SOIL SCIENCE ANNUAL
2022, 73(2), 156099

https://doi.org/10.37501/soilsa/156099

Humic acids in permanent grasslands of the Czersk Meadows Complex, north Poland

Magdalena Banach-Szott[1]*, Andrzej Dziamski[2]

[1] Bydgoszcz University of Science and Technology, Faculty of Agriculture and Biotechnology, Department of Biogeochemistry and Soil Science, 6 Bernardynska St., 85-029 Bydgoszcz, Poland
[2] Bydgoszcz University of Science and Technology, Faculty of Agriculture and Biotechnology, Department of Botany and Ecology, 7 Kaliskiego St., 85-796 Bydgoszcz, Poland

* dr inż. M. Banach-Szott, e-mail: mbanach@pbs.edu.pl, ORCID iD: https://orcid.org/ 0000-0002-9981-0841

Received: 2022-05-28
Accepted: 2022-10-27

Associated editor: B. Glina

Key words:

Meadow soil
Humus
Elemental composition
Hydrophobicity/hydrophilicity
UV-VIS

Abstract

The research objective was to determine basic soil properties and the stability of humic acids (HAs) in individual layers of the A horizon of meadow soils. Soil samples were collected from the unique Czersk Meadow Complex in north Poland, 25 years after the end of "slope-and-flooding" irrigation that had lasted for 150 years. It is a continuation of research being carried out on the Czersk Meadows. In the previous studies (Banach-Szott et al. 2021a), continuously irrigated soils were analysed. The total organic carbon content (TOC), total nitrogen content (Nt) and grain size composition were determined in soil samples. Humic acids were extracted by Schnitzer method and analysed for: elemental composition, spectrometric parameters in the UV-VIS range and hydrophilic and hydrophobic properties. The tested soils consisted largely of sand fraction, with only small amounts of clay. The TOC, Nt and TOC/Nt ratio values all depended on soil sampling depth and distance from irrigation ditch. The TOC, Nt and TOC/Nt ratio were all highest for soils collected from a depth of 0–10 cm and for those taken 25 m from the irrigation ditch. The research revealed that the HA molecules of soils collected from a depth of 0–10 cm had higher H/C ratios and spectrometric parameters and lower values of the ω parameter and HIL/HOB ratio than those from deeper layers. This indicates that the degree of maturity of HAs increases with depth. On the basis of the obtained atomic ratios (H/C, O/C, O/H), ω parameter and spectrometric properties ($A_{2/6}$, $A_{4/6}$ and ΔlogK), the degree of maturity for HAs molecules was highest in the soil samples taken furthest from the irrigation ditch. The results indicate that relatively high-stability HAs were formed by the processes of transformation of the organic matter of the mineral meadow soils.

Abbreviations:
H/C – ratio of hydrogen content to carbon content
O/C – ratio of oxygen content to carbon content
O/H – ratio of oxygen content to hydrogen content
$A_{2/4}$ – 280 nm and 465 nm absorbance ratio
$A_{2/6}$ – 280 nm and 665 nm absorbance ratio
$A_{4/6}$ – 465 nm and 665 nm absorbance ratio
HIL/HOB – ratio of share of HIL fraction to share of HOB fraction

1. Introduction

Due to the sequestration process, soils constitute the largest store of carbon. It is therefore important to study the condition of soils – and to protect them – on global, regional and local scales (COM, 2006; Wiesmeier et al., 2019).

The average humus content in soils in Poland is currently 2.90% (GIOS, 2022). In past years it has been lower, ranging from 1.90 to 1.97%. According to international standards, an OC content of 2.0% represents soil degradation. For this reason, solutions are being sought to reduce OC losses from soil. It has been shown that meadow soils provide some of the best conditions for accumulating and immobilizing organic matter (Lal, 2011; Kämpf et al., 2016). To increase carbon sequestration in the environment, it is therefore desirable to create meadow ecosystems and to protect natural ones (Lal 2011; EIP-AGRI 2014). However, when meadow ecosystems are formed on soils that are poor in organic matter, only long-term use results in the permanent accumulation of OC. One example of this is the permanent pasture complex known as the Czersk Meadows, which are unique in Europe. This extensive complex located in various parts of the Tuchola Pinewoods was created in the mid-19th century to limit the emigration of people from these areas and to provide farm animals with sufficient amounts of feed. The meadows were created partly on peat soils and partly on mineral soils, i.e., in sandur areas of former pinewoods. Because these meadows are located on sandur areas of the upper Wda and Brda rivers, where loose sands dominate and the natural water table is deeper than 2 m b.g.l., the only possible way of irrigating them was to use a slope-and-flooding system. The systematic irrigation of sandy mineral soils allowed diverse plant communities to grow. This translated into an intensification of processes leading to the formation of a humic horizon in subsurface soil layers, enriching them with organic matter (Sabiniarz, 2006; Sabiniarz and Kozłowski, 2009a, 2009b)

It should be emphasized that, to date, most research on organic matter in grasslands has mainly concerned hydrogenic soils. By contrast, research on organic matter in mineral soils that have been developed as permanent grasslands is niche. Organic matter is undeniably the main component of soil quality. Its contents depend on such factors as soil aggregate stability, water retention, biodiversity, and the density of soils – especially mineral soils (Sapek, 2009). The main component of organic matter is humic substances, which are the most common organic compounds in nature (Orsi, 2014; Weber et al., 2018). Therefore, the quality of organic matter is largely determined by the quality of humic substances (Canellas et al., 2010; Lanyi, 2010; Weber et al., 2018). Humic substances have a complex structure and are the result of those processes of transformation and decomposition of organic matter known as "humification". Research on the properties of these compounds requires several instrumental methods (Weber et al., 2018). One of the main parameters characterizing humic acids (HAs) is elemental composition, which is conditioned by both habitat and anthropogenic factors (Canellas et al., 2010; Trubetskaya et al., 2013; Boguta et al., 2016). Important criteria reflecting the nature and origin of HAs are the absorbance value of their solutions: A_{280}, A_{465}, A_{665} and their absorbance coefficients $A_{2/4}$, $A_{2/6}$, $A_{4/6}$, $\Delta\log K$ (Kumada, 1988; Vieyra et al., 2009; Polak et al., 2011; Rodríguez et al., 2016). It is assumed that the absorbance at 280 nm (A_{280}) corresponds to the content of lignin compounds, the absorbance at 465 nm (A_{465}) denotes the content of matter in the initial stage of decomposition, and absorbance at 665 nm (A_{665}) correlates with the content of highly humified matter. The value of the $A_{2/4}$ ratio reflects the amount of matter in the initial stage of decomposition, $A_{2/6}$ corresponds to the ratio of the content of humification-resistant compounds to the strongly humidified organic matter, and the $A_{4/6}$ ratio corresponds to the ratio of the content of matter in the initial stage of decomposition to the content of highly humified matter and is correlated with the degree of condensation of aromatic rings and molecular mass (Chen et al., 1977). They can also be used to determine how advanced the humification of organic materials is. The degree of humification of organic matter is also related to the hydrophilic–hydrophobic properties of HAs (Preuße et al., 2000; Dębska et al., 2007; 2010).

Thus, the properties of HAs can be used to estimate the degree of transformation and the quality of organic matter. This study therefore aimed to determine the basic properties of soils and selected properties of HAs in the meadow soils of the Czersk Meadow Complex, 25 years after the discontinuation of 150 years of slope-and-flooding irrigation.

