An integraded chemical and micromorphological investigation of humic substances in three podzolized soils of the Netherlands

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Summary

The humic substances in three podzolized soils of the Netherlands, viz a 'Holt' podzol (Entic Haplorthod), a 'Haar' podzol (Typic Haplohumod) and a 'Veld' podzol (Typic Haplaquod), were analysed chemically and micromorphologically. Tiurin's method was used for total C analysis and for fractional analysis of humic substances. The absorption spectra of Na-humates in visible light and infrared spectra were determined for the humic acids. The results of the mentioned analyses were compared with the micromorphology of the organic matter occurring in the three soils.

A distinct difference was found in the translocation and distribution of the principal humus compounds in the 'Holt' podzol on the one hand, and the 'Haar' podzol and the 'Veld' podzol on the other hand. The 'Holt' podzol is characterized by a 'mechanical' illuviation, and the other two profiles by translocation in solution. Good correlations were found between the micromorphological images and the chemical composition of the humic substances. Illuviation cutans occurring in the B horizons of the 'Haar' podzol and the 'Veld' podzol appeared to consist mainly of fulvic acids. The dark humus micro-aggregates characteristic of the 'Haar' podzol and the Ap horizon of the 'Veld' podzol differ in composition of humic substances from the brown micro-aggregates of the 'Holt' podzol. Correlations of the stability of micro-aggregates and their composition were found.

Introduction

In most mineral soils the content of humic substances is relatively small. Nevertheless, those substances are very important from the pedogenetic point of view. This is particularly evident in podzolized soils where clear profile differentiation

results from the illuviation of humic substances and their role in the transloca-
tion of mineral components.

Consequently, the humic substances in podzolized soils have been the subject
of chemical investigations for some decades. Several authors, among others Ko-
nonova (1966), Scharpenseel et al. (1964), Scheffer & Ulrich (1960), Tiurin
(1937) and Turski & Lipińska (1965), have shown that the fractional humus
composition in podzolized soils differs considerably from that in other soils. In
particular, podzolized soils have higher contents of mobile humus fractions and
a lower C-humic acids/C-fulvic acids ratio ($C_{h.ac}/C_{f.ac}$). Humic acids in podzo-
lized soils have a relatively simple molecular structure, i.e. a low degree of poly-
merization (Orlow, 1968; Sapek, 1971; Springer, 1934; Sytek, 1972; Welte,
1956); this has been found by chemical methods as well as by spectroscopic cha-
racterization (a rather low absorption in the visible light region and a high opti-
cal density ratio E4/E6).

Recently more attention has been paid to the study of functional groups oc-
curring in the humic substances of podzolic soils.

Infrared spectrophotometry has shown that humic acids and fulvic acids iso-
lated from the Bh horizon of podzolic soils contain similar functional groups
and have almost identical molecular structures. The existing differences are
mainly due to different amounts of COOH groups (Schnitzer, 1971).

Nevertheless chemical and physicochemical methods alone do not give us an
insight into the relation between the composition of organic matter and its
morphology. Probably the only way of answering that question is through a
combined chemical, physico-chemical and micromorphological investigation of
the organic matter.

This paper deals with such an investigation that was done on three podzolized
soils of the Netherlands. Our questions were of two kinds, i.e.:
1) Is there a certain profile differentiation in the composition and morphology
of the humus in the soils investigated?
2) Is the fractional humus composition reflected by the micromorphology of or-
ganic matter in different podzolized soils?

Materials and methods

Three soil profiles were investigated, i.e.:
— Profile I: an Entic Haplorthod[1] or Leptic Podzol[2] or 'Holt' podzol soil[3] or
Rusty podzolized soil (Gleba rdzawa)[4].
— Profile II: a Typic Haplohumod[1] or Humic Podzol[2] or 'Haar' podzol soil[3] or
Iron-humus soil (Bielica żelasisto-próchniczna)[4].
— Profile III: a Typic Haplaquod[1] or Gleyic Podzol[2] or 'Veld' podzol soil[3] or
Mucky podzolic soil (Gleba bielicowa murszasta)[4].

[1] According to the U.S. Soil Taxonomy (Soil Survey Staff, 1975).
[2] According to the FAO soil classification.
[3] According to the Dutch system of soil classification (de Bakker & Schelling, 1966).
[4] According to the Polish system of soil classification (Kuźnicki et al., 1974).

Table 1. Fractional humus composition of some Dutch podzolic soils.

Profile and horizon	Depth (cm)	Total C*	Bitu-mens*	Frac-tion 1a*	Fraction 1*			Fraction 2*			$C_{h.ac.}/C_{f.ac.}$ in fractions 1a, 1 and 2	Mobile forms of h.ac. (%)	Humins*
					isola-ted	$C_{h.ac.}$	$C_{f.ac.}$	isola-ted	$C_{h.ac.}$	$C_{f.ac.}$			
Profile I. 'Holt' podzol													
A1(2)	7-15	6119	311	125	3305	1627	1678	75	55	20	0.9	100	2332
		100	5.0	2.0	54.0	26.5	27.5	1.1	0.9	0.2			38.1
AB	15-30	1602	220	157	818	393	425	66	34	32	0.7	100	345
		100	13.5	9.8	51.0	24.5	26.5	4.1	2.1	2.0			21.5
B2	30-45	1268	90	166	382	216	166	36	23	23	0.7	75	590
		100	7.0	13.0	30.1	17.1	13.0	2.8	1.8	1.0			46.5
B3	45-60	675	60	114	260	146	114	30	20	10	0.7	86	198
		100	8.8	16.8	38.5	21.6	16.9	4.4	3.2	1.2			29.3
Profile II. 'Haar' podzol													
A1	0-2	8611	1016	80	3523	1609	1914	296	121	175	0.8	100	3791
		100	11.8	0.9	40.9	18.6	22.3	3.4	1.4	2.0			44.0
A21	5-12	2308	547	24	814	471	343	58	25	33	1.2	100	873
		100	23.6	1.0	35.2	20.4	14.8	2.5	1.0	1.5			37.8
A22	15-25	1843	401	32	886	485	401	30	16	14	1.1	100	490
		100	21.7	1.7	48.1	25.5	22.6	1.6	0.9	0.7			26.5
B2h	29-34	3268	462	221	1992	866	1126	61	23	38	0.6	100	549
		100	14.1	6.7	60.9	26.5	34.9	1.9	0.7	1.2			16.8
B22	37-47	2400	313	332	1344	569	775	34	10	24	0.5	100	306
		100	13.0	13.8	56.0	23.6	32.4	1.4	0.4	1.0			12.7
B3	52-62	903	25	287	459	258	201	20	13	7	0.5	100	117
		100	2.7	31.7	50.8	28.5	22.3	2.2	1.4	0.8			12.9
Profile III. 'Veld' podzol													
Ap	5-15	4106	858	77	2040	1283	757	75	38	37	1.5	100	1056
		100	20.9	1.8	49.7	31.2	18.5	1.8	0.9	0.9			25.7
B2	30-40	2117	354	129	1308	746	562	20	13	7	1.1	100	306
		100	16.7	6.1	61.8	35.2	26.6	0.9	0.6	0.3			14.4
B3	45-55	1042	65	218	673	349	324	6	n.d.	n.d.	0.6	100	53
		100	6.2	20.9	64.6	33.5	31.1	0.6					5.0

* The top row of figures indicates the C content in mg/100 g of soil; the lower line gives the content as % (m/m) of total C.

