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## Transformation of some organic matter components in organic soils exposed to drainage

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**Abstract:** In drained Histosols used as pastures or arable fields the muck-forming process transforms organic soil formations into muck. The rush vegetation (*Caricetum acutiformis* and *Glycerietum maximae*) covering Histosols in the organic matter accumulation stage is replaced by meadow vegetation (*Molinietalia* order). During sustained drainage mucks are transformed into muck-like formations that contain less than 12% organic carbon. The aim of this study was to report the changes in organic matter initiated by the muck-forming process. Soil organic matter was fractionated into humic-acid carbon, fulvic-acid carbon, and humins. The amount of carbon susceptible to oxidation with  $\text{KMnO}_4$  was also determined and, based on these results, lability, carbon pool, and management indices were calculated. Additionally, hot-water extractable carbon, corresponding to microbial biomass, was determined. The study's results show that the muck-forming process caused a decrease in organic carbon and the concentration of total nitrogen, indicating a reduction in carbon sequestration in the soils. The humin fraction was predominant in untransformed soils and was positively correlated with clay, total nitrogen, and non-oxidizable carbon. Drainage of Histosols contributed to increasing the solubility of humus compounds. The humification index, and the content of humic and fulvic acids was higher in drained soils. Humic acids and fulvic acids content was 24% and 11%-12% of organic carbon, respectively. Muck formations contained more humic acids than muck-like formations. Higher  $\Sigma\text{CHCF}:\text{humins}$  ratios were also observed in drained soils. In muck-like formations this ratio was 0.91 (11-fold higher than in reference soils). Drainage contributed to an increase in hot-water extractable carbon. Carbon indices were higher in mucks than in muck-like formations.

**Key words:** Degradation of Histosols, hot water-extractable carbon, humic substances, reclamation of organic soils

### Introduction

Soil organic matter (SOM) plays an important role in the soils of almost every ecosystem. It affects the chemical and physical properties of soil, such as the formation of stable aggregates, water retention, cation exchange capacity, nutrient abundance, and nitrogen

and carbon reserves (Kononova 1966). On the other hand, soil type, water regime, and the composition of the mineral fraction (quantities of sand, silt, and clay) can influence SOM properties. Organic matter content in soil depends on the balance between the rates of addition and decomposition of organic

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material (Blair et al. 1995). On a global scale, organic soils (Histosols) are an important reservoir of organic carbon (Rabenhorst and Swanson 2000). Carbon in these soils is stored in the form of plant remnants in various stages of decomposition, as well as in the form of heterogeneous organic (humic) compounds, which can be described as a complex mixture of polyelectrolyte-like macromolecules of variable chemical composition, shape, and size (Zavarzina et al. 2002). As a result of humification, the humic substances content in organic soils increases. They participate in sorption processes in the soil, and form soluble and insoluble complexes with metallic ions (Stevenson 1994). Humic substances are the main constituents of the adsorptive complex that affects soil properties. Humic substances of different origins differ in composition and chemical structure (Lishtvan et al. 1989). Humic substances are complex and have high molecular weight. The classic fractionation of humus is based on extracting fulvic acids, humic acids, and humins that differ in solubility in various solutions of variable pH (Valladares et al. 2007).

In northern and central Europe organic soils occur mainly near lakes or in depressions where the groundwater level is high. They also frequently occur in river valleys. For the present study we chose some specific parts of river valleys in Poland (central Europe), where simultaneous accumulation of well-decomposed organic matter (of autogenous origin as well as transported by river water) and fine-grained mineral particles occur. In the depressions on floodplains vegetation is submerged for 4-8 months a year. Simultaneously, the water is oxidized by megaplankton. These factors lead to the formation of well-decomposed organic matter that resembles low-moor peat. Low-moor peat, in contrast to high-moor peat (bog peat), contains little or no *Sphagnum* spp. Peat material can be fibric, hemic, or sapric, depending on the degree of decomposition.