2. Materials and methods

2.1. Materials

Permanent pasture soils were taken for testing from the unique Czersk Meadow Complex, north Poland. The Polish name *Kompleks Łąk Czerskich* is a historical term for perennial grasslands totalling almost 2,000 hectares throughout various parts of the Tuchola Pinewoods that have been used as permanent grasslands (Sabiniarz, 2006). In the years 1842–49, the Podlesie meadow was created, and in 1857–60 the Zielona Łąka meadow was created. The main rivers of the Tuchola Pinewoods, the Brda and the Wda, were used to irrigate the meadows. Extraordinarily, the water from the irrigation ditches was distributed across the meadows by a system of channels, ditches and flood-

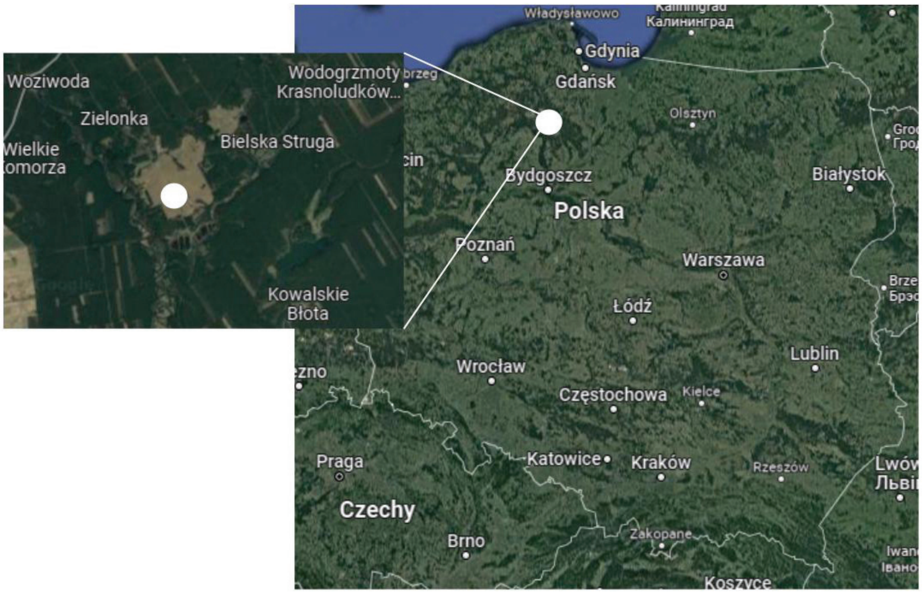

Fig. 1. Soil sampling locations (source: https://www.google.pl/maps/@52.3900175,17.7007785,931922m/data=!3m1!1e3)

ing furrows that constituted a unique irrigation system that has been described as "slope-and-flooding" or "flooding". The newly developed "districts" were meadow plots carefully profiled and shaped depending on the terrain to form gentle slopes of about 1–5%, down which water flowed freely from the irrigation ditch and flooding furrows. This infrastructure, despite being significantly damaged, is still in use. Currently, the study area includes areas that have been irrigated continuously until the present day, and areas where the process was abandoned approximately 25 years before sampling. Soil samples were collected from a non-irrigated meadow – Zielona Łąka. Three transects with representative vegetation were selected there. Because irrigation was abandoned there, meadows of ryegrass developed that mostly transformed into *Diantho–Armerietum* communities with a dominance of *Festuca ovina*. Soil samples were taken in three replications from the A horizon at depths of 0–10 cm, 10–20 cm and 20–30 cm in spring. The soils (*Albic Brunic Arenosol*) were sampled in three replications at distances of 5, 15 and 25 m from an irrigation ditch. These soils were formed from fluvioglacial sands. The average annual temperature in this area for 2008–12 was 7.9°C, and the annual sum of precipitation was 648.6 mm. Soil samples were dried at room temperature and sieved through a 2-mm mesh. In total, the research covered nine soil profiles for each of the objects (a total of 27 soil samples).

2.2. Methods

2.2.1. Soil analysis

For air-dried soil samples, the following analyses were made:

The contents of total organic carbon (TOC) and total nitrogen (Nt) were assayed with a Vario Max CN analyser from Elementar (Germany) (Dębska et al., 2016).

The pH was assessed in the suspension of distilled water and soil with a MultiCal pH 540 GLP WTW pH meter (van Reeuwijk, 2002).

The grain size composition was determined by areometric method (Kobierski, 2010).

2.2.2. Extraction of humic acids

Humic acids (HAs) were extracted from the samples following the standard procedure described by Dębska et al. (2010):

Decalcification was performed (24 h) with 0.05 M HCl (1:10 w/v). After centrifugation, the residue was washed with distilled water until neutral. Then, we performed extraction (24 h) of the remaining solid with 0.5 M NaOH (1:10 w/v), with occasional mixing, followed by centrifugation. Precipitation (24 h) of the HAs was performed from the resulting alkaline extract with 2 M HCl to pH=2 and centrifugation. This was followed by purification of the resulting HAs: the HA residue was treated with a mixture of HCl/HF (950 mL H_2O, 5 mL HCl, 5 mL HF) over a 24-h period, followed by centrifugation. The residue was also treated with distilled water until zero reaction to chloride was achieved.

The preparations were lyophilized and powdered in agate mortar. The ash content in the HA preparations was lower than 2%.

The properties of the HAs were investigated using the following analyses:

- C, H, N and ash content with a Perkin Elmer Series II 2400 CHN analyser (Dębska et al., 2012). The H/C, O/C, O/H, and N/C atomic ratio and ω (internal oxidation degree) were calculated using the following formula:
  $\omega = (2O+3N-H):C$
  where O, N, H, C – content in atomic %.
- optical properties in the UV-VIS range using a Perkin Elmer Lambda 20 spectrophotometer (Dębska et al., 2002). VIS spectra were obtained from 0.02% HAs solutions in 0.1 M NaOH and UV-spectra after fivefold dilution. The absorbance was measured at 280 nm (A_{280}), 400 nm (A_{400}), 465 nm (A_{465}), 600 nm (A_{600}) and 665 nm (A_{665}) and used to calculate the coefficient values:
  $A_{2/4}$ – 280 nm and 465 nm absorbance ratio
  $A_{2/6}$ – 280 nm and 665 nm absorbance ratio
  $A_{4/6}$ – 465 nm and 665 nm absorbance ratio
  $\Delta\log K = \log A_{400} - \log A_{600}$ (Kumada 1988);
- hydrophilic and hydrophobic properties using a Perkin Elmer HPLC series 200 liquid chromatograph (Dębska et al., 2010). The separation involved the use of column X-Terra C18, 5 µm, 250 × 4.6 mm. The solutions of HAs were applied in 0.01 M NaOH of the concentration of 2 mg mL^{-1}; the injection of the sample was 10 µL; solvent – acetonitrile – water; solvents flow in the gradient (ratio H_2O:ACN (v/v) over 0–6 min – 99.5:0.5, 7–13 min – 70:30, 13–20 min – 10:90); detection – at the excitation/emission wavelength (λex/λem) of 270/330 nm. Based on the areas determined under peaks, the share of HIL and HOB fractions in HAs molecules and parameter HIL/HOB were determined.

2.2.3. Statistical analysis

The statistical analyses of the properties of soils and HAs included an analysis of data variance from a single, two-factor, split-plot experiment. The tables show the mean values of the triplicates. The significance of differences was assessed by Fishers' Least Significant Difference (LSD) at a significance level of α=0.05. Additionally, single-factor analysis of variance (ANOVA) was performed using Tukey's test. The relationships between the shares of clay, silt and sand fraction and the selected parameters of HAs were defined using the Pearson's correlation coefficients (P≤0.05). Statistical analyses were performed in MS Statistica 12.0.