Table 2. Laboratory data of Profile I.

Horizon	Sampling depth (cm)	pH (KCl)	Clay (%)	Silt (%)	Sand (%)
A1(2)	0- 6	3.0	5.0	15.0	80.0
B2	25- 35	4.0	5.0	16.0	79.0
B3	50- 60	4.3	4.5	15.0	80.5
C	90-100	4.7	1.5	10.0	88.5

Profile I (de Bakker & Edelman-Vlam, 1964a; de Bakker, 1979)
This noncalcareous loamy sand soil is situated on an ice-pushed ridge near Doorwerth (about 10 km west of Arnhem). Permeability is high, and the water-table is very deep. The vegetation is an oak coppice which has not been cut for some decades. The ground-cover consists of bracken (*Pteridium aquilinum*) and some wavy hair grass (*Deschampsia flexuosa*).

Under a thin A0 a dark, very friable A1(2) horizon occurs up to 15 cm below the surface. This is underlain by a greyish AB. Underneath is a very friable, pellety, dark brown B2 horizon (30-45 cm below surface), which gradually passes into a brownish yellow B3 horizon. The laboratory data[5] are given in Table 2.

Profile II (de Bakker & Edelman-Vlam, 1964b; de Bakker, 1979)
The soil is situated a few km north of Arnhem (Schaarsbergen) on a Late Pleistocene dune ridge which rises approx. 5 m above the surrounding ground. The parent material is a noncalcareous sand. Permeability is high and the water-table is found at more than 10 m depth. The vegetation is heather (*Calluna vulgaris*) and some seedlings of Scots Pine (*Pinus silvestris*).

Under a thin sod (A1) a well developed A2 is present. This horizon is underlain by a black horizon (24-36 cm below the surface) rich in illuviated organic matter (B2h); underneath this a brown illuvial horizon with ferri-humic cutans occurs (B22). Laboratory data are given in Table 3.

Profile III (de Bakker & Edelman-Vlam, 1964c; de Bakker, 1979)
The profile is situated near Maarsbergen, approx. 20 km east of Utrecht. The soil developed in a noncalcareous medium sand that was deposited by wind during the Late Würm. Permeability is moderate. The water-table fluctuates between about 30 cm in winter and 100 cm in summer. Before World War I the area was marshy heathland, but since then it has been used as grassland.

[5] The laboratory data (pH and granular composition) of this and the other two profiles are taken from the publications of de Bakker & Edelman-Vlam and refer to sites that are near the profiles we investigated. This explains differences between the depths of the sampled zones and the depths of the described soil horizons. The organic matter contents (expressed as total C) of the soils investigated are given in Table 1.

Table 3. Laboratory data of Profile II.

Horizon	Sampling depth (cm)	pH (KCl)	Clay (%)	Silt (%)	Sand (%)
A1	0- 5	3.6	2.0	4.5	93.5
A2	10-15	3.8	0.5	3.5	96.0
B2h	18-20	3.9	0.0	5.5	94.5
B22	25-30	4.4	1.5	2.5	96.0
B3	50-75	4.6	0.0	1.0	99.0

Underneath a very dark grey Ap horizon a brownish grey B2 horizon occurs (approx. 30-40 below the surface), characterized by coatings of illuviated organic matter on the sand grains. This horizon is underlain by a B3 horizon which shows a gradual thinning of the coatings. The A and B horizons are devoid of iron, as can be proved by the fact that they turn white on ignition. Laboratory data are given in Table 4.

From these soils, samples of the different horizons were taken for:
— total C analysis and fractional analysis of humic substances according to Tiurin's method (1937);
— physical characterization of humic acids by spectroscopic methods (absorption in the visible light region and infrared spectrophotometry);
— micromorphologic investigations of thin sections.

Tiurin's method
This method (for a good description see Kononova, 1966) was used because it makes the results of our investigation comparable with those of several other publications on this topic (among others Kononova, 1966; Kozakiewicz, 1966; Tiurin, 1951).

By Tiurin's method the following fractions of humic substances were isolated and determined — as C content — successively (Fig. 1 and Table 1).
1. Humic substances that are soluble in a 1 : 1 mixture of ethanol and benzene. These substances are waxes, fats, resins and related compounds. Although strictly a misnomer, for convenience sake the collective term 'bitumens' has been used by several authors (e.g. Tiurin, 1937; Drozd & Kowalinski, 1972) to

Table 4. Laboratory data of Profile III.

Horizon	Sampling depth (cm)	pH (KCl)	Clay (%)	Silt (%)	Sand (%)
A11	0- 8	4.6	4.0	6.5	89.5
Ap	8-20	4.3	1.5	7.5	91.0
B2	30-55	3.9	0.0	0.5	99.5
B3	60-80	4.2	0.0	0.5	99.5

.designate this group of substances. We have followed suit in this paper.

2. Humic substances that are soluble in 0.1 N H_2SO_4 (decalcification). This *Fraction 1a* consists of very mobile low-molecular compounds, i.e. free fulvic acids (Kononova, 1966; Kozakiewicz, 1966; Scheffer & Ulrich, 1960; Springer, 1934; Tiurin, 1937, 1951).

3. Humic substances separated from the decalcified sample by repeated extraction with 0.1 N NaOH. This *Fraction 1* mainly consists of humic acids and fulvic acids which partly are free, partly combined with mobile forms of R_2O_3 and with calcium.

4. Humic substances separated during further alternate extraction with 0.1 N H_2SO_4 and 0.1 N NaOH. The H_2SO_4 breaks down the links between the humic substances and the stable forms of R_2O_3 and the clay minerals. The bulk of the liberated humic substances is found in the alkaline extract (*Fraction 2*).

5. Humic substances occurring in the soil residue. These are the very stable non-hydrolysable compounds which belong to the *humins*.

6. Humic substances that are soluble in 0.1 N NaOH without previous decalcification of the sample. They mainly consist of humus compounds that are free and/or combined with mobile forms of R_2O_3 (*free humus compounds fraction*).

By acidification to pH$\sim$ 1 and heating to 80 °C the extracts of Fractions 1 and 2 and those of the free humus compounds were separated into:

— humic acids (which precipitate as a dark brown gel)
— fulvic acids (which stay in solution).

After isolation of the precipitates by infiltration, and repeated washing with distilled water to remove the SO_4 ions, the humic acids were dissolved in hot 0.02 N NaOH. The solution was dried on a water bath, and the C content of the humic acids was determined. Once the C contents of Fractions 1 and 2 of the free humus compounds fraction were known, those of the fulvic acids could be calculated by subtraction.

The amount of humic acids bound with calcium was also found by calculation, being the difference between the amount of humic acids of fraction 1 and that of the free humus compounds fraction.

Spectroscopic methods
Supplementary qualitative spectroscopic investigations were carried out on the most important group of humic acids, i.e. those separated from Fraction 1.

— Absorption in the visible light region (400-800 μm wavelength), measured in humic acid solutions that were prepared according to the Kononova method (1966), i.e. solution in 0.02 N $NaHCO_3$ to a concentration of 10 mg C/100 ml. Results are presented in Fig. 1.

