THERMAL DECOMPOSITION CHARACTERISTICS OF HUMUS HORIZONS FROM CULBIN FOREST

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Differential thermal analysis in an oxygen atmosphere and pyrolysis in vacuo combined with mass spectrometry have been used to follow the transformations occurring during the humification of vegetation. Two processes are indicated, one, apparently enhanced by liming consisting of oxidative degradation and the other corresponding to degradation of organic components with high thermal dissociation energies. At the base of some profiles the humus has characteristics close to those of translocated humus in freely drained soils.

At Culbin (Laigh of Moray) Forest, Morayshire, planting of trees directly on dune sand began in 1922. Since the sand itself contains only about 0.06% carbon, the soil profiles that have developed are derived from a known and well-defined vegetation type and complications arising from changes in vegetation and land use are absent. These soils are therefore suitable for thermoanalytical study of the transformations occurring during the change from freshly deposited vegetation to humified material.

In a differential thermal analysis (DTA) study of pine needles, using an oxygen atmosphere, Mitchell and Birnie [1] have noted marked changes in the exothermic peak pattern after leaf fall. The same DTA technique has been employed in the present study and supplementary evidence is provided by rapid vacuum pyrolysis followed by mass spectrometric examination of the volatile products [2].

Experimental

Materials and methods

The typical soil profile is still essentially as described by Ovington [3] in 1950, consisting of a continuous organic layer up to 7 cm thick overlying the dune sand. In the organic layer, beneath the surface covering of recently fallen litter, two layers can usually be distinguished: an upper *L* layer of relatively undecomposed litter and a lower more darkly coloured *F* or F/H layer of decomposing plant remains. In places the underlying sand is stained by organic matter for some 2—3 cm below the base of the organic layer and at its base there is a sharp boundary to the aeolian sand.

In the autumn of 1972 four profiles were selected and sampled for study:

Profile 1: Under Scots pine (Pinus sylvestris), the litter consisting entirely of pine needles. Freshly picked needles, newly fallen needles, the L layer and the F layer were sampled.

Profile 2: Under Birch (Betula alba) on the top of a knoll, the litter consisting almost entirely of birch leaves. Fresh leaves, recently fallen leaves, the L layer and the F layer were sampled.
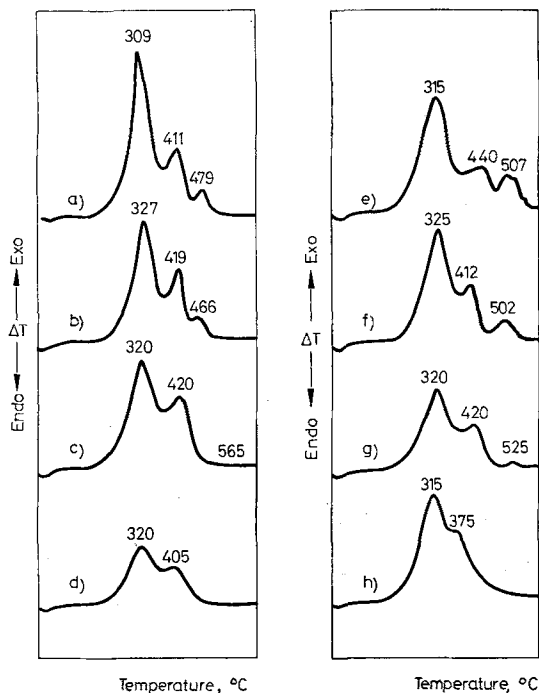

Fig. 1. DTA curves for samples from Profiles 1 (a—d), and 2 (e—h): (a) — fresh pine needles (7 mg); (b) — recent litter (3 mg); (c) — L horizon (3 mg); (d) — F horizon (3 mg); (e) — fresh birch leaves (5 mg); (f) — recent litter (3 mg); (g) — L horizon (3 mg); (h) — F horizon (3 mg)

Profile 3: Under Scots pine where there was a predominant ground cover of moss, mainly Hypnum cupressiforme var. ericetorum. The moss, a very dark brown (10YR3/2.5) fibrous L/F layer with abundant decaying pine needles, and the underlying organic-stained sand were sampled.