3. Results and discussion

3.1. Basic soil parameters

The pH values of the studied soils ranged from 5.2 to 6.9 (Table 1) and were similar to the soil pH values obtained in previous studies (Banach-Szott et al., 2021a) and in peat soils of north-eastern Germany (Heller and Zeitz, 2012). Soil samples were characterized by an increase in pH with depth, with soils collected from 10–20 cm differing significantly from those taken from 20–30 cm (P=0.029, Table 2). The Czersk Meadow Complex was established in the second half of the 19th century on mineral soils previously covered with forests. Sand fraction (2.0–0.05 mm) dominated the granulometric composition of the soils, ranging from 88.7% to 92.0%. The percentage of clay fraction (<0.002 mm) was very low, ranging from 0.2% to 0.7% (Table 1). The results confirm previous research by Banach-Szott et al. (2021a) for soils sampled in the same area but continuously irrigated by the slope-and-flooding system. Moreover, with depth, the amount of sand was seen to decrease and the amount of clay to increase (Table 1). A low percentage of clay in meadow soil (2.1%) was also obtained by Jonczak (2013), but those soils contained less sand fraction (61%). In turn, Norton et al. (2011) and Kenngott et al. (2021) obtained much lower contents of sand fraction and higher contents of clay fraction. The soil samples collected from a depth of 10–20 cm had significantly more sand fraction on average than the soil collected from 20–30 cm (P=0.0124, Table 2). In turn, the average amount of clay differed significantly between successive soil layers (P=0.005 and P=0.004, Table 2).

The TOC and Nt contents in the tested soils averaged, respectively, 40.3 g kg^{-1} and 3.61 g kg^{-1} in the 0–10 cm layer, 25.7 g kg^{-1} and 2.53 g kg^{-1} in the 10–20 cm layer as well as 16.1 g kg^{-1} and 1.67 g kg^{-1} in the 20–30 cm layer. It was found that, relative to the meadow soil results of Drąg et al. (2007), Khalid et al. (2007), Sapek and Burzyńska (2009) and Jonczak (2013), the studied meadow soils had higher TOC and Nt contents. This underlines that conditions were favourable for the development of meadow vegetation, which translated into the development of biomass and carbon sequestration (Pizzeghello et al., 2017).

With regard to the results obtained by Banach-Szott et al. (2021a), the distributions of TOC and Nt differed between analogous soil layers. Particularly, the contents of TOC and Nt were highest in soil samples from the 0–10 cm layer, ranging from 35.7 to 44.6 g kg^{-1} and from 3.48 to 3.83 g kg^{-1}, respectively (Table 3). The analysis of variance confirmed that the samples from the 0–10 cm layer had higher average TOC and Nt than the soils collected from either the 10–20 cm or 20–30 cm layer (P=0.0001, Table 2). As TOC and Nt decreased with depth, and in the 20–30 cm layer they ranged from 12.9 to 21.3 g kg^{-1} and from 1.45 to 2.18 g kg^{-1}, respectively.

Table 1
The pH and grain size composition of the soil samples

Factor		pH	Sand (%)	Silt (%)	Clay (%)
Transect I					
Distance (m)	5	5.2–6.5	90.3	9.3	0.4
	15	5.8–6.6	89.3	10.4	0.3
	25	5.7–6.2	91.6	7.6	0.7
LSD		–	0.338	0.189	0.253
Depth (cm)	0–10	5.2–5.9	91.2	8.6	0.2
	10–20	5.8–5.9	90.4	9.1	0.5
	20–30	6.2–6.6	89.6	9.7	0.7
LSD		–	0.152	0.179	0.100
Transect II					
Distance (m)	5	5.6–5–9	91.6	8.2	0.2
	15	5.6–5.9	92.0	7.6	0.4
	25	5.8–6.1	91.9	7.4	0.7
LSD		–	0.162	0.152	0.112
Depth (cm)	0–10	5.6–5.8	92.0	7.7	0.3
	10–20	5.6–5.8	92.0	7.6	0.4
	20–30	5.9–6.1	91.4	7.9	0.7
LSD		–	0.142	0.112	0.157
Transect III					
Distance (m)	5	6.5–6.9	88.7	10.9	0.4
	15	6.0–6.4	91.3	8.4	0.3
	25	6.3–6.7	90.3	9.0	0.7
LSD		–	0.208	0.117	0.189
Depth (cm)	0–10	6.0–6.5	91.0	8.7	0.3
	10–20	6.2–6.7	90.4	9.2	0.4
	20–30	6.4–6.9	88.9	10.5	0.6
LSD		–	0.144	0.114	0.137

LSD (Least significant difference, α=0.05)

Table 2
Analysis of variance (ANOVA) with the Tukey test

Parameter	A 0–10 cm n=27	B 10–20 cm n=27	Significant level (P)* A and B	C 20–30 cm n=27	Significant level (P)* B and C
TOC ($g\ kg^{-1}$)	40.3	25.7	0.0001	16.1	0.0001
Nt ($g\ kg^{-1}$)	3.61	2.53	0.0001	1.67	0.0001
TOC/Nt	11.2	10.3	0.015	10.0	0.52
Sand (%)	91.4	90.9	0.120	90.0	0.0124
Silt (%)	8.32	8.63	0.331	9.36	0.062
Clay (%)	0.27	0.44	0.005	0.67	0.004
pH	6.49	6.66	0.20	6.96	0.029
H/C	1.36	1.33	0.008	1.29	0.001
ω	0.126	0.159	0.0001	0.164	0.614
$A_{4/6}$	5.32	4.99	0.0006	4.42	0.0001
ΔLogk	0.725	0.694	0.001	0.626	0.0001
HIL (%)	39.1	40.1	0.105	41.5	0.002
HIL/HOB	0.644	0.670	0.103	0.710	0.003

Table 3
Basic chemical parameters of soils

Factor		TOC ($g\ kg^{-1}$)	Nt ($g\ kg^{-1}$)	TOC/Nt	TOC ($g\ kg^{-1}$)	Nt ($g\ kg^{-1}$)	TOC/Nt	TOC ($g\ kg^{-1}$)	Nt ($g\ kg^{-1}$)	TOC/Nt
		Transect I			Transect II			Transect III		
Distance (m)	5	27.1	2.51	10.51	25.4	2.27	10.94	29.12	3.09	9.43
	15	27.0	2.37	11.20	25.3	2.56	9.37	24.10	2.43	9.90
	25	29.8	2.57	11.80	30.0	2.74	11.29	28.81	2.89	9.95
LSD		1.309	0.190	1.085	0.580	0.063	1.171	2.837	0.034	0.075
Depth (cm)	0–10	44.6	3.83	11.68	40.6	3.48	11.75	35.72	3.53	10.14
	10–20	25.1	2.26	11.18	27.1	2.64	10.29	24.99	2.71	9.34
	20–30	14.1	1.37	10.64	12.9	1.45	9.56	21.32	2.18	9.79
LSD		1.680	0.123	0.841	0.428	0.130	1.165	0.663	0.130	0.572

LSD (Least significant difference, α=0.05)

On the other hand, the levels of TOC and Nt in continuously irrigated soils were highest in the soil samples taken from the 10–20 cm layer and lowest in the 0–10 cm layer, 49.5 and 14.7 $g\ kg^{-1}$ respectively (Banach-Szott et al., 2021a). This proves that mineralization processes dominated over humification processes in the 0–10 cm layer. Thus, the discontinuation of irrigation over the last 25 years may have affected the accumulation of organic matter in the upper (0–10 cm) layer of the studied soils' A horizon. Distance from the irrigation ditch also determined the contents of TOC and Nt in the soil samples taken from transects I and II. These components were most abundant at 25 m from the watercourse (Table 3).