— Measurement of infrared spectra (4000-600 cm^{-1} wave number; 2.5-15.4 μm wavelenght) of humic acids mixed with KBr in a 1 : 200 ratio. The humic acids were first purified by electro-dialysis to a pH of 3.4, and then freeze-dried to preserve their natural properties as much as possible. Results are presented in Fig. 2. For details concerning spectroscopic methods, see among others Schnitzer & Khan (1972).
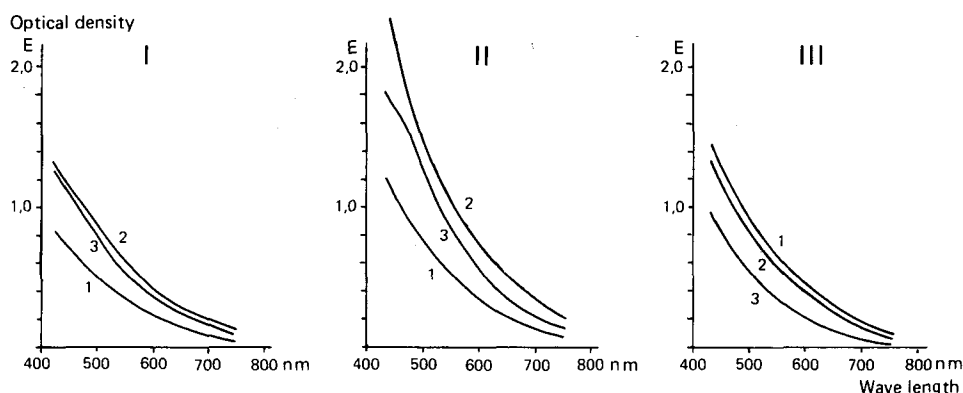
Fig. 1. Absorption spectra in visible light of Na-humates obtained from the three podzolized soils investigated. (Concentration of humic acids: 10 mg C in 100 ml 0.02 N NaHCO$_3$; pH $= 7.4$; E(extinction) $= \log_{10} Io/I$.)
I - 'Holt' podzol soil; 1 = A1(2) horizon, 2 = AB horizon, 3 = B2 horizon.
II - 'Haar' podzol soil; 1 = A1 horizon, 2 = A21 horizon, 3 = B2h horizon.
III - 'Veld' podzol soil; 1 = Ap horizon, 2 = B2 horizon, 3 = B3 horizon.

Thin sections

Thin sections were made according to the method of Jongerius and Heintzberger (1975). In the description of the sections the term *humus micro-aggregates* is used in the sense of Jongerius (1957): aggregates some hundreds of micrometers in maximum size, which are composed of aged excrements. Other terms used in the descriptions are: *polymorphic* (De Coninck et al., 1974; Bullock et al., 1978): organic material without recognizable plant or animal structure which forms a discontinuous mass consisting of small variously coloured patches that usually have diffuse boundaries; *monomorphic* (De Coninck et al., 1974; Bullock et al., 1978): organic material without recognizable plant of animal structure which forms a continuous mass relatively uniform in colour or density; *debris cutan* (Jongerius, 1970): a free grain cutan (Brewer, 1964) consisting of an intimate mixture of silt- en clay-sized material, brownish yellow, and usually showing a rough surface; *humican* (Bal, 1973): a cutan consisting almost entirely of humic substances.

The fractional humus composition

In this chapter the analytic results as presented in Table 1 will be discussed. The relation with soil micromorphology and the genetic interpretation of the data will be dealt with in the general discussion.

Bitumens
In the type of soils and horizons analysed, the compound showed a wide variation in fraction of the soil as well as in fraction of total C. In every soil investiga-
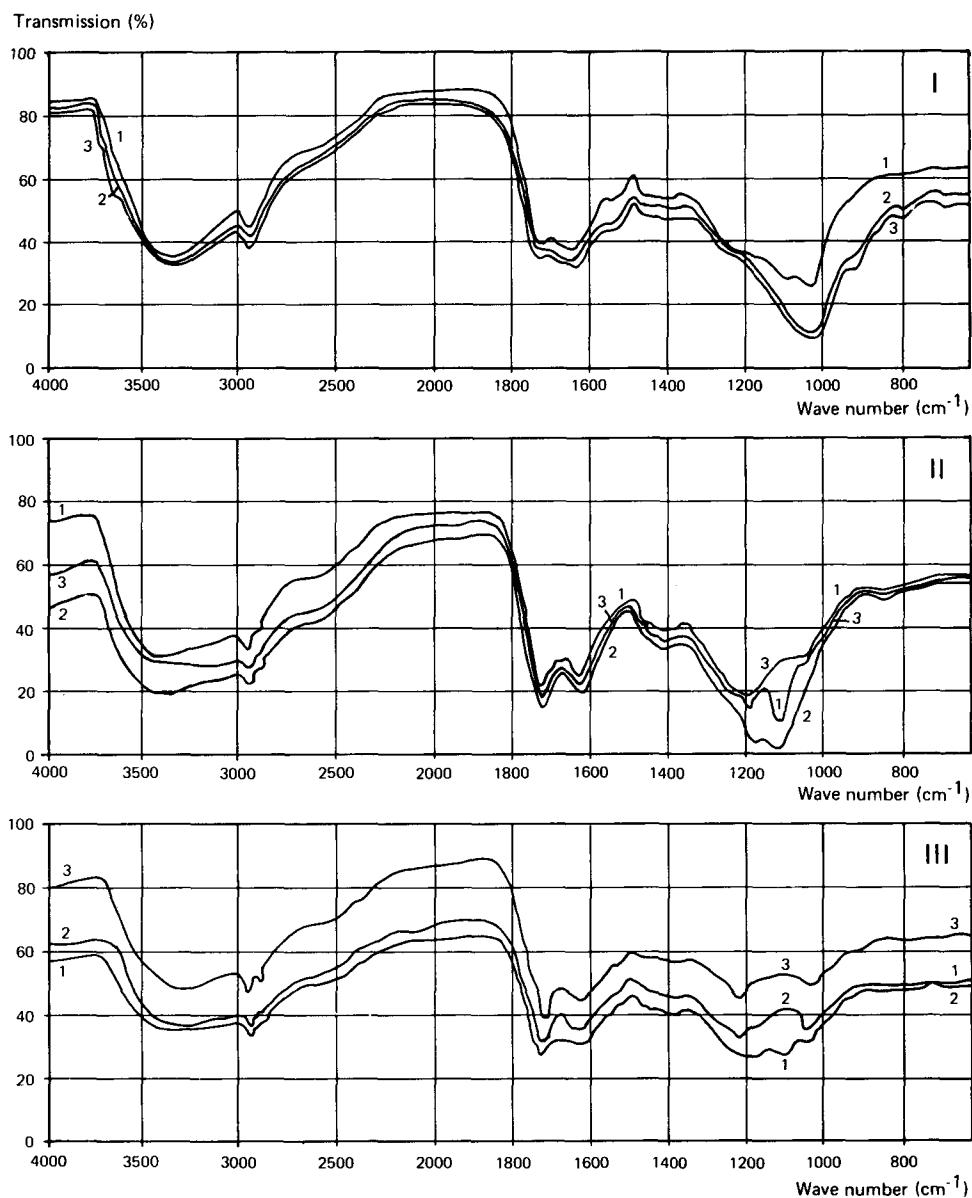
Transmission (%)

Fig. 2. Infrared spectra of humin acids extracted from:
I - 'Holt' podzol soil; 1 = A1(2) horizon, 2 = AB horizon, 3 = B2 horizon.
II - 'Haar' podzol soil; 1 = A1 horizon, 2 = A21 horizon, 3 = B2h horizon.
III - 'Veld' podzol soil; 1 = Ap horizon, 2 = B2 horizon, 3 = B3 horizon.

ted bitumen fraction of the soil decreased with depth, but in Profile II a small increase should be noted in the B2h horizon. However the situation is different for the bitumen fraction of total C. Profiles I and II showed a maximum in the AB and A21 horizons respectively, whereas in Profile III it gradually decreased with depth. In contrast, in the B3 horizon of Profile I there was an increase in this fraction. Finally, bitumen fractions of soil and of total C occurring in the A1, Ap and A2 horizons of Profiles II and III were markedly higher than those in the corresponding horizons of Profile I.