Profile 4: Similar to Profile 3, but treated in 1968 with ground limestone at the rate of 2500 kg/ha as part of a study on nitrogen mineralization [4]. The surface moss, a very dark greyish brown (10YR3/2) fibrous F layer, a very dark grey

(10YR3/1) more humified F/H layer, a second very dark greyish brown (10YR3/2) fibrous *F* layer and the underlying organic-stained sand were sampled.

Samples were passed through a 5 mm sieve to remove twigs and stones, dried at 100° and ground in an agate ball mill to approximately 30 μm diameter. For DTA a sample of a few mg (actual weights are indicated in connection with the curves in Figs 1 and 2) was placed in a shallow aluminium pan in the differential scanning calorimeter cell of a Du Pont 900 Differential Thermal Analyzer, an empty pan being used as reference. The heating rate was 10°/min and the oxygen flow-rate was 200 ml/min.
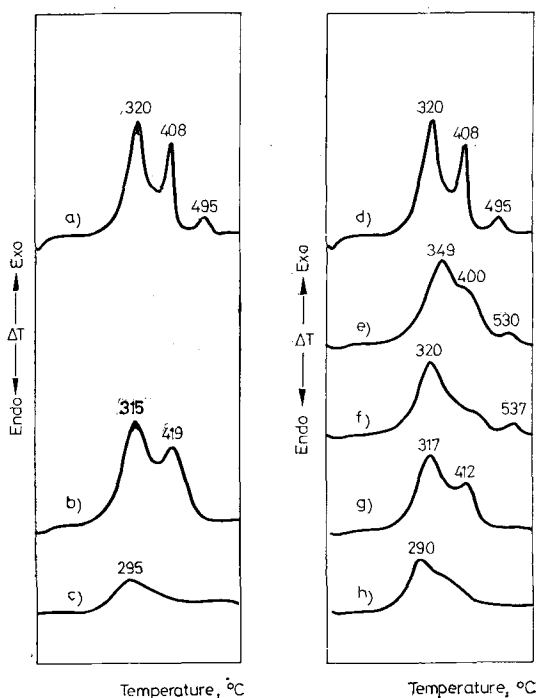

Fig. 2. DTA curves for samples from profiles 3 (a—c) and 4 (d—h): (a) — fresh moss (3 mg); (b) — L/F$_i$ horizon (3 mg); (c) — stained sand (60 mg); (d) — fresh moss (3 mg); (e) — upper F horizon (3 mg); (f) — F/H horizon (3 mg); (g) — Lower F horizon (3 mg); (h) — stained sand (52 mg)

Samples of 1 mg were used for pyrolysis combined with mass spectrometry. The samples were pyrolysed at 770° in vacuo (10^{-3} torr.) in a Curie-point pyrolyser, the volatile products being examined on an AEI MS10c2 mass spectrometer as already described [2].