The basic parameter describing the intensity of decomposition of organic matter in soils (which translates into the properties of the forming HAs) is the value of the TOC/Nt ratio. In general, the values of this ratio were lowest (from 9.43 to 10.51) for the soils collected closer to the irrigation ditches (Table 3). Generally, the greater the distance, the higher the ratio. For the soils collected 25 m from the irrigation ditch, the TOC/Nt ratio ranged from 9.95 to 11.29. The values of this parameter also depended on depth. The TOC/Nt ratio was highest for the soils with the highest carbon content, i.e., those from a depth of 0–10 cm, where it ranged from 10.14 to 11.75 (Table 3). However, the analysis of variance found that the values of this parameter differed significantly between soil samples from the 0–10 cm and 10–20 cm layers only (P=0.015, Table 2). According to Becher and Kalembasa (2011), the values of this parameter obtained for the soils from the 0–10 cm layer indicate favourable conditions for the transformation of organic matter.

3.2. Properties of humic acids

Humic acids are complex macromolecular compounds, so several instrumental methods are used to determine their structures and properties. Because there was ample experimental material, the properties of the tested compounds could be evaluated and, consequently, indirect conclusions could be drawn as to the degree of transformation of the organic matter. The key elements in HAs are carbon, hydrogen, oxygen and nitrogen (Chen et al., 1977; Kumada 1985; Orlov, 1986; Gonet et al., 2007; Dębska et al., 2012; Gomes de Melo et al., 2016; Zhang et al., 2017). Atomic ratios were calculated based on the shares of individual elements in the HA molecules. The numerical values of the atomic ratios allow the structure of HA molecules to be approximately determined by assessing the degree of condensation of aromatic rings (the H/C ratio) and their degree of maturity (O/C, O/H, ω) (Van Krevelen, 1950; Dębska et al., 2012; Tan, 2012; Ferreira et al., 2013; Tinoco et al., 2015).

The obtained H/C ratio values ranged from 1.26 to 1.38, whereas it is expected to be around 1 in soil HAs. Thus, the studied HAs are built of aromatic systems coupled with aliphatic chains containing up to ten carbon atoms (Visser, 1983). The values of the H/C atomic ratios indicate that aromatic ring groups predominate over aliphatic chains. This makes it possible to determine the degree of maturity of HA molecules (Sanchez-Monedero et al., 2002; Gonet et al., 2007; Canellas et al., 2010; Boguta et al., 2016). It is worth adding that the examined HA molecules had similar H/C ratios to those obtained by Zdenek and Tesarova (2004), Drąg et al. (2007) and Banach-Szott et al. (2021b). Dergacheva et al. (2012) emphasize that the value of the H/C ratio depends on the conditions under which the HAs formed. Let us also not forget that not only the properties of HA molecules of a given soil type, but also the degree and direction of changes in them, depend primarily on the chemical composition of plant remains. Furthermore, the conditions under which humification takes place are also important. Thus, the dynamics of transformations of a certain type of plant residue will differ between soil types. Changes in the aromaticity of HAs subject to environmental perturbations such as changes in soil use (reforestation, clearing and cultivation, or bush encroachment) have been demonstrated by Tinoco et al. (2015). Our results indicate that the direction of changes in elemental composition depended on depth and distance from irrigation ditch (Table 4). The H/C parameter decreased with distance from the irrigation

Table 4
Values of atomic ratio of humic acids

Factor		H/C	N/C	O/C	O/H	ω
Transect I						
Distance (m)	5	1.36	0.080	0.635	0.467	0.150
	15	1.26	0.067	0.607	0.484	0.160
	25	1.27	0.069	0.617	0.486	0.169
LSD		0.003	0.001	0.011	0.008	ns
Depth (cm)	0–10	1.33	0.075	0.616	0.462	0.123
	10–20	1.29	0.073	0.630	0.488	0.186
	20–30	1.26	0.067	0.614	0.488	0.170
LSD		0.002	0.001	0.007	0.006	0.015
Transect II						
Distance (m)	5	1.36	0.081	0.625	0.458	0.126
	15	1.34	0.078	0.619	0.463	0.136
	25	1.31	0.080	0.610	0.467	0.151
LSD		0.011	ns	0.014	ns	ns
Depth (cm)	0–10	1.36	0.080	0.621	0.457	0.123
	10–20	1.35	0.082	0.619	0.458	0.134
	20–30	1.30	0.077	0.613	0.472	0.157
LSD		0.011	0.003	ns	0.009	0.021
Transect III						
Distance (m)	5	1.37	0.086	0.621	0.455	0.136
	15	1.35	0.085	0.616	0.456	0.137
	25	1.32	0.080	0.629	0.478	0.178
LSD		0.004	0.002	ns	0.013	0.027
Depth (cm)	0–10	1.38	0.085	0.629	0.455	0.132
	10–20	1.35	0.085	0.625	0.464	0.157
	20–30	1.30	0.081	0.611	0.470	0.163
LSD		0.003	0.003	ns	ns	ns

LSD (Least significant difference, α=0.05)

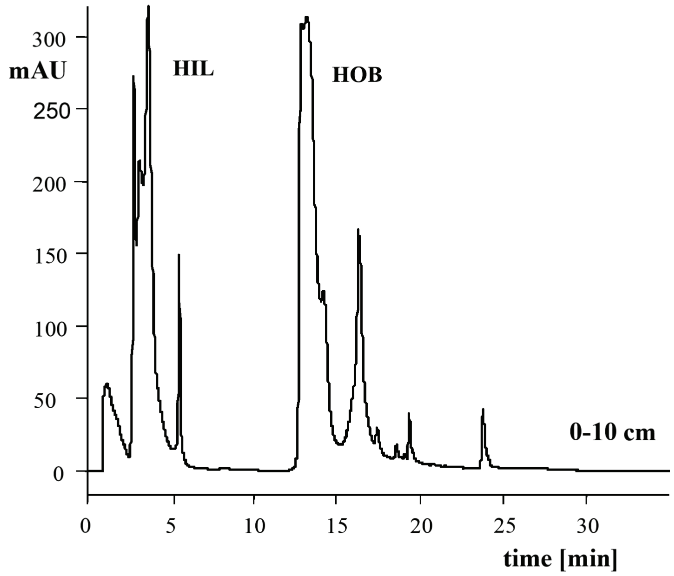

Fig. 2. RP-HPLC chromatogram of humic acids of the soils sampled in Transect II, 5 m away from the watercourse

ditch and with depth. Inverse relationships were obtained for the O/H ratio and the ω parameter. The N/C and O/C ratios values were 0.067–0.086 and 0.607–0.635, respectively (Table 4). Despite depth and distance having significantly influenced the values of these ratios, no unequivocal dependencies were found. It was only found that the N/C values were lowest for HAs in the soil from the 20–30 cm layer. According to Sanchez-Monedero et al. (2002) and Gonet et al. (2007), HA molecules with higher ω, O/C and O/H values and lower H/C values have a higher degree of maturity. Thus, the HAs of the soils collected closest to the ditch and from the 0–10 cm layer alike had the lowest degree of maturity. This is also confirmed by the significant differences found between the H/C ratio values for the HA molecules of soils collected from the 0–10 cm and 10–20 cm layer and between the H/C values of the HA molecules of soils collected from the depths of 10–20 cm and 20–30 cm (P=0.008 and P=0.001, respectively) (Table 2). The mean value of the ω parameter for HA molecules of soils collected from the 0–10 cm layer was 0.126, which was significantly lower than for HAs in the 10–20 cm layer (P=0.008, Table 2). The results of the meadow soil tests presented by Drąg et al. (2007) corresponded with the examined HA molecules, exhibiting similar values of H/C, O/H and the ω parameter. However, compared to the properties of HAs in peat soils (Becher et al., 2022) and Chernozems (Łabaz, 2010), the tested HAs had a lower degree of maturity, as evidenced by higher H/C ratios and lower ω parameter values.