Fraction 1a (free fulvic acids)

In every profile investigated, the content of Fraction 1a in total C increased with depth, but in Profiles I and III this trend was rather weak, whereas the increase was very pronounced in Profile II (from 0.9 % in the A1 horizon to 31.7 % in the B3). The same tendency was apparent in the content of Fraction 1a in soil, except that in Profiles I and II it again decreased markedly below that of the B2 and B22 horizons respectively. The considerable drop occurring in the A2 horizon of Profile II is very striking.

Fraction 1

From the quantitative point of view this is the most important fraction in the samples investigated.

In Profiles I and III the content of Fraction 1 in soil decreased with depth, but there is a considerable difference between both cases. Profile III showed a very gradual decrease, whereas in Profile I — which was very high in the A1 horizon — this content dropped sharply to the AB horizon. In Profile II the course of this content is entirely different: a sharp decrease in the A2 horizon, followed by a pronounced increase in the B2h, and then a gradual decrease in the B horizons below. Content of Fraction 1 in total C showed the same tendency in the latter profile. In Profile I a gradual decrease was visible up to and including the B2 horizon, but in the B3 this content was again somewhat higher. Profile III showed an increase with depth.

Fraction 2

In all samples the content of this fraction in total C was very small (4.4 % maximum). This is mainly due to the fact that these soils are very sandy. The extremely low value (0.6 %) in the B3 horizon of Profile III is interesting, because it proves that in that horizon no humic substances were combined with stable R_2O_3 forms.

The $C_{h.ac.}/C_{f.ac.}$ ratio

In research on the chemistry of humus, this ratio (calculated from Fractions 1a, 1 and 2) is considered to be the best measure of the podzolization process. For an explanation of the ratios presented in Table 1, see the general discussion.

The mobile humus compound fraction
In nearly all soil horizons investigated, the humic acids were entirely of mobile form. In the B2 and B3 horizons of Profile I, however, the contents of mobile humic acids in total C were 75 and 86 % respectively. This means that in these horizons 25 % and 14 % respectively of the humic acids were bound to calcium.

Non-hydrolysable compounds (humins)
In its B2 horizon Profile I showed a relative maximum of humin content in soil as well as in total C. In Profile II the same tendency is visible with regard to the content in soil, i.e. there was a relative maximum in the B2h horizon, but the content in total C gradually decreased with depth. Profile III showed a distinct decrease with depth for both contents.

Spectroscopic characterization of humic acids isolated from fraction 1

Optical properties of Na-humates
The absorption spectra of Na-humates in visible light indicate, among other things, the molecular weight and total carbon content of humic acids. High optical densities point to the occurrence of humic acids that have a relatively high content of chromophore groups, i.e. a more complicated molecular structure (Flaig, 1971; Kononova, 1966; Welte, 1956; Scheffer & Ulrich, 1960).

From Fig. 1 it can be seen that the soils investigated showed clear differences in density of Na-humates. In the A1 (or Ap) horizons the highest density of Na-humates was derived from Profile III. In this profile the density decreased with depth, whereas in Profiles I and II the density was lowest in the A1(2) and A1 horizons and at a maximum in the AB and A21 horizons respectively. The differentiation of densities throughout the soil was strongest in Profile II.

Infrared spectra of humic acids
The infrared spectra presented in Fig. 2 indicate that the humic acids investigated had an essentially similar chemical structure.

All spectra showed a wide and distinctly visible absorption band in the 3250-3500 cm^{-1} region. This is attributed to the occurrence of OH groups which are probably alcoholic and phenolic (Drozd, 1971; Kononova, 1966; Scheffer & Ulrich, 1960; Schnitzer et al., 1959; Schnitzer, 1971; Schnitzer & Khan, 1972; Sklodowski, 1974). Two other bands occurring in all spectra were situated in the 2930 cm^{-1} region and in the 2860 cm^{-1} region respectively. The first band, which was narrow but very distinct, is characteristic for CH_3 and CH_2 groups, and the (less distinct) second one reflects the vibration of Ch in aliphatic CH_3 groups (Drozd, 1971; Kononova, 1966; Scheffer & Ulrich, 1960; Schnitzer et al., 1959; Schnitzer, 1971; Sklodowski, 1974).

The most characteristic bands, however, were found in the 1720 cm^{-1} and the 1630 cm^{-1} region. The first one proves the occurrence of $C=O$ in carboxylic groups and $C=O$ stretch of ketonic carbonyl, while the 1630 cm^{-1} band corresponds with chinonic $C=O$ bands (Drozd, 1971; Kononova, 1966; Rosochacka,

1969; Schnitzer, 1971; Schnitzer & Khan, 1972; Theng & Posner, 1967). As both bands were present in all spectra, this means that all the humic acids investigated had aromatic rings and aliphatic chains that contained similar function groups. The intensity of the bands, however, was not the same in all cases, and this enabled us to discern two groups in these humic acids, i.e. those occurring in Profile I and those derived from Profiles II and III. The first group is characterized by a lower intensity in the 1720 cm^{-1} band compared with that in the 1630 cm^{-1} band, whereas the second group shows the reverse. Based on Schnitzer's (1971) investigations, this difference can partly be explained by the fact that there were fewer COOH groups in the humic acids of the 'holt' podzol soil (Profile I) compared with the humic acids occurring in Profiles II and III.

