both peats, even due to a treatment at temperatures as low as 50° and 75°. The moist heat brought about a more intensive transformation of nitrogen than the dry heat, as could be expected.

Table 3. NH_4-nitrogen and NO_3-nitrogen in the peat samples treated by moist heat for two hours. Expressed as ppm of dry matter.

Temperature	SC-peat		BC-peat	
	NH_4-N	NO_3-N	NH_4-N	NO_3-N
75°	710	20	720	20
100°	740	20	820	20
120°	800	20	810	20
Original	330	30	390	50

Table 4. NH_4-nitrogen and NO_3-nitrogen in the peat samples treated by dry heat for three hours. Expressed as ppm of dry matter.

Temperature	SC-peat		BC-peat	
	NH_4-N	NO_3-N	NH_4-N	NO_3-N
50°	500	20	520	20
75°	420	20	420	20
100°	470	20	420	20
125°	500	20	440	20
150°	340	20	300	20
200°	720	40	650	20
Original	330	30	390	50

It is of interest to note that accumulation of ammonia nitrogen in the samples treated by dry heat does not increase when the temperature increases from 50° to 125°. At 150° a drop in the values precedes the maximum of these experiments lying at 200°.

These data for the ammonia and nitrate nitrogen contents of the peat samples cannot, however, give any reliable picture of the transformations brought about by the heat treatments. The losses of organic matter and, particularly, of total nitrogen are more important points. Tables 5 and 6 reveal that these losses were nearly negligible at temperatures below 125°. At 150° and especially at 200° a considerable amount of organic matter was burnt up. The losses of total nitrogen at these highest temperatures were about one half of the corresponding decreases in the dry matter. The nitrogen in the BC-peat seems to have been more resistant than that of the SC-sample.

The relations between the losses of nitrogen and organic matter probably depends on the nature and on the degree of decomposition of the peat. For example, in the experiments reported by Potter and Snyder (10) the loss of total nitrogen was more than twice as large as that of dry matter when a well-decomposed peat sample was heated at 200° for two hours.

The changes of acidity deserve some attention. A fairly regular decrease in the

Table 5. Acidity and losses of dry matter and total nitrogen in peat samples treated by moist heat for two hours

Temperature	SC-peat			BC-peat		
	pH	Losses of		pH	Losses of	
		dry matter %	tot. N %		dry matter %	tot. N %
75°	4.53	0	0	4.91	1	0
100°	4.41	2	0	4.85	1	0
120°	4.49	1	0	4.80	3	0

Table 6. Acidity and losses of dry matter and total nitrogen in peat samples treated by dry heat for three hours.

Temperature	SC-peat			BC-peat		
	pH	Losses of dry matter %	Losses of tot. N %	pH	Losses of dry matter %	Losses of tot. N %
50°	4.92	0	0	5.09	0	0
75°	4.83	0	1	5.05	1	0
100°	4.79	0	4	4.96	2	0
125°	4.62	0	3	4.80	2	0
150°	4.57	13	7	4.74	9	2
200°	5.33	32	17	5.80	37	16

pH-values with increasing temperature can be demonstrated within the range from 50° to 150°. This is in accordance with several earlier investigations. (3, 6), and probably due to changes in the state of peat colloids. At 200°C, however, the structure of the organic material must have been partly destroyed, and a decrease in the amount of organic acids has brought an increase in the corresponding pH-values.

Summary and conclusions

The preliminary experiments the results of which are recorded in the present paper, have been carried out in order to obtain some information on the microbiological and chemical mobilization of peat nitrogen at various temperatures.

In the incubation experiment at 5°, 20°, 35°, 50°, and 65°C the accumulation of ammonia nitrogen increased with a rising temperature except in the limed series where a minimum was found at 20°. The maximum of nitrate-nitrogen lay at 20° in both the series. The amount of nitrite-nitrogen was almost negligible in all the samples.