According to de Aguiar et al. (2022), HA molecules isolated from different soil types had a similar structural pattern but differed in their amounts of the same chemical structures. The presence of different amounts of the same structures results in different HA properties, such as hydrophilicity, hydrophobicity, aromaticity and aliphaticity. The structural patterns for HS obtained by de Aguiar et al. (2022) justify the existence of HS structured as self-assembled, hydrophilic and hydrophobic domains that, under certain conditions, can undergo transformations, altering the balance of organic carbon in the environment. An HS structure consisting in a self-assembly of fragments in the soil in order of decreasing polarization is also confirmed in research by Fischer (2017). The highly polar superstructural subunits are arranged on the surface of the HS structure, and the less polar subunits are arranged toward the interior. Thus, the most polar subunits protect the humic fragments from being solubilized by the soil solution.

The hydrophilic–hydrophobic properties of the analysed HAs were determined by chromatographic analysis. Exemplary humic acid chromatograms are shown in Fig. 2. Fractions with a retention time of 3.0–8.0 mins show greater hydrophilic properties, while fractions with a retention time between 12.0 and 25.0 mins are increasingly hydrophobic. The share of hydrophobic fractions (HOB) in the examined HA molecules was higher than the share of hydrophilic fractions (HIL) and was at 58.11–61.24% (Table 5). The share of the discussed fractions in HAs generally depended on depth. It was shown that the HAs of soils collected from the 0–10 cm layer had more HOB fraction than did the HAs of deeper soil layers. In the case of the HIL fraction, the inverse relationship was found. The analysis of variance found that the share of the HIL fraction was highest in the HA molecules of soils from the 20–30 cm layer (41.5%) and differed significantly from the share in the HA molecules of soils from the 10–20 cm layer (P=0.002, Table 2). Changes in the HIL/HOB parameter express changes in the relative shares of the HIL and HOB fractions. The value of this ratio ranged from 0.640 to 0.723 and generally increased with depth (Table 5). The analysis of variance, too, showed that values of this parameter depended on depth. The HAs of the soils from the 20–30 cm layer had higher values of this parameter than did the HA molecules of the soils from the 10–20 cm layer (P=0.003, Table 2). According to Rusanov and Anilova (2009), a lower ratio corresponds to a higher content of hydrophobic humic components. Milanovskii (2000) and Milanovskii and Shein (2002) hold that a ratio of hydrophilic to hydrophobic fractions of close to 0.5–0.6 indicates a good balance of these fractions. This is evidence of sufficient content of hydrophobic substances to create stable soil aggregates and of the necessary content of hydrophilic components that form the

Table 5
Percentage share of hydrophilic (HIL) and hydrophobic (HOB) fractions in the molecules of humic acids

Factor		HIL (%)	HOB (%)	HIL/HOB	HIL (%)	HOB (%)	HIL/HOB	HIL (%)	HOB (%)	HIL/HOB
		Transect I			Transect II			Transect III		
Distance (m)	5	40.94	59.06	0.694	39.03	60.97	0.642	39.97	60.03	0.668
	15	40.32	59.68	0.676	39.00	61.00	0.642	39.54	60.46	0.655
	25	40.12	59.88	0.670	41.89	58.11	0.723	41.15	58.85	0.702
LSD		ns	ns	ns	ns	ns	ns	ns	ns	ns
Depth (cm)	0–10	39.57	60.43	0.655	38.76	61.24	0.636	38.95	61.05	0.640
	10–20	40.38	59.62	0.678	39.79	60.21	0.664	40.00	60.00	0.669
	20–30	41.43	58.57	0.708	41.38	58.62	0.706	41.71	58.29	0.716
LSD		1.242	1.242	0.035	ns	ns	ns	2.446	2.446	0.066

LSD (Least significant difference, α=0.05)

main reserve of readily available nutrients and that are easily distributed throughout the soil profile. In line with the results of Preuße (2000), Dębska et al. (2010), Becher et al. (2021) and Banach-Szott et al. (2021b), the hydrophilic–hydrophobic properties of HAs are related to the degree of humification of organic matter. Based on the obtained results, it is found that the degree of maturity of HA molecules increases with depth.

Distance had a negligible effect on the hydrophilic–hydrophobic properties of HAs. However, the HA molecules of soils collected at 25 m from the watercourse (Transects II and III) had a higher degree of humification (higher values of the HIL/HOB ratio) than did the HA molecules of soils collected at a distance of 5 m.

The results confirm the relationship found in previous studies of HAs in meadow soils conducted by Banach-Szott et al. (2021a).

The important parameters used to determine the properties of HAs and to evaluate the transformations of organic matter in the soils are spectrometric parameters in the UV-VIS range. The absorbance coefficients obtained were as follows: $A_{2/4}$: 5.80–7.30; $A_{2/6}$: 26.07–40.41; $A_{4/6}$: 4.35–5.27; and ΔlogK: 0.623–0.747. Compared against the results of Jonczak (2013), Drąg et al. (2007) and Kobierski et al. (2018), it was found that the tested HA molecules had lower $A_{4/6}$ absorbance coefficients and ΔlogK absorbance coefficients. It is worth emphasizing that the tested HAs had slightly higher values of the $A_{4/6}$ and ΔlogK absorbance coefficients than do HAs in peat soils (Becher et al., 2022). Filcheva et al. (2018) hold that there is a direct relationship between the groups with prevailing HAs or FAs in the humic products and the $A_{4/6}$ ratio. Results published by other authors also prove that $A_{4/6}$ ratios of HAs of around 4.04 indicate high quality. When FAs dominate, the $A_{4/6}$ ratio reaches values of up to 6.17; when HAs dominate, the value is 4.34 (Eshwar et al., 2017). Thus, the obtained values of the $A_{4/6}$ absorbance coefficient (4.35–5.27) are evidence of a relatively high degree of transformation of organic matter and confirm the maturity of the tested HAs (Kumada, 1988; Tinoco et al., 2015; Filcheva et al., 2018).

The absorbance coefficients were found to decrease with depth (Table 6). Based on the results reported by Kumada (1988), Tinoco et al. (2015) and Filcheva et al. (2018), this proves that the degree of humification of the tested HAs increases with depth. The analysis of variance showed that the values of the $A_{4/6}$ and ΔlogK parameters of HAs in soils collected from the depth of 0–10 cm differed from those in soils from 10–20 cm (P=0.0006 and P=0.001) and that those of soils collected from the depth of 10–20 cm differed from those of soils from 20–30 cm (P=0.0001 and P=0.0001) (Table 2). It was also shown that distance from the irrigation ditch had a significant impact on the discussed absorbance coefficients. For the HAs of soils collected from Transects II and III, the $A_{2/4}$, $A_{2/6}$, $A_{4/6}$ and ΔlogK values were lowest at 25 m from the watercourse. Thus, the results show that the HA molecules of the soils collected farthest from the ditch had the highest degree of humification. It is worth noting that the spectrometric parameter values were highest for the HAs of soils collected 15 m from the irrigation ditch. This may indicate that humic substances are more abundant in the initial stage of decomposition than in the soil collected closest to and farthest from the ditch. According to Vieyra et al. (2009), the value of the $A_{4/6}$ absorbance ratio is higher for non-humified materials due to the presence of proteins and carbohydrates. Moreover, the high value of this parameter reflects the low degree of condensation of aromatic rings (Albrecht et al., 2011).