Absorption also occurred in the 1450-1400 cm^{-1} region. This can be attributed to the occurrence of aliphatic C-H. The absorption at about 1400 cm^{-1} also proves the presence of carboxylic groups, mostly in the form of salts or anions (Kasatochkin et al., 1964; Kononova, 1966; Schnitzer et al., 1959; Schnitzer, 1971). Absorption bands occurring in the 1200 cm^{-1} region of the spectra belonging to Profiles II and III were characteristic for C-O stretch or OH deformation of CO$_2$H (Kononova, 1966; Schnitzer et al., 1959; Schnitzer, 1971). According to other authors (including Farmer & Morrison, 1960; Turski & Wincenciak, 1969) the 1200 cm^{-1} band corresponds with O directly bound to C of aromatic rings. The absorption in the 1150-1050 cm^{-1} region was probably caused by bending vibration of OH, stretching vibration of C-O of secondary and tertiary alcohols and C-O-C of cyclic ethers (Drozd, 1971; Farmer & Morrison, 1960).
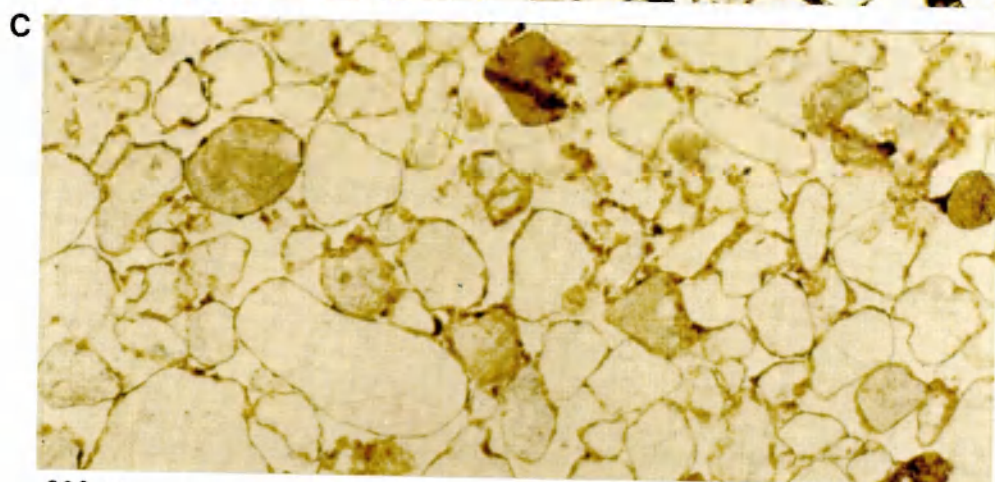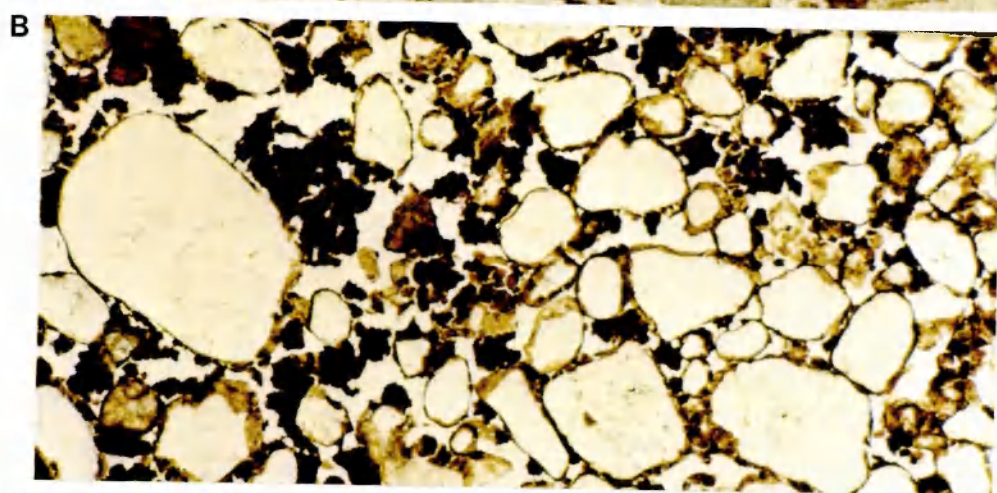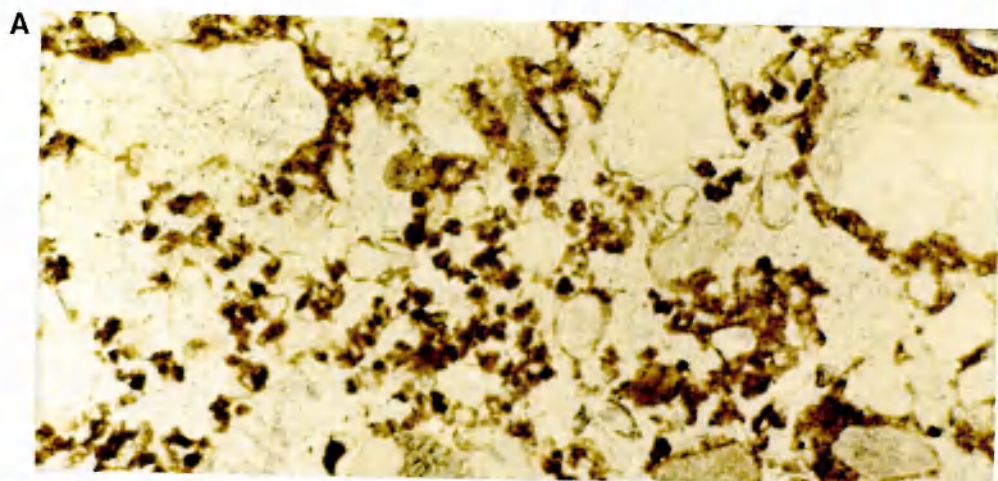
According to Sklodowski (1974) humic acids of high molucular weights show a maximum absorption in the 1000-1100 cm^{-1} region, whereas those of lower molecular weight are characterized by a maximum absorption in the 1100-1200 cm^{-1} region. This would imply that the humic acids of the 'Holt' podzol soil (Profile I) had higher molecular weight than those of the 'Haar' podzol soil (Profile II). The spectra of Profile III were not clear in this respect. One should be aware, however, that the 1050 cm^{-1} bands could partly have been caused by Si-O impurities resulting from preparation (Scharpenseel et al., 1964).

Micromorphology

Profile I

A1(2) hor.   *0-15 cm*   *Upper part:* abundant rounded faecal pellets (approx. 40 μm) and many
(Fig.3)   larger excrements (up to more than 1 mm) produced by earthworms and millipedes. Several excrements are intact, but many others are disintegrating due to ageing (Bal, 1973). The excrements consist of brown polymorphic organic matter in which are embedded many cells and very fine usually dark tissue fragments, and much fine silty mineral material only a part of which is loosely bound with the organic matter. Moderate separate fragments of organs and rather large tissue fragments, predominantly rather fresh (much cellulose visible under crossed nicols), but mostly showing continuing humification. Relatively few bare sand grains.

(Fig. 4)   *Deeper:* predominantly rounded faecal pellets of approx. 40 μm, separate

200 μm

or in loose clusters and ageing larger excrements. In the dark brown polymorphic organic matter many dark to opaque very fine tissue fragments and silty mineral grains. A small content of charcoal. Some brown to dark brown root fragments in different stages of decomposition. Moderate fungal hyphae. More bare sand grains than in the upper part of the horizon.

AB hor.   *15-30 cm*   Much less organic matter but still abundant rounded pellets of approx. 40
(Fig. 5) μm, separate and in loose clusters; deeper an increasing number of porous humus micro-aggregates. The polymorphic organic matter is dark brown, downwards grading into brown. Many very fine embedded organic bodies, the content of which decreases with depth, and many loosely bound silt- and sand-sized mineral grains. A few fungal hyphae. Few root fragments. In the deeper part of the horizon some traces of thin, brown debris cutans on the free sand grains which are predominantly bare.