The soils presented herein resemble sapric, mostly decomposed peats. Due to the substantial admixture of mineral particles, the organic matter content in the studied soil formations was 20%-60%, i.e. it was lower than generally observed in peats. As in all organic soils, after drainage they undergo the process of organic matter transformation, known as

the muck-forming process (Okruszko 1993; Ilnicki and Zeitz 2003; Okruszko and Ilnicki 2003). During this process intense mineralization, humification, and changes in the composition of SOM take place. As a result, drained soils have lower SOM content. It has been proposed that drainage of organic soils leads to changes in the physico-chemical properties of these soils and humic substances content (Sokołowska et al. 2005), and degradation of SOM (Szajdak et al. 2007).

SOM is the most important factor affecting soil quality (Yangchun Xu et al. 2007). Soil transformation caused by drainage affects the accumulation and distribution of the forms of organic compounds in the soil. Labile forms of humus are fulvic acids and brown humic acids (Kononova 1966). Fulvic acids are associated with the part of organic carbon referred to as dissolved organic carbon. Less labile forms are humic acids bound to cations and humins (Andriulo et al. 1991; Stevenson 1994; Six et al. 2002). Labile carbon measurement should be used more widely in order to examine soil properties (Craswell and Lefroy 2001; Schulz 2004), as this part of organic carbon has the potential to be easily oxidized to CO<sub>2</sub> and therefore contributes to the greenhouse effect. The oxidation of SOM in cultivated soils causes the release of approximately 50 Pg of C to the atmosphere (Ingram and Fernandes 2001). In Histosols, which are predominated by organic matter, the importance of examining humic substances is crucial (Valladares et al. 2007).

Interest is growing in understanding the changes in SOM in organic soils affected by transformation due to drainage. The aim of the present study was to examine changes in SOM in riverine organic matter-rich soils caused by drainage. The analyses included extraction of humic and fulvic acids, potentially oxidizable carbon, and hot water-extractable carbon. The examined soils required our attention because many river valleys are subjected to hydrotechnical projects and land reclamation. The soil processes taking place in these types of soil have an effect on carbon cycling and river water quality. Increases in SOM in riverine soils during the accumulation stage may contribute to carbon sequestration; however, drainage and degradation of these soils release carbon compounds (CO<sub>2</sub>).

## Materials and methods

In the present study soils were selected from 2 river valleys (Rozoga and Omulew) in northeastern Poland. Both valleys are located on a sandy outwash plain formed during the Vistula (Weichelian) Glaciation. There are morainal hills in the northern part of the catchment areas, which contain the rivers' sources. In the 1930s and 1950s the rivers became regulated and their valleys were drained to obtain more land for agricultural use. As a slow rate of SOM accumulation is characteristic for such soils in river valleys, the organic layer is generally thin (up to 40-50 cm) and underlying deposits consist of alluvial loose sands. Mineral deposits were excluded from this study.

Soil samples were taken from depths of 0-20 cm and 20-40 cm. We took 4 samples of surface soil undergoing organic matter accumulation (in this study they are regarded as reference samples) and 16 samples from drained soils. Among the drained soils samples, 10 represent surface layers and 6 represent subsurface layers. The surface soil samples differed in total organic carbon (TOC) content and therefore were divided into 2 groups: muck formations representing the first stage of SOM transformation that contained more than 12% TOC, and muck-like formations representing the second stage of SOM transformation that contained less than 12% TOC. Due to further mineralization of organic matter in the mucks, TOC decreased. The soil formations with less than 12% TOC are referred to as 'muck-like formations'. They are considered degraded organic soils (Okruszko 1993). All subsurface samples were the underlying muck formations and contained more than 12% TOC, but 2 samples also contained less than 12% TOC. General characteristics of the examined soils are given in Table 1.