To assess how soil properties affect HA properties, Table 7 presents the correlation between the grain-size composition content (%) and selected HA parameters. Humic acid molecules with a higher “degree of maturity” (i.e., a significant negative correlation between the clay content and the values of H/C, $A_{2/4}$, $A_{2/6}$, $A_{4/6}$, ΔlogK and a significant positive correlation between the clay content and ω parameter) are characteristic for the soils with a higher clay fraction content and a lower sand fraction content. The importance of the interaction between organic matter (including humic substances) and the clay fraction is emphasized by, among others, Theng (1979) Cornejo and Hermosin (1996) and Tan (2012). Jindaluang et al. (2013) noted the effect that grain-size composition (especially the content of the clay fraction) had on the content and properties of SOM. The obtained dependencies also confirm previous research presented by Banach-Szott et al. (2021a).

Table 6
Values of humic acids absorbance coefficients

Factor		$A_{2/4}$	$A_{2/6}$	$A_{4/6}$	ΔlogK
Transect I					
Distance (m)	5	6.35	31.0	4.88	0.678
	15	6.17	28.7	4.65	0.655
	25	6.18	29.4	4.75	0.658
LSD		ns	0.589	0.166	0.023
Depth (cm)	0–10	6.53	33.6	5.15	0.700
	10–20	6.16	29.4	4.78	0.666
	20–30	6.02	26.2	4.35	0.624
LSD		0.369	0.331	0.310	0.023
Transect II					
Distance (m)	5	6.73	34.3	5.08	0.697
	15	6.95	37.0	5.27	0.719
	25	6.38	31.3	4.81	0.666
LSD		0.132	1.562	0.283	0.007
Depth (cm)	0–10	7.30	40.4	5.52	0.747
	10–20	6.97	36.1	5.17	0.712
	20–30	5.80	26.1	4.47	0.623
LSD		0.074	1.537	0.218	0.007
Transect III					
Distance (m)	5	6.599	33.712	5.028	0.686
	15	6.896	35.789	5.171	0.721
	25	6.111	28.315	4.556	0.654
LSD		0.131	2.336	0.130	0.037
Depth (cm)	0–10	7.201	38.080	5.286	0.728
	10–20	6.546	33.404	5.023	0.703
	20–30	5.858	26.332	4.446	0.630
LSD		0.083	1.566	0.145	0.019

LSD (Least significant difference, α=0.05)

Table 7
Correlations between the grain size composition content (%) and selected parameters of humic acids

	H/C	ω	$A_{2/4}$	$A_{2/6}$	$A_{4/6}$	ΔlogK
Clay	–0.602*	0.740*	–0.691*	–0.708*	–0.753*	–0.749*
Silt	–0.153	0.301	–0.393	–0.408	–0.412	–0.380
Sand	0.261	–0.429	0.512*	0.529*	0.540	0.509*

* Significant correlations for $p \leq 0.05$

4. Conclusions

The studied soils consisted largely of sand fraction and contained little in terms of clay fraction. The TOC and Nt contents were highest for the soils collected from a depth of 0–10 cm. Consequently, this soil layer had the TOC/Nt ratio values most conducive to the decomposition of organic matter. The research has identified that HA properties depended on clay content. Soils with a higher content of clay fraction include HAs with a higher “degree of maturity”. On the basis of the obtained atomic ratios (H/C, O/H and ω) and spectrometric parameters ($A_{2/6}$, $A_{4/6}$ and ΔlogK), the degree of maturity of the HAs was found to increase with depth and was highest in the soil samples taken farthest from the irrigation ditch. The results indicate that relatively high-stability HAs were formed by the processes of transformation of the organic matter of the mineral meadow soils.

Acknowledgments

The research was made as part of 1047/B/P01/2010/39 research project, financed by the Ministry of Science and Higher Education (Poland).

References

Albrecht, R., Petit, J.L., Terrom, G., Périssol, C., 2011. Comparison between UV spectroscopy and Nirs to assess humification process during sewage sludge and green wastes co-composting. Bioresource Technology 102(6), 4495–4500. https://doi.org/10.1016/j.biortech.2010.12.053

Banach-Szott, M., Dębska, B., Tobiasova, E., 2021b. Properties of humic acids depending on the land use in different parts of Slovakia. Environmental Science and Pollution Research 28, 58068–58080. https://doi.org/10.1007/s11356-021-14616-9

Banach-Szott, M., Dziamski, A., Markiewicz, M., 2021a. Properties of humic acids in meadow soils irrigated with the slope-and-flooding system. Agronomy 11(12), 2553. https://doi.org/10.3390/agronomy11122553

Becher, M., Banach-Szott, M., Godlewska, A., 2021. Organic matter properties of spent button mushroom substrate in the context of soil organic matter reproduction. Agronomy 11(2), 204. https://doi.org/10.3390/agronomy11020204

Becher, M., Kalembasa, D., 2011. Frakcje azotu i węgla w poziomach próchnicznych ornych gleb brunatnoziemnych wysoczyzny siedleckiej. Acta Agrophysica 18(1), 7–16.

Becher, M., Tołoczko, W., Godlewska, A., Pakuła, K., Żukowski, E., 2022. Fractional composition of organic matter and properties of humic acids in the soils of drained bogs of the Siedlce Heights in eastern Poland. Journal of Ecological Engineering 23(3), 208–222. https://doi.org/10.12911/22998993/146679

Boguta, P., D'Orazio, V., Sokołowska Z., Senesi, N., 2016. Effects of selected chemical and physicochemical properties of humic acids from peat soils on their interaction mechanisms with copper ions at various pHs. Journal of Geochemical Exploration 168, 119–126. https://doi.org/10.1016/j.gexplo.2016.06.004

Canellas, L.P., Piccolo, A., Dobbss, L.B., Spaccini, R., Olivares, F.L., Zandonadi, D.B., Façanha, A.R., 2010. Chemical composition and bioactivity properties of size-fractions separated from a vermicompost humic acid. Chemosphere 78, 457–466. https://doi.org/10.1016/j.chemosphere.2009.10.018

Chen, Y., Senesi, N., Schnitzer, M., 1977. Information provided on humic substances by $E_{4/6}$ ratios. Soil Science Society American Journal 41, 352–358. https://doi.org/10.2136/sssaj1977.03615995004100020037x

COM 231 final. 2006. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. Thematic Strategy for Soil Protection, Brussels. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52006DC0231&from=EN (accessed on 26 September 2006).

Cornejo, J., Hermosin, M.C., 1996. Interaction of humic substances and soil clays. [In:] Piccolo, A. (Ed), Humic substances in terrestrial ecosystems. Elsevier, Amsterdam, The Netherlands, 595–624.

de Aguiar, C., de Oliveira Torchia, D.F., van Tol de Castro, T.A., Tavares, O.C.H., de Abreu Lopes S., de Souza da Silva, L., Castro, R.N., Berbara, R.L.L., Pereira, M.G., García, A.C., 2022. Spectroscopic–chemometric modeling of 80 humic acids confirms the structural pattern identity of humified organic matter despite different formation environments Tamiris. Science of the Total Environment 833, 155133. http://dx.doi.org/10.1016/j.scitotenv.2022.155133

Dębska, B., Banach-Szott, M., Dziamski, A., Gonet, S.S., 2010. Chromatographic characteristics (HPLC, HPSEC) of humic acids of soil fertilised with various organic fertilisers. Chemical Ecology 26, 49–57. https://doi.org/10.1080/02757540.2010.501027

Dębska, B., Długosz, J., Piotrowska-Długosz, A., Banach-Szott, M., 2016. The impact of bio-fertilizer on the soil organic matter status and carbon sequestration–results from a fiel-scale study. Journal of Soils and Sediments 16, 2335–2343. https://doi.org/10.1007/s11368-016-1430-5

Dębska, B., Drąg, M., Banach-Szott, M., 2007. Molecular size distribution and hydrophilic and hydrophobic properties of humic acids isolated from forest soil. Soil and Water Research 2, 45–53. https://doi.org/10.17221/2113-SWR

Dębska, B., Drąg, M., Tobiasova, E., 2012. Effect of post-harvest residue of maize, rapeseed, and sunflower on humic acids properties in various soils. Polish Journal of Environmental Studies 21, 603–613.