B2 hor.   *30-45 cm*   Moderate faecal pellets of approximately 40 μm, partly as loose tubulic fil-
(Plate I,A)   lings, partly grouped in small very porous clusters in the groundmass. Many rather compact humus micro-aggregates. The brown polymorphic organic matter contains a moderate amount of very fine dark to opaque organic bodies, some of which have a still recognizable plant structure, and a high amount of mineral grains of silt and fine sand size. Few root fragments. Most free sand grains are partly or entirely covered with brown, rather thick debris cutans of the same composition as the pellets and micro-aggregates.

B3 hor.   *>45 cm*   Many humus micro-aggregates, resembling those of the B2 horizon, but
(Fig. 6)   still more compact. More and thicker debris cutans. Micro-aggregates and debris cutans are composed of yellowish brown polymorphic organic matter, very fine tissue fragments and many silt and fine sand-sized mineral grains.
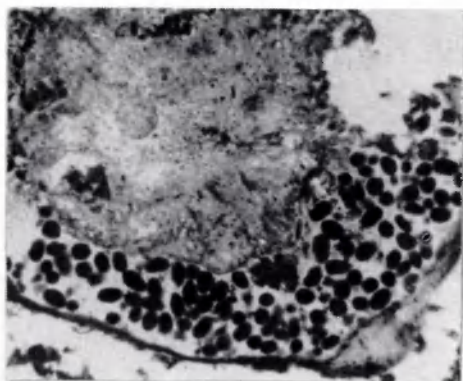
Profile II

A1 hor.   *0-2 cm*   Abundant porous humus aggregates, varying greatly in size, and composed
(Fig. 7)   of a mixture of dark, mostly opaque pellets, approx. 40 μm, and fine brown tissue fragments with fairly recognizable structures. Few single excrements, approx. 40-150 μm in diameter, composed of dark brown polymorphic and opaque organic material, and very fine brownish fragments. Many larger plant fragments, varying from mostly brownish well preserved ones with recognizable parenchymatic structures, to dark nearly opaque remnants of bark, vessels, etc. Few fungal hyphae. Relatively few sand grains, free partly bare, partly covered with very small humus aggregates, or loosely embedded in the organic material.

A21 hor.   *2-12 cm*   Many humus micro-aggregates, approx. 50-200 μm; mainly weakly porous
(Fig. 8)   to compact, consisting of very small opaque particles (partly plant fragments) and brown material with faintly recognizable plant structures; few


Plate 1.
A. Very loose clusters of faecal pellets of approx. 40 μm, predominantly consisting of brown polymorphic organic matter. Some rather compact humus micro-aggregates of the same colour and composition. Debris cutans around a part of the sand grains. Profile I, B2 horizon, 35 cm depth.
B. Dark, mainly opaque humus micro-aggregates. Brown monomorphic humicans on the sand grains. Profile II, B2h horizon, 30 cm depth.
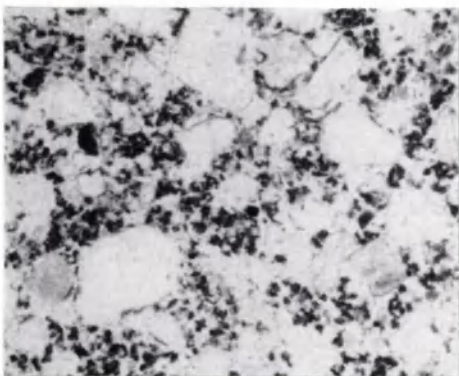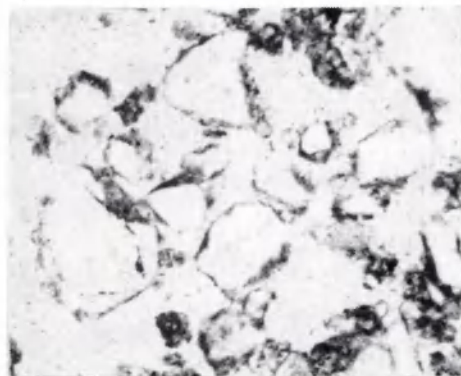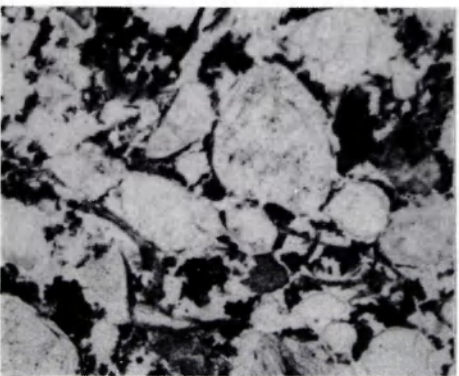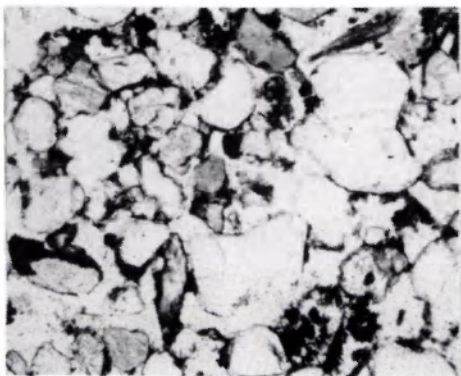C. Brownish red humicans on the sand grains. Profile III, B3 horizon, 42 cm depth.
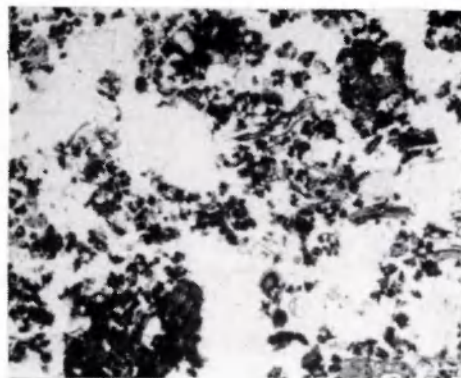
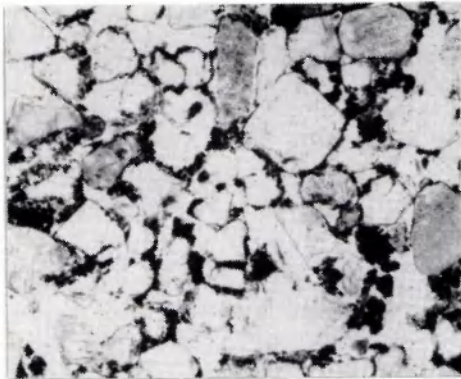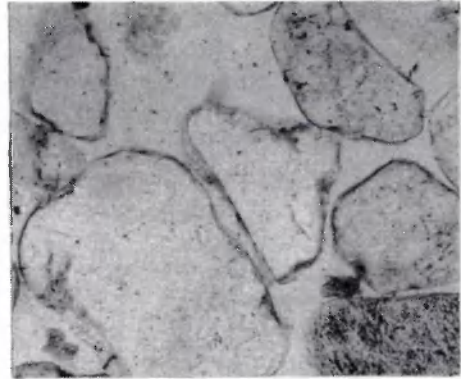Fig. 3. Large fragment of an organ with a zone of intact faecal pellets. Profile I, A1(2) horizon, 7 cm depth. × 25.
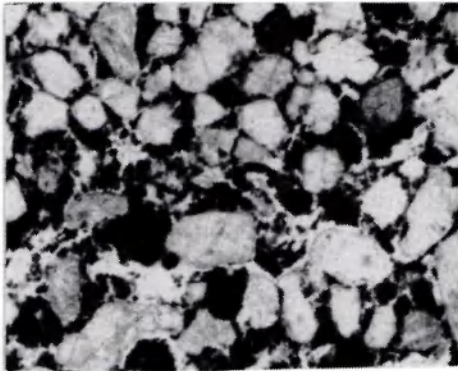
Fig. 4. Ageing larger excrements (right-hand top corner and left-hand bottom corner) and loose clusters of dominantly dark brown pellets. Profile I, A1(2) horizon, 11 cm depth. × 25.
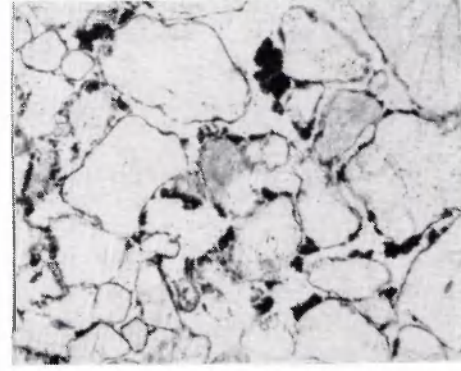
Fig. 5. Porous brown humus micro-aggregates filling the simple packing voids. Profile I, AB horizon, 21 cm depth. × 25.