The threshold value of 12% TOC content distinguishes organic soil formations from mineral formations (IUSS Working Group WRB 2006), and was chosen because the investigated soil formations had low clay content (<10%) in their mineral matter (Table 1). Generally, the WRB system classifies organic soils as those that have a histic horizon containing more than 12% TOC and no clay, or 12%-18% TOC when clay content is 0%-60% or 18% TOC when the clay content is more than 60%. In this respect, muck-like formations are classified as mineral

formations, but their genetic connections with organic soils are obvious. The soils representing the organic matter accumulation stage were covered by rush vegetation (*Caricetum acutiformis* and *Glycerietum maximae*), whereas drained soils were covered by meadow vegetation of the order *Molinietalia*. According to the WRB soil classification system (IUSS Working Group WRB 2006), the soils in the SOM accumulation stage were Rhei-sapric Histosols and Eutric Fluvisols, drained soils in the first stage of SOM transformation were Eutri-sapric Histosols and Eutric Fluvisols, and the soils in the second stage of SOM transformation were Gleyic Fluvisols, Eutric Gleysols, and Distric Gleysols.

Soil samples were air-dried and visible plant remnants were removed by hand. For mineral fraction analysis, samples were sieved on 2-mm mesh and the percentage of fractions 2000-50  $\mu\text{m}$  in diameter (sand), 50-2  $\mu\text{m}$  (silt), and less than 2  $\mu\text{m}$  (clay) was determined using a Malvern Mastersizer 2000 laser analyzer after organic matter was removed by oxidation with 30%  $\text{H}_2\text{O}_2$ . For chemical analysis soil samples were ground to pass through a 0.25-mm sieve. Loss-on-ignition (LOI) was determined after dry ashing the soil samples over 6 h at 550 °C. TOC content was measured with a spectrophotometer after oxidation with potassium dichromate (ISO 14235 1998), and total nitrogen (TN) was measured by the Kjeldahl method. Cation exchange capacity (CEC) and base saturation (BS) were calculated based on exchangeable cation content in a solution after extraction with 1 M ammonium acetate ( $\text{CH}_3\text{COONH}_4$ , pH 7.0) (van Reeuwijk 1995).

Various procedures for isolation of humus fractions were employed. For humic and fulvic acid extraction the scheme described by Duchaufour and Jacquin (1966) was used. Humic substance fractioning was performed using 3 extraction solvents: a mixture of 0.1 M sodium diphosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ) and 7.5% sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) at pH 7.0 was used to extract the most mobile (free) humus compounds; 0.1 M sodium diphosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ) was used to extract humus compounds bound to cations; 0.1 M sodium hydroxide (NaOH) was used to extract strongly bound humus compounds and those with high molecular weight.

The analyzed soil samples were amorphous in character and did not contain any undecomposed organic remains; therefore, the separation of “free” organic matter was omitted. Five grams of soil and 100 cm<sup>3</sup> of the first solvent were used with a contact time of 24 h. Then the solutions were centrifuged for 30 min at 4000 rpm and filtered through qualitative paper filters (Eurochem BGD, 150 mm in diameter). The residue was washed with the second solvent and left for 24 h, and then was centrifuged and filtered, as described above. The residue was again washed with the third solvent with a contact time of 24 h, and then was centrifuged and filtered. These 3 extracts were collected for determination of carbon content (fulvic and humic acids). Humic acids (CH) were precipitated with 0.05 M sulfuric acid in an aliquot of 50 cm<sup>3</sup> of the 3 extracts, and then were redissolved with 0.1 M sodium hydroxide to determine their carbon content. The carbon content of the extracts was determined with a spectrophotometer (Shimadzu UV 1201V), following oxidation with a solution of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>). The carbon content of fulvic acids (CF) was determined based on the difference between the carbon content of the extracts and the carbon content of humic acids. The sum of CH and CF reported as a percentage of TOC in the soil sample is referred to as the degree of humification (Ciavatta et al. 1990). The content of humic acids in the 3 extracts enabled us to determine the amount of respectively “free”, bound, and strongly bound organic compounds within the mineral matrix. The CH:CF ratio was calculated to determine the types of humus: humic (CH:CF >1.5), fulvic-humic (CH:CF 1.0-1.5), and humic-fulvic (CH:CF 0.5-1.0) (Grishina 1986). Part of SOM was not extracted because heterogeneous organic compounds, called humins, are resistant to chemical solvents. Humins are an insoluble part of humus, which is tightly bound to clay minerals, or colloidal iron hydroxide and aluminum hydroxide.