Dębska, B., Maciejewska, A., Kwiatkowska, J., 2002. The effect fertilization with brown coal on Haplic Luvisol humic acids. Rostlinna Vyroba 48(1), 33–39. https://doi.org/10.17221/4203-PSE

Dergacheva, M.I., Nekrasova, O.A., Okoneshnikova, M.V., Vasileva, D.I., Gavrilov, D.A., Ochur, K.O., Ondar, E.E., 2012. Ratio of elements in humic acids as a source of information on the environment of soil formation. *Contemporary Problems* of Ecology 5, 497–504. https://doi.org/10.1134/S1995425512050022

Drąg, M., Dębska, B., Dziamski, A., 2007. Properties of humic substances of forest and meadow soil in the area of the Wierzchlas Reserve. Humic Substances in Ecosystems 7, 141–151.

EIP-AGRI, Focus Group. Profitability of Permanent Grassland 2014. Available online: https://ec.europa.eu/eip/agriculture/sites/default/files/fg9_permanent_grassland_profitability_starting_paper_2014_en.pdf (accessed on 28 May 2014).

Eshwar, M., Srilatha, M., Rekha, K.B., Sharma, S.H.K., 2017. Characterization of humic substances by functional groups and spectroscopic methods. *International Journal* of *Current Microbiology* and *Applied* Sciences 6(10), 1768–1774. https://doi.org/10.20546/ijcmas.2017.610.213

Ferreira, F.P., Vidal-Torrado, P., Otero, X.L., Buurman, P., Martin-Neto, L., Boluda, R., Macias, F., 2013. Chemical and spectroscopic characteristics of humic acids in marshes from the Iberian Peninsula. Journal of Soils and Sediment 13, 253–264. https://doi.org/10.1007/s11368-012-0607-9

Filcheva, E., Hristova, M., Nikolova, P., Popova, T., Chakalov, K., Savov, V., 2018. Quantitative and qualitative characterisation of humic products with spectral parameters. Journal of Soil Sediments 18(8), 2863–2867. https://doi.org/10.1007/s11368-018-2021-4

Fischer, T., 2017. Humic supramolecular structures have polar surfaces and unpolar cores in native soil. Chemosphere 183, 437–443. https://doi.org/10.1016/j.chemosphere.2017.05.125

GIOS, 2022. Monitoring chemizmu gleb ornych w Polsce w latach 2020––2022. https://www.gios.gov.pl/images/dokumenty/pms/monitoring_jakosci_gleb/raport_chemizm_gleb_2022.pdf

Gomes de Melo, B.A., Motta, F.L., Santana, M.H.A., 2016. Humic acids: Structural properties and multiple functionalities for novel technological developments. Materials *Science* and *Engineering* C 62, 967–974. https://doi.org/10.1016/j.msec.2015.12.001

Gonet, S.S., Dębska, B., Zaujec, A., Banach-Szott, M., Szombathova, N., 2007. Wpływ gatunku drzew i warunków glebowo-klimatycznych na właściwości próchnicy gleb leśnych. [In:] Gonet, S.S., Markiewicz, M. (Eds.), Rola materii organicznej w środowisku – Role of organic matter in the environment. PTSH, Wrocław, Poland, 61–98. (in Polish)

Heller, Ch., Zeitz, J., 2012. Stability of soil organic matter in two northeastern German fen soils: the influence of site and soil development Journal of Soils and Sediment 12, 1231–1240. https://doi.org/10.1007/s11368-012-0500-6

Jindaluang, W., Kheouenromne, I., Suddhiprakam, A., Singh, B.P., Singh, B., 2013. Influence of soil texture and mineralogy on organic matter content and composition in physically separated fractions soil in Thailand. Geoderma 195–196, 207–219. https://doi.org/10.1016/j.geoderma.2012.12.003

Jonczak, J., 2013. Soil organic matter properties in Stagnic Luvisols under different land use types. Acta Agrophysica 20, 565–576.

Kämpf, I., Hölzel, N., Störrle, M., Broll, G., Kiehl, K., 2016. Potential of temperate agricultural soils for carbon sequestration: A meta-analysis of land-use effects. Science of the Total Environment 566, 428–435. https://doi.org/10.1016/j.scitotenv.2016.05.067

Kenngott, K.G.J., Riess, K., Mu*ń*oz, K., Schaumann, G.E., Buhk, C., Diehl, D., 2021. Flood pulse irrigation of meadows shapes soil chemical and microbial parameters more than mineral fertilization. Soil Systems 5, 24. https://doi.org/10.3390/soilsystems5020024

Khalid, M., Soleman, N., Jones, D.L., 2007. Grassland plants affect dissolved organic carbon and nitrogen dynamics in soil. Soil Biology and Biochemistry 39, 378–381. https://doi.org/10.1016/j.soilbio.2006.07.007

Kobierski, M., 2010. Uziarnienie gleb różnych typów wytworzonych z gliny lodowcowej w aspekcie klasyfikacji PTG 2008. Roczniki Gleboznawcze – Soil Science Annual 61, 67–76. (in Polish with English abstract)

Kobierski, M., Kondratowicz-Maciejewska, K., Banach-Szott, M., Wojewódzki, P., Castejón, J.M.P., 2018. Humic substances and aggregate stability in rhizospheric and non-rhizospheric soil. Journal of Soils and Sediment 18, 2777–2789. https://doi.org/10.1007/s11368-018-1935-1

Kumada, K., 1985. Elementary composition and absorption spectra of humic and fulvic acids. Soil Science and Plant Nutrition 31(3), 437–448.

Kumada, K., 1988. Chemistry of Soil Organic Matter. Elsevier, Amsterdam, The Netherlands.

Łabaz, B., 2010. Właściwości kwasów huminowych gleb czarnoziemnych występujących w rejonie Kłodzka. Woda – Środowisko – Obszary wiejskie 10(3), 153–164. (in Polish)

Lal, R., 2011. Sequestering carbon in soils of agro-ecosystems. Food Policy 36, 533–539. https://doi.org/10.1016/j.foodpol.2010.12.001

Lanyi, K., 2010. Assessment of the relations between the spectroscopic characteristics of soils and their ability to adsorb organic pollutants. Microchemical Journal 79, 249–256. https://doi.org/10.1016/j.microc.2004.08.008

Milanovskii, E.Y., 2000. Amphiphilous components of soil humic substances. Eurasian Soil Science 33(6), 617–625.

Milanovskii, E.Y., Shein, E.V., 2002. Functional role of amphiphilic humus components in humus structure formation and soil genesis. Eurasian Soil Science 35(10), 1064–1075.

Norton, J.B., Jungst, L.J., Norton, U., Olsen, H.R., Tate, K.W., Horwath, W.R., 2011. Soil carbon and nitrogen storage in upper montane riparian meadows. Ecosystems 14, 1217–1231. https://doi.org/10.1007/s10021-011-9477-z

Orlov, D.S., 1986. Humus acids of soils, first ed. AA Balkema, Rotterdam.