Fig. 6. Debris cutans around sand grains, and (right-hand top and bottom corner) yellowish brown, rather compact humus micro-aggregates. Profile I, B3 horizon, 55 cm depth. × 40.

Fig. 7. Porous humus aggregates of strongly varying size. Many of the smallest aggregates are on the bare sand grains. Brownish intact roots are visible, particularly in the centre. Profile II, A1 horizon, 1 cm depth. × 40.

Fig. 8. Many, usually very small, weakly porous to compact, brownish black humus micro-aggregates, partly on the otherwise bare sand grains. Profile II, A21 horizon, 12 cm depth. × 40.

Fig. 9. Moderate humus micro-aggregates, more opaque than in the A21 horizon. Many sand grains are partly or entirely covered with very small opaque organic matter particles. Profile II, A22 horizon, 22 cm depth. × 40.

Fig. 10. Thin, light brown monomorphic humicans around sand grains. Profile II, B3 horizon, 60 cm depth. × 100.

Fig. 11. Many humus micro-aggregates of varying size. The organic matter is dark blackish brown, grading into opaque. Most sand grains are bare, but locally there are organic cutans. Profile III, Ap horizon, 6 cm depth. × 40.

Fig. 12. Rather few and small humus micro-aggregates, reddish brown and black. On the sand grains brownish red monomorphic humicans, locally covered by small micro-aggregates. Profile III, B2 horizon, 33 cm depth. × 40.

		compact opaque bodies, subangular, maximum size approx. 50 μm (probably plant remnants); many intact root remnants; sand grains partly bare, partly covered with very small humus aggregates.
A22 hor. (Fig.9)	*12-24 cm*	Moderate humus micro-aggregates, approx. 150 μm maximum; partly weakly porous and somewhat botryoidal, partly compact with flat faces and rounded edges; predominantly opaque, some composed of opaque particles and brown polymorphic organic matter. Sand grains are partly bare, but several are entirely or partly covered with very small, opaque organic matter particles. Some brown or blackish root fragments usually with still recognizable structure. In the lower part of the horizon traces of yellow brown, monomorphic free grain humicans.
B2 hor. (Plate I, B)	*24-36 cm*	Abundant humus micro-aggregates (approx. 100-150 μm) and organic bodies of approx. 40 μm. The latter are for a small part typical rounded pellets, but in general they are flat-faced and sharp-edged. Some micro-aggregates are weakly porous and botryoidal, but most are compact and subangular; predominantly opaque. Sand grains are surrounded by brown monomorphic humicans, the thickness of which increases with depth. On several sand grains small opaque organic particles that partly or wholly cover the humicans. Some usually dark brown, more or less intact root fragments.
B22 hor.	*36-52 cm*	Relatively few humus micro-aggregates, predominantly not larger than 60 μm, varying in shape from rounded to very irregular sharp-edged, for a small part larger (approx. 100-150 μm), rather compact to compact, weakly botryoidal to subangular; partly opaque, but predominantly dark brown and polymorphic. Strongly developed brown monomorphic humicans on sand grains, locally covered by some small opaque organic aggregates. Some strongly humified dark brown to blackish opaque root fragments.
B3 hor. (Fig. 10)	*>52 cm*	Sand grains covered by thin, light brown monomorphic humicans; fibres the same, but cutans are much thicker.

Profile III

Ap hor. (Fig. 11)	*0-30 cm*	Abundant humus micro-aggregates, strongly varying in size, mainly up to 400 μm maximum, but also some that are up to 1 cm; ranging from porous botryoidal to compact subangular. Organic matter essentially polymorphic, but mainly very dark blackish brown, frequently grading to opaque. Mainly bare sand grains, but locally cutans of the same composition as the micro-aggregates. Some strongly humified woody plant fragments.
B2 hor. (Fig. 12)	*30-40 cm*	Few humus micro-aggregates, mainly 50-150 μm rather compact, subangular and angular, mainly polymorphic, reddish brown and black. Former root channels containing larger root fragments with still partly recognizable structure, reddish brown to brownish black, and small dark reddish brown polymorphic faecal pellets (approx. 25-35 μm). Some isotubules containing brownish polymorphic humus in which many sand grains are embedded. Free grain humicans brownish red, monomorphic, locally covered by small micro-aggregates.
B3 hor. (Plate I, C)	*>40 cm*	Same kind of humicans as in the A2 horizon, gradually becoming thinner with depth. Sporadic small humus micro-aggregates of the same colour and morphology as in the A2.

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General discussion

Profile I

As can be seen from Table 1, the quantity and relative content of humins, i.e. non-hydrolysable compounds that partly or entirely consist of very fine remnants of plant tissue, were largest in the B2 horizon. This peak is in good agreement with the concept of mechanical illuviation (Jongerius, 1957; Jongerius & Schelling, 1960) or mecaconcentration (Jongerius, 1970). According to this concept, in 'Holt' podzol soils aged faecal pellets (which still contain very fine plant fragments) or their fragments are transported from the A0 and A1(2) horizons by percolating water to a certain depth (the B horizons), where they form humus micro-aggregates.

The content of Fraction 1 in soil and its component substances (humic acids and fulvic acids) decreased with depth in this profile, as did the contents of that fraction in total C, at least up to and including the B2 horizon. This means that humic substances belonging to Fraction 1 did not translocate, even though they were free and/or mobile compounds. This agrees with the results obtained from the infrared investigation, which revealed that in this profile the molecular weight of the humic acids belonging to Fraction 1 was fairly high.

Because contents of Fraction 2 both in soil and in total C were low in Profile I (as in the other profiles), Fraction 2 is not important for genetic interpretation.