Potentially oxidizable carbon content was estimated with the method described by Blair et al. (1995). Soil samples containing 20 mg of TOC and 50 mL of 0.0333 M potassium permanganate (KMnO<sub>4</sub>) were used and shaken for 30 min on a BIOSAN PSU 20 multi-shaker. Then the solutions were passed through glass filters and the change in KMnO<sub>4</sub> concentration was estimated using 0.05 M oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>). On the basis of the change in KMnO<sub>4</sub>

concentration, the amount of carbon that oxidized was calculated. The amount of oxidized carbon was estimated to be the labile carbon (C<sub>L</sub>) and the difference between the TOC and C<sub>L</sub> was assumed to be non-labile carbon (C<sub>NL</sub>). The carbon pool index (CPI) was calculated based on changes in TOC in drained soils, as compared to the TOC content in the reference samples (CPI = TOC<sub>sample</sub>/TOC<sub>reference</sub>). The lability index (LI) was determined based on changes in the proportion of C<sub>L</sub> in the soil samples in the SOM accumulation stage (a reference site) and in drained soils (muck and muck-like) (LI = L<sub>sample</sub>/L<sub>reference</sub>, where L = C<sub>L</sub>/C<sub>NL</sub>). The LI and CPI indices were used to calculate the carbon management index (CMI) (CMI = CPI × LI × 100).

Hot-water extractable C was determined in air-dried soil samples, according to the method described by Sparling et al. (1998). Briefly, 4 g of air-dried soil was incubated with 20 mL of filtered water in a capped test-tube at 70 °C for 18 h. The tubes were shaken by hand at the end of incubation, and were then filtered through Whatman ME 25/21 ST 0.45-µm membrane filters (mixed cellulose ester). Hot-water soluble carbon (HWC) was measured on a Shimadzu 5000 TOC analyzer.

All analyses were performed in duplicate. All results are expressed on an oven-dry soil weight basis (drying temperature: 105 °C). Statistical analyses were conducted with Statistica v. 7.0. Pearson's linear correlations were used to assess the relationships between various organic carbon fractions.

## Results

The process of transformation of SOM (after drainage of organic soils) led to a decrease in TOC. The investigated soils in the SOM accumulation stage contained about 30% TOC (Table 1). In drained soils, especially muck-like soils, it dropped to approximately 5%; however, great variability in TOC content in the investigated soils should be noted. The mineralization of organic carbon compounds was also demonstrated by the narrowing C:N ratio, which dropped from about 11-14 in soils in the SOM accumulation stage to below 10 in muck-like soils. A drop in pH values was also indicative of the process of soil transformation. Soil processes intensified by



Table 1. General chemical properties and mineral fraction composition of the studied soils.