The mineral nitrogen in the samples incubated at 50° and 65° represented 10—20 % of the total nitrogen. Thus, the organic nitrogen in peat soils can be mobilized to a marked extent, if the conditions are favourable. Accumulation of mineral nitrogen could be stated also at the lower temperatures where the reutilization of released nitrogen in the synthesis of new microbial substance is always more intensive than in the range of thermophilic organisms. Even at 5° a release of nitrogen was noticable.

In these experiments liming did not show any beneficial effect upon the accumulation of mineral nitrogen, on the contrary, the values for total nitrogen and ammonia nitrogen were lower in the limed series. The nitrate formation was generally somewhat higher in the limed samples than in the corresponding unlimed ones.

It was supposed that the considerable increase in the ammonia content of the samples incubated at 50° and 65° was partly due to purely chemical transformations, since the mere heating of moist samples at 75° for two hours brought about a marked accumulation of ammonia nitrogen. The treatment with dry heat was less effective except when the temperature was raised to 200° in which case a carbonization of the peat took place. The losses of organic matter and of total nitrogen due to the heating were almost negligible at the temperatures below 150°. At 150° and at 200°, respectively, about one tenth and one third of the organic matter was burnt up, and the losses of total nitrogen corresponded to approximately one half of the decrease in dry matter.

On the basis of the results reported above valid conclusions ought not to be drawn, since the material is too scarce. However, these experiments indicate that reasons for further research exist.

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SELOSTUS:

LÄMPÖTILAN VAIKUTUKSESTA TURPEEN TYPEN MOBILISOITUMISEEN

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Yliopiston maanviljelyskemian laitoksessa käynnissä olevien Pohjois-Suomen soiden typen käyttökelpoisuutta koskevien tutkimusten yhteydessä on kiinnitetty huomiota myös lämpötilan vaikutukseen typen mobilisoitumista säätelevänä tekijänä. Edellä on selostettu eräitä laboratoriokokeita, joilla pyrittiin selvittämään turpeen typen mikrobiologista ja kemiallista mobilisoitumista eri lämpötiloissa.

Kun verraten heikosti maatuneita SC- ja BC-turpeita muhitettiin 100 vrk. 5°, 20°, 35°, 50° tai 65° lämpötilassa, todettiin näytteiden ammoniumtypen lisääntyneen sitä enemmän, mitä korkeampi oli muhituslämpötila. Poikkeuksen muodostivat kuitenkin kalkittujen sarjojen 20°:ssa muhitetut näytteet, joiden ammoniumtypen pitoisuus oli muita alempi. Nitraattityppeä kertyi eniten 20°:ssa. Nitriittityppeä oli näytteissä häviävän pienet määrät.

Näissä kokeissa ei kalkitus lisännyt näytteiden mineraalitypen määrää, vaan päinvastoin kalkittujen sarjojen ammoniumtypen ja mineraalitypen määrät olivat pienemmät kuin kalkitsemattomien. Korkeampi pH oli myös edistänyt nitraattitypen muodostumista.

50° ja 65° lämpötiloissa muhitettujen näytteiden mineraalityppi oli 10—20 % näytteiden kokonaistypestä. Alemmissa lämpötiloissa, joissa typen biologinen pidättyminen on voimakkaampaa kuin termofiilien mikro-organismien alueella, oli kertyneen mineraalitypen määrä huomattavasti pienempi, vain muutama prosentti kokonaistypestä.

On todennäköistä, että korkeammissa lämpötiloissa vapautuu ammoniumtyppeä puhtaasti kemiallistenkin tekijöiden vaikutuksesta, sillä pelkkä kosteiden näytteiden kuumentaminen kahden tunnin aikana 75°:ssa lisäsi huomattavasti ammoniumtypen määrää. Kuivien näytteiden kuumentaminen johti tehokkaaseen ammoniumtypen kertymiseen vasta, kun lämpötila oli 200°, jolloin turve jo melkoisesti hiiltyi ja noin kolmannes sen kuiva-aineesta paloi. Typen häviö tässä lämpötilassa oli vain noin puolet orgaanisen aineksen häviöstä.