Results and discussion

In addition to a small endothermic peak below 100°, the DTA curves (Figs 1 and 2) for freshly picked or newly fallen vegetation show three well-defined exothermic peaks — in agreement with previous observations [1, 5]. For purposes of discussion these will be termed peaks I, II and III, peak I being in the range 200 – 380° with peak temperatures at 300 – 320°, peak II in the range 370 – 455°
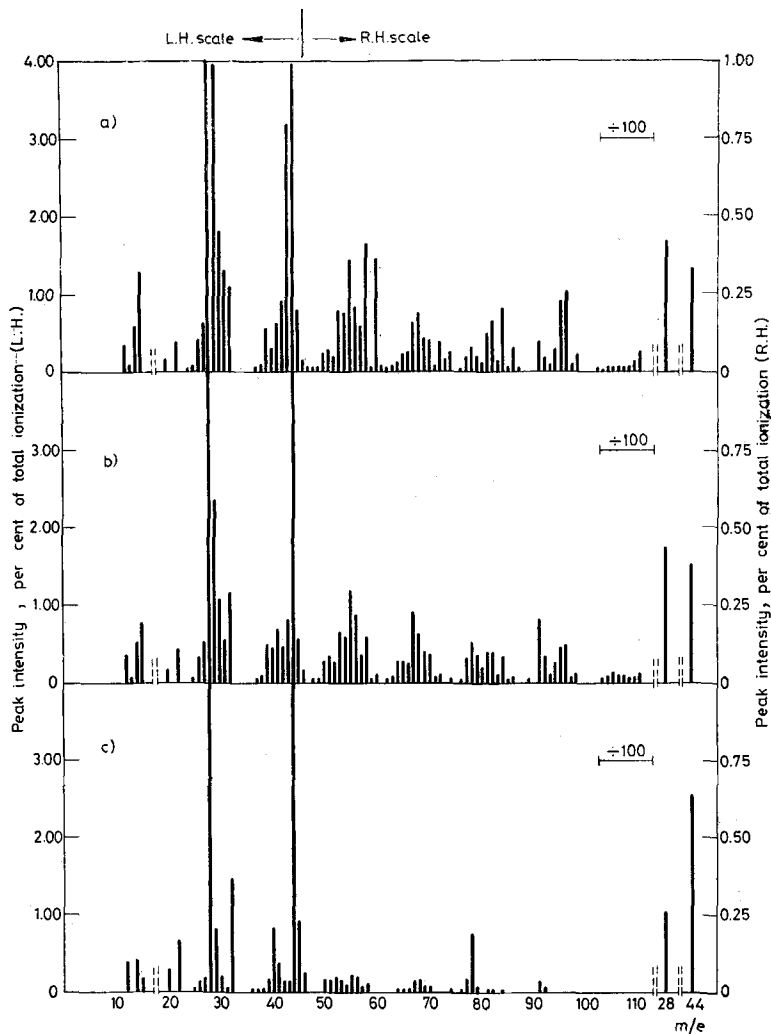

Fig. 3. Mass spectra of pyrolysis products from samples of profile 3: (a) — fresh moss; (b) — L/F horizon; (c) — stained sand

with peaks at about 410° and peak III in the region 450 – 550° with peak temperatures at 465 – 505°.

Two changes in the DTA curve occur with depth: (a) peak III tends to decrease in size, eventually disappearing (cf. [1]); (b) peaks I and II tend to broaden and merge. These features are particularly clear for Profiles 1 and 2 (Fig. 1) where peak III is poorly developed for the L layer and is absent on the curve for the F layer whilst peaks I and II broaden and partially superpose in the F layer. The surface vegetation of profiles 3 and 4 yields three clear peaks (Fig. 2). In the L/F layer of profile 3 peak III is absent and peaks I and II are broader; the stained sand yields no separate peak II but the tailing towards high temperatures suggests that it has merged with peak I. The curves for both the stained sand and the lower F layer of profile 4 are similar to those for the stained sand and L/F layer of profile 3, respectively. The F/H and upper F layers of this profile, however, whilst showing pronounced merging of peaks I and II reveal no marked decrease in size of peak III. This less common pattern presumably reflects the effects of liming some four and a half years earlier, since below the F/H layer the normal trend is observed.

As an example the mass spectra of pyrolysis products of samples from profile 3 are reproduced in Fig. 3, relative peak heights at the various mass numbers (m/e) indicating relative amounts of CO, CO_2, various hydrocarbon groups, etc. [2]. The amounts of hydrocarbons and other organic molecules decrease down the profile and the underlying stained sand yields a pyrolysis pattern characteristic of the translocated humus found in the B horizons of freely drained soils [6] – i.e. a low CO : CO_2 (m/e 28 : m/e 44) ratio and very small amounts of hydrocarbons and minor volatile products, except for benzene at m/e 78. The pattern from other layers with a high CO : CO_2 ratio and a large amount of hydrocarbons resembles that for more humus [2].