Sample no.	LOI [%]	TOC [%]	TN [%]	C:N	pH in KCl	CEC [cmol(+)kg <sup>-1</sup> ]	BS [%]	Sand [%]	Silt [%]	Clay [%]
Reference samples (ongoing process of SOM accumulation)										
1	73.93	32.06	2.99	10.72	6.53	86.63	71.83	18.73	72.78	8.49
2	48.19	24.18	1.75	13.82	7.18	82.90	82.63	59.78	36.15	4.07
3	50.27	28.18	2.23	12.64	6.26	89.29	77.15	22.64	67.83	9.53
4	69.18	31.33	2.76	11.35	5.58	89.56	72.31	13.95	76.32	9.73
Surface muck formations of drained soils (the first stage of transformation)										
5	74.34	33.01	2.35	14.05	5.03	104.45	66.30	27.92	66.66	5.42
6	77.98	33.10	2.23	14.84	5.50	159.98	72.00	16.09	78.34	5.57
7	41.80	16.44	1.56	10.54	4.99	92.15	53.99	33.89	51.64	4.47
8	36.90	14.34	1.18	12.15	5.77	84.48	70.41	91.32	8.00	0.68
Surface muck-like formations of drained soils (the second stage of transformation)										
9	13.97	7.74	0.71	10.90	5.24	52.12	63.55	83.80	14.62	1.58
10	10.75	4.38	0.50	8.76	5.87	38.56	61.61	20.33	75.04	4.63
11	8.93	3.59	0.44	8.16	6.54	16.59	63.84	96.19	3.76	0.05
12	9.99	5.86	0.55	10.65	5.10	19.17	19.65	87.32	11.61	1.07
13	6.21	2.68	0.28	9.57	5.24	10.87	28.26	94.56	5.36	0.08
14	25.83	9.21	0.95	9.69	5.62	55.34	65.30	95.23	4.56	0.21
Subsurface soil formations of drained soils										
15	66.88	29.82	1.80	16.57	6.15	146.48	78.56	31.83	63.51	4.66
16	61.78	31.34	1.69	18.54	6.14	129.42	87.02	36.44	58.15	5.41
17	22.38	9.03	0.84	10.75	5.28	78.15	58.80	41.08	55.80	3.12
18	24.30	13.36	0.83	16.10	5.58	66.28	68.92	87.44	11.32	1.24
19	34.97	18.61	1.07	17.39	6.09	86.62	77.60	73.16	24.70	2.14
20	21.71	8.63	0.74	11.66	6.36	60.42	79.81	94.85	4.89	0.26

LOI – loss-on-ignition; TOC – total organic carbon; TN – total nitrogen; CEC – cation exchange capacity; BS – base saturation; Sand – mineral particles of  $\phi$  2000-50  $\mu\text{m}$ ; Silt – mineral particles of  $\phi$  50-2  $\mu\text{m}$ ; Clay – mineral particles of  $\phi$  < 2  $\mu\text{m}$

aeration in drained soils led to the production of protons ( $H^+$ ) and soil acidification. The base saturation (BS) was higher in the soils in the SOM accumulation stage (72%-82%) and lower in drained soils. In muck-like soils BS was generally lower than 65% and in some cases as low as 20%-30%.

A quantitative distribution of humic and fulvic acids in the analyzed soils proves there was transformation of SOM (Table 2). In the soils in the SOM accumulation stage most of the carbon was accumulated in insoluble humus compounds (humins and particulate organic matter). Mean humic and

fulvic acids content in these soils accounted for 7.34% of TOC. In the surface soil formations of the muck soils the humic acids content increased 5-fold and fulvic acids content increased 4-fold, as compared to the reference samples. Transformation of SOM also caused an increase in the amount of "free" or labile humic compounds, defined as CH I. The content of humic compounds bound to cations (CH II) decreased in muck-like soils. The quantity of humic substances strongly bound to the mineral matrix (CH III) decreased only in muck soils. The quantity of CH and CF was strongly and positively correlated with TOC (Table 3).

Table 2. Content of humic acids, fulvic acids, humins, and hot water-extractable carbon.