The $C_{h.ac.}/C_{f.ac.}$ ratios are more interesting in this respect. The relatively small decrease of $C_{h.ac.}/C_{f.ac.}$ ratios from 0.9 in the A1(2) horizon to 0.7 in the lower horizons indicates that there is only a weak tendency for fulvic acids to accumulate in the B horizons. As shown in the analytic data, this particularly concerns the very mobile fulvic acids of Fraction 1a. It is remarkable that there were no micromorphological indications of translocation of fulvic acids, for these were visible in Profiles II and III as light brown humicans around sand grains (see below). This means that, if fulvic acids have translocated, they have been absorbed by the humus micro-aggregates. However, it is also possible that the downward increase of Fraction 1a is due to continuing formation of fulvic acids during the process of mechanical illuviation of pellety material.

The brown micro-aggregates particularly common in the B2 horizon of Profile I are not stable. They disintegrate easily, a process that results in the formation of debris cutans around the sand grains. In our opinion, this rather low stability is due to the occurrence of fulvic acids in the micro-aggregates.

Profile II

The A1 horizon of this profile had the highest quantity of total C of all the horizons investigated. This quantity decreased markedly in the A21 horizon and (in particular) in the A22 horizon, was rather high again in the B2h horizon, and then gradually decreased in the B horizons below. The quantities (and relative contents) of Fraction 1 and of the humins followed the same trend. In contrast, bitumens reached a maximum content in the A21 horizon.

The content of Fraction 1a in soil (which represents very mobile low-molecu-

lar humus compounds) was low in the A2 horizons, and then increased sharply to a maximum in the B22 horizon. The content of Fraction 1a in total C increased strongly from the A1 horizon to the B3 horizon.

To a certain extent, both contents followed the same trend, i.e. a minimum in the A21 horizon and a maximum in the B2h horizon.

The $C_{h.ac.}/C_{f.ac.}$ ratios showed the reverse tendency, i.e. they were at a maximum in the A21 horizon and decreased with depth in the B horizons.

These results clearly point to a translocation of some fractions of humus compounds, and especially to a strong illuviation of fulvic acids into the B horizons. The removal of fulvic acids from the A horizons brought about the relatively high content of bitumens in the A2 horizons. This fact probably led to the rather high physical stability of the micro-aggregates occurring in these horizons.

Summarizing, it can be said that in this profile the distribution of the fractional humus compounds throughout the profile (in particular that of Fractions 1a and 1, and of the bitumens) very clearly reflects the typical podzolization process.

The micromorphological observations confirm the above-mentioned conclusions. The brown, monomorphic humicans that envelop the sand grains in the B horizons are, in our view, mainly composed of fulvic acids: it should be stressed that the humicans also contain some iron and probably some bitumen, but their colour is predominantly determined by the fulvic acids. The dark humus micro-aggregates that occurred in the intergranular spaces in the B2h horizon and (to a lesser extent) in the B22 horizon are, in our opinion, mainly composed of a mixture of humic and fulvic acids.

Profile III
The Ap horizon of this profile showed a lower content of total C than was the case with the top horizons of Profiles I and II. Furthermore, unlike the situation in Profile II, the content of total C gradually decreased downwards, i.e. there was no peak in the B2 horizon.

The content of bitumens in total C in the Ap horizon was much higher than was the case in the A1(2) and A1 horizons of Profiles I and II respectively. Such a high bitumen content is characteristic for soils that have developed under stronger hydromorphic conditions. This means that in the Ap horizon of this soil reducing conditions periodically prevail.

The contents of humins both in soil and in total C were lower in this profile than in Profiles I and II. In particular, the humin content in total C in the B3 horizon was remarkably low.

The $C_{h.ac.}/C_{f.ac.}$ ratios in the Ap and B2 horizon were relatively high due to the translocation of fulvic acids from the Ap horizon to the B3 horizon. This phenomenon is confirmed by the fact that the contents of Fraction 1a both in soil and in total C increased with depth, and by the results of micromorphological observations, which also in other respects agreed well with the chemical data.

The relatively large dark micro-aggregates that were characteristic of the Ap horizon, are considered to be rather rich in bitumens and humus substances that

are mainly humic acids of high molecular weight.

In the B2 horizon there were fewer dark micro-aggregates and they were also smaller than those occurring in the Ap horizon. It is possible that these micro-aggregates like those in the Ap horizon, contain high fractions of bitumens. Furthermore, in the B2 horizon the sand grains were coated by brownish red, mono-morphic (amorphous) humic substances (humicans). It is probable that the hu-micans are composed mainly of humic substances of low molecular weight. This view fits in very well with the lower $C_{h.ac.}/C_{f.ac.}$ ratio in this horizon.

In the B3 horizon nearly all organic matter occurred as humicans identical to those of the A2 horizon. This phenomenon is clearly connected to the low $C_{h.ac.}/C_{f.ac.}$ in the Bh2. The very low content of humins in the B3 horizon is in good agreement with the fact that there were hardly any micro-aggregates.

Conclusions

From our investigations several conclusions can be drawn.

1. A comparison of the fractional humus compositions of the three podzolic soils investigated did show a distinct difference in the translocation and distribution of the principal humus compounds in the 'Holt' podzol soil on the one hand, and the 'Haar' podzol and the 'Veld' podzol on the other hand.

2. The translocation processes of humus compounds were less pronounced in the 'Holt' podzol soils than in the other profiles. Humic acids isolated from the 'Holt' podzol soil were predominantly characterized by higher molecular weight and contained fewer carboxylic groups compared with the acids extracted from the 'Haar' and 'Veld' podzol. This means that the humic acids in the 'Holt' podzol are less acid and less mobile.

3. The occurrence of a maximum of humins in the B2 horizon of the 'Holt' podzol indicates a pronounced illuviation of very fine remnants of plant tissue, which is in good agreement with the concept of mechanical illuviation proposed by Jongerius (1957) and Jongerius & Schelling (1960).

4. Translocation processes of humus compounds in solution were most pronounced in the 'Haar' podzol soil and less so in the 'Veld' podzol. In this respect, the removal of fulvic acids from the upper horizons to the B horizons is most striking.

5. The fractional humus composition of the soils investigated played an essential role in the development of micro-aggregates and their water stability, and in the formation of cutans. This was confirmed by micromorphological investigations.

6. In thin sections two kinds of micro-aggregates could clearly be distinguished, i.e. blackish brown to black, usually opaque ones and brownish ones. The first type was dominant in the 'Haar' podzol soil, whereas the 'Holt' podzol was characterized by the brownish micro-aggregates. In the upper horizons of the 'Veld' podzol both types occurred but downwards the brownish type became more dominant.

7. The humic substances of the dark micro-aggregates were mainly composed

of bitumens, humins and humic acids of higher molecular weight. The humic substances of the brownish micro-aggregates in the 'Veld' podzol mainly consisted of fulvic acids and probably also of humic acids of lower molecular weight. This also holds for the brownish micro-aggregates in the 'Holt' podzol soil, but in this case quite a lot of humins also occurred.

8. The dark micro-aggregates probably have a higher stability than the brownish ones. The lower stability of the brownish aggregates is, in our opinion, due to the high amount of fulvic acids. This also explains the phenomenon of debris cutan formation in the B horizons of the 'Holt' podzol. These cutans are the product of the brown micro-aggregates disintegrating in the B horizon.

9. The brownish red free grain cutans of the 'Veld' podzol probably mainly consist of fulvic acids, whereas the brown cutans that occurred in the 'Haar' podzol are predominantly composed of fulvic acids, bitumens and some iron-humus complexes.

Acknowledgements

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