In some instances variations in peak heights parallel changes on the DTA curves. For example, from the selected information in Table 1, the m/e 28 : m/e 44 ratio varies in the same manner as peak II, both showing similar step-wise decreases in size with depth in profiles 1, 2 and 3 and a more complex behaviour in profile 4 where they decrease for the upper F and F/H layers, increase in the lower F layer, and subsequently decrease for the stained sand. The values for m/e 15 and m/e 30 also show some correlation with the size of peak II. Of the many peaks that decrease in size down the profile only those at the m/e values 29, 31, 42, 43, 58, 60, 74 and 86 – which are those mass numbers likely to arise from oxygen-containing products such as alcohols, aldehydes and ketones – do so in steps approximately parallel to the decrease in size of peak III.

Since the increasing degree of humification with depth that is visible in these profiles is accompanied by the decrease in the amounts of almost all the minor volatile products of pyrolysis, it could be assessed from the decrease in abundance of any of these. On the other hand, DTA curves show two kinds of change namely, the decrease in size of peak III and the decrease in resolution of peaks I and II. The decrease in size of peak III and concomitantly of certain mass peaks suggests the degradation of materials that are present in the undecomposed litter. Although

Table 1

Mass spectra of pyrolysis products. Selected peak heights

Profile	Sample or layer	m/e 28:m/e 44	m/e 15*	m/e 29	m/e 30	m/e 31	m/e 42	m/e 43	m/e 58	m/e 60	m/e 74	m/e 78	m/e 86
1. Birch	Fresh Vegetation	0.58	2.33	4.21	1.3	2.8	1.2	4.6	0.58	0.49	0.12	0.19	0.16
	Recent Litter	1.13	1.92	5.01	2.2	3.3	1.2	4.1	0.55	0.54	0.10	0.14	0.13
	L	1.02	1.94	3.66	1.7	1.6	0.9	2.2	0.31	0.21	0.04	0.14	0.05
	F	1.17	1.55	2.81	1.2	1.2	0.6	1.2	0.20	0.05	0.02	0.16	0.03
2. Pine	Fresh Vegetation	0.91	2.14	5.37	2.2	3.5	1.3	4.2	0.73	0.43	0.12	0.26	0.13
	Recent Litter	1.33	2.07	5.87	2.8	3.2	1.2	4.2	0.65	0.43	0.11	0.15	0.12
	L	1.00	2.07	4.10	2.2	1.7	0.8	2.1	0.32	0.13	0.04	0.15	0.05
	F	1.14	1.68	3.48	1.7	1.0	0.7	1.8	0.29	0.08	0.03	0.16	0.04
3. Moss (untreated)	Fresh Vegetation	1.17	1.82	5.15	2.5	2.2	1.3	4.7	0.61	0.65	0.77	0.10	0.12
	F	1.10	1.01	2.70	1.2	0.6	0.5	0.9	0.17	0.03	0.01	0.16	0.02
	Stained sand	0.55	0.33	1.28	0.4	0.08	0.2	0.3	0.04	0.01	0.01	0.21	0
4. Moss (limed)	Fresh Vegetation	1.17	1.82	5.15	2.5	2.2	1.3	4.7	0.61	0.65	0.77	0.10	0.12
	Upper F	0.91	2.05	4.35	2.1	1.4	0.9	2.6	0.37	0.18	0.06	0.16	0.07
	F/H	0.92	1.54	3.51	1.7	1.0	0.8	2.2	0.31	0.11	0.04	0.17	0.05
	Lower F	1.23	1.35	2.83	1.3	0.8	0.6	1.5	0.24	0.10	0.03	0.16	0.04
	Stained Sand	0.67	0.58	1.25	0.4	0.2	0.4	0.4	0.07	0.03	0.02	0.20	0.01

* All peak heights are expressed as a ratio % to the sum of peak heights m/e 28 + m/e 44

no specific plant component could be associated with peak III in earlier studies, humic acid from peat yields a third peak in the region of 500°, which is chiefly associated with the fraction soluble in alcohol-benzene [1, 7]. From the high temperature of decomposition the materials yielding this peak must have strong bonds and high dissociation energies.