Orsi, M., 2014. Molecular dynamics simulation of humic substances. Chemical and Biological Technologies in Agriculture 1(1), 1–14. https://doi.org/10.1186/s40538-014-0010-4

Pizzeghello, D., Francioso, O., Concheri, G., Muscolo, A., Nardi, S., 2017. Land use affects the soil C sequestration in alpine environment, NE Italy. Forests 8(6), 197. https://doi.org/10.3390/f8060197

Polak, J., Bartoszek, M., Żądło, M., Kos, A., Sułkowski, W.W., 2011. The spectroscopic studies of humic acid extracted from sediment collected at different seasons. Chemosphere 84, 1548–1555. https://doi.org/10.1016/j.chemosphere.2011.05.046

Preuße, G., Friedrich, S., Salzer, R., 2000. Retention behavior of humic substances in reversed phase HPLC. Fresenius Journal of Analytical Chemistry 368, 268–273. https://doi.org/10.1007/s002160000457

Rodriguez, F.J., Schlenger, P., García-Valverde, M., 2016. Monitoring changes in the structure and properties of humic substances following ozonation using UV-Vis, FTIR and H NMR techniques. Science of the Total Environment 541, 626–637. https://doi.org/10.1016/j.scitotenv.2015.09.127

Rusanov, A.M., Anilova, L.V., 2009. The humus formation and humus in forest-steppe and steppe chernozems of the southern cisural region. Eurasian Soil Science 42(10), 1101–1108. https://doi.org/10.1134/S1064229309100044

Sabiniarz A., Kozłowski S., 2009b. Łąki Czerskie w aspekcie paszowym. Łąkarstwo w Polsce – Grassland Science in Poland, 12, 155–163. (in Polish with English abstract)

Sabiniarz, A., 2006. Łąki Czerskie w aspekcie historycznym. Łąkarstwo w Polsce – Grassland Science in Poland, 9, 184–194. (in Polish with English abstract)

Sabiniarz, A., Kozłowski, S., 2009a. Łąki Czerskie w aspekcie krajobrazowym. Łąkarstwo w Polsce – Grassland Science in Poland, 12, 141–154. (in Polish with English abstract)

Sanchez-Monedero, M.A., Cegarra, J., Garcia, D., Roig, A., 2002. Chemical and structural evolution of humic acids during organic wast e composting. Biodegradation 13, 361–371. https://doi.org/10.1023/a:1022888231982

Sapek, B., 2009. Zapobieganie stratom i sekwestracja węgla organicznego w glebach łąkowych. Inżynieria Ekologiczna – Ecological Engineering 21 48–61. (in Polish)

Sapek, B., Burzyńska, I., 2009. Węgiel organiczny w glebie łąkowej na tle jej użytkowania, nawożenia i uwilgotnienia. Woda – Środowisko – Obszary wiejskie 9 (1), 111–127. (in Polish)

Tan, H.K., 2012. Humic matter in soil and the environment (2nd ed.). CRC Press, Boca Raton. https://doi.org/10.1201/b17037

Theng, B.K.G., 1979. Formation and properties of clay-polymer complexes. Elsevier, Amsterdam, The Netherlands.

Tinoco, P., Almendros, G., Francisco, J., Gonzalez-Vila, F.J., Sanz, J., Gonzalez-Perez, J.A., 2015. Revisiting molecular characteristics responsive for the aromaticity of soil humic acids. Journal of Soils and Sediment 15, 781–791. https://doi.org/10.1007/s11368-014-1033-y

Trubetskaya, O.E., Trubetskoj, O.A., Voyard, G., Richard, C., 2013. Determination of hydrophobicity and optical properties of soil humic acids isolated by different methods. *Journal of Geochemical Exploration* 132, 84–89. https://doi.org/10.1016/j.gexplo.2013.06.004

Van Krevelen, D.W., 1950. Graphical-statistical method for investigation of the structure of coal. Fuel 26, 269–284.

van Reeuwijk, L.P., 2002. Procedures for Soil Analysis. International Soil Reference and Information Centre, Wageningen, The Netherlands.

Vieyra, F.E.M., Palazzi, V.I., de Pinto, M.I.S., Borsarelli, C.D., 2009. Combined UV–Vis absorbance and fluorescence properties of extracted humic substances-like for characterization of composting evolution of domestic solid wastes. Geoderma 151, 61–67. https://doi.org/10.1016/j.geoderma.2009.03.006

Visser, S.A., 1983. Application of van Krevelen's graphical statistical method for the study of aquatic humic material. Environmental Science and Technology 17(7), 412–417.

Weber, J., Chen, Y., Jamroz, E., Miano, T., 2018. Preface: humic substances in the environment. Journal of Soils and Sediment 18, 2665–2667. https://doi.org/10.1007/s11368-018-2052-x

Wiesmeier, M., Urbański, L., Hobley, E., Lang, B., von Lützow, M., Marin--Spiotta, E., van Wesemael, B., Rabot, E., Ließ, M., Garcia-Franco, N., Wollschlager, U., Vogel, H., Kögel-Knabner, I., 2019. Soil organic carbon storage as a key function of soils – A review of drivers and indicators at various scales. Geoderma 333, 149−162. https://doi.org/10.1016/j.geoderma.2018.07.026

Zdenek, F., Tesarova, M., 2004. Microbial degradation and transformation of humic acids from permanent meadow and forest soils. *International Biodeterioration* and *Biodegradation* 54, 225−231. https://doi.org/10.1016/j.ibiod.2004.06.006

Zhang, J., Wang, J., An, T., Wei, D., Chi, F., Zhou, B., 2017. Effects of long-term fertilization on soil humic acid composition and structure in Black Soil. Plos One 12(11), 1−14. https://doi.org/10.1371/journal.pone.0186918

Kwasy huminowe wieloletnich użytków zielonych Kompleksu Łąk Czerskich

Słowa kluczowe

Gleby łąkowe
Humus
Skład pierwiastkowy
Hydrofilowość/Hydrofobowość
UV-VIS

Streszczenie

Celem badań było określenie podstawowych właściwości gleb oraz stabilności kwasów huminowych (KH) w poszczególnych warstwach poziomu A gleb łąkowych. Próbki gleb pobrano na terenie unikalnego „Kompleksu Łąk Czerskich" w północnej Polsce, po 25 latach od zaprzestania nawadniania systemem stokowo-zalewowym trwającego 150 lat. Jest to kontynuacja badań prowadzonych na Łąkach Czerskich. We wcześniejszych badaniach (Banach-Szott i in. 2021a) analizowano gleby nieprzerwanie nawadniane. W próbkach gleb oznaczono zawartość całkowitego węgla organicznego (TOC) i całkowitego azotu (Nt) oraz skład granulometryczny. Kwasy huminowe wyekstrahowano metodą Schnitzera i analizowano pod kątem składu pierwiastkowego, parametrów spektrometrycznych w zakresie UV-VIS i właściwości hydrofilowych i hydrofobowych. Badane gleby charakteryzowały się wysoką zawartością frakcji piasku i niską zawartością frakcji ilastej. Zawartości TOC, Nt, wartości stosunku TOC/Nt zależały od głębokości pobrania próbek gleb i odległości od rowu nawadniającego. Najwyższe zawartości TOC i Nt oraz wartości stosunku TOC/Nt otrzymano dla gleb pobranych z głębokości 0–10 cm i tych pobranych 25 m od rowu nawadniającego. Badania wykazały, że cząsteczki KH gleb pobranych z głębokości 0–10 cm charakteryzowały się wyższymi wartościami stosunków H/C i parametrami spektrometrycznymi oraz niższymi wartościami parametru ω i stosunku HIL/HOB niż kwasy huminowe głębszych warstw gleby. Wskazuje to na wzrost „stopnia dojrzałości" kwasów huminowych ze wzrostem głębokości. Na podstawie otrzymanych wartości stosunków atomowych (H/C, O/C, O/H), parametru ω i współczynników absorbancji ($A_{2/6}$, $A_{4/6}$ and ΔlogK) stwierdzono najwyższy stopień dojrzałości cząsteczek KH w próbkach gleb pobranych najdalej od rowu nawadniającego. Wyniki wykazały, że w wyniku procesów transformacji materii organicznej mineralnych gleb łąkowych powstały stosunkowo stabilne kwasy huminowe.