Earlier studies [1] on peaks I and II have suggested that the latter results from the oxidative decomposition of compounds containing relatively non-volatile or strongly bound carbon atoms whereas peak I results from the oxidation of more readily volatile materials with oxygen-containing groups. Thus, oxygen-rich materials such as cellulose, holocellulose and simple sugars yield a curve with a large peak I and a small peak II whilst materials with higher carbon contents, such as humic acids, lignin and p-aminohippuric acid yield a curve with a small peak I and a large peak II [1]. The present study has shown the size of peak II to be associated with that of the $CO : CO_2$ ratio in the volatile products, which is itself related to the degree of oxidation of the organic matter. This is in agreement with previous observations from DTA and DTG which have shown an association between degree of humification and the proportion of oxygen-containing functional groups [1, 8]. The beginning of such a process is therefore indicated here by the changes in peaks I and II, particularly in those horizons that show the influence of liming in profile 4.

From the results for profile 4 it is also apparent that the two processes envisaged − i.e. decrease in amount of strongly-bonded compounds with high dissociation energies and increase in the number of oxygen-containing functional groups − do not necessarily occur together, nor is one a necessary precursor of the other. Experimental evidence also shows that the staining of the underlying sand is due to humus very similar to the translocated humus found in the B horizons of freely drained soils − i.e. it is highly oxidized and relatively simple in chemical structure.

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References

1. B. D. MITCHELL and A. C. BIRNIE, in Differential Thermal Analysis, ed. R. C. MACKENZIE, Academic Press, London and New York, 1970. 685.
2. J. M. BRACEWELL and G. W. ROBERTSON, J. Soil Sci., 24 (1973) 421.
3. J. D. OVINGTON, J. Ecol., 38 (1950) 303.
4. B. L. WILLIAMS, Forestry, 45 (1972) 177.
5. J. M. STEWART, A. C. BIRNIE and B. D. MITCHELL, Agrochimica, 11 (1966) 92.
6. J. M. BRACEWELL, Geoderma, 6 (1971) 163.
7. B. D. MITCHELL, Scient. Proc. R. Dubl. Soc., A 1 (1960) 105.
8. M. SCHNITZER and I. HOFFMAN, Proc. Soil Sci. Soc. Am., 30 (1966) 63.

Résumé — Afin de suivre les variations qui ont lieu lors de l'humification des substances végé-
tales on a utilisé l'analyse thermique différentielle en atmosphère d'oxygène et la pyrolyse sous
vide combinées avec la spectrométrie de masse. Deux processus sont indiqués: l'un d'eux
semble être intensifié par la calcification et consiste en une dégradation oxydante tandis que
l'autre correspond à une dégradation de composés organiques avec une énergie d'activation
élevée. A la base de quelques profils, l'humus montre des caractéristiques similaires à celles
observées chez les humus déplacés des sols à infiltration libre.

ZUSAMMENFASSUNG — Differentialthermoanalyse in Sauerstoff-Atmosphäre sowie mit Massen-
spektrometrie kombinierte Vakuumpyrolyse wurden zur Verfolgung der Veränderungen
während der Humifizierung der Vegetation eingesetzt. Zwei Prozesse werden angedeutet, der
eine, welcher anscheinend durch Verkalkung verstärkt wird, besteht in einer oxidativen Zer-
setzung und der andere in der Zersetzung organischer Komponenten von hoher thermischer
Dissoziationsenergie. Aufgrund einiger Profile besitzt der Humus Eigenschaften, welche den
der übertragenen Humus-Arten frei sickernder Böden nahe stehen.

Резюме — Дифференциальный термический анализ в атмосфере кислорода и пиролиз в
вакууме в комбинации с масс-спектрометрией был использован, чтобы проследить за
превращениями, происходящими при гумификсации растительности. Установлено два
процесса, из которых один, очевидно, заключается в окислительной деградации и который
повышается при известковании. Другой же заключается в соответствующей деградации
органических компонент с высокими термическими энергиями диссоциации. В общих чер-
тах исследованный гумус имеет характеристики близкие к гумусу осушенных почв.