	$\Sigma$ CH	$\Sigma$ CF	CH I	CH II	CH III	$\Sigma$ CH: $\Sigma$ CF	$\Sigma$ CHCF: Humins	Humins	HWC
	% of TOC		% $\Sigma$ CH					% of TOC	
Reference samples (ongoing process of SOM accumulation)									
min-max	3.3-6.3	1.9-3.6	22.3-32.5	20.6-32.5	35.0-56.9	1.6-1.8	0.05-0.11	90.11-94.80	0.8-1.5
MN	4.62	2.72	26.89	27.15	45.96	1.69	0.08	92.66	1.06
SD	1.32	0.69	5.23	5.68	8.93	0.07	0.02	2.01	0.29
Surface muck formations of drained soils (the first stage of transformation)									
min-max	15.8-29.5	8.3-15.1	32.6-36.5	22.5-33.1	30.4-44.9	1.6-3.0	0.35-0.71	58.52-74.21	1.2-1.7
MN	23.72	10.80	34.34	28.12	37.54	2.28	0.54	65.48	1.55
SD	5.87	2.94	1.92	4.55	6.37	0.71	0.17	7.24	0.22
Surface muck-like formations of drained soils (the second stage of transformation)									
min-max	19.5-28.3	9.8-15.2	25.0-40.9	19.3-30.5	32.7-51.6	1.9-2.2	0.42-0.77	56.55-70.65	0.6-1.5
MN	24.45	11.96	31.27	26.59	42.19	2.05	0.58	63.58	0.89
SD	3.56	1.85	5.48	4.08	7.44	0.13	0.13	5.26	0.35
Subsurface soil formations of drained soils									
min-max	17.8-37.2	11.6-26.7	21.1-41.1	17.4-30.3	37.4-59.4	0.8-2.3	0.42-1.77	36.07-70.54	1.2-2.7
MN	26.41	18.43	29.38	22.17	48.45	1.53	0.91	55.16	2.08
SD	7.89	6.96	7.20	4.28	7.21	0.49	0.50	12.94	0.60

MN – mean; SD – standard deviation; CH – humic acid; CF – fulvic acid; I – active humus compounds extracted with  $Na_4P_2O_7$  and  $Na_2SO_4$ ; II – humus compounds bound to cations educed during extraction with  $Na_4P_2O_7$ ; III – strongly bound humus compounds educed during extraction with NaOH; HWC – hot-water extractable carbon

Table 3. Linear correlation coefficients among soil properties (n = 20). Critical values of the correlation coefficient: 0.400 at the significance level of 0.05, and 0.543 at the significance level of 0.01.

	% of mineral matter		cmol(+) kg <sup>-1</sup>			g kg <sup>-1</sup>			ΣCHCF/Humins		g kg <sup>-1</sup>		
	Clay	TOC	TN	CEC	ΣCH I, II, III	ΣCF I, II, III	CH I	CH II	CH III	Humins	HWC	C <sub>L</sub>	
TOC	0.794												
TN	0.870	0.938											
CEC	0.556	0.853	0.709										
ΣCH	0.150	0.599	0.360	0.798									
ΣCF	0.177	0.568	0.335	0.799	0.957								
CH I	0.153	0.582	0.360	0.782	0.988	0.934							
CH II	0.186	0.621	0.393	0.786	0.981	0.925	0.986						
CH III	0.111	0.564	0.313	0.777	0.969	0.948	0.924	0.909					
Humins	0.878	0.947	0.969	0.687	0.311	0.281	0.296	0.345	0.279				
ΣCHCF/Humins	-0.479	-0.571	-0.643	-0.372	0.045	0.094	0.070	0.014	0.045	-0.701			
HWC	0.688	0.798	0.829	0.650	0.503	0.491	0.541	0.551	0.405	0.744	-0.383		
C <sub>L</sub>	0.799	0.895	0.922	0.652	0.384	0.363	0.369	0.411	0.355	0.909	-0.551	0.666	
C <sub>NL</sub>	0.788	0.999	0.932	0.860	0.610	0.578	0.592	0.631	0.575	0.942	-0.568	0.801	0.881

C<sub>L</sub> – fraction of organic matter oxidized by KMnO<sub>4</sub>; C<sub>NL</sub> – non-oxidizable fraction of organic matter

The CH:CF ratio of all 3 humus fractions was related to the degree of SOM transformation (Table 2). In soils in the SOM accumulation stage this ratio was lower than in muck soils. In the reference soils, as well as in muck soils, the humic type of humus (CH:CF >1.5) dominated; however, in muck-like soils, a drop in the CH:CF ratio was observed, and also fulvic-humic (CH:CF 1.0-1.5) and humic-fulvic (CH:CF 0.5-1.0) types of humus were observed. This indicates that when the muck-forming process was advanced there were less humic acids in the soil.

The degree of humification in the soils in the SOM accumulation stage was very low (ΣCH and ΣCF <10%). Drained soils had a high (ΣCH and ΣCF between 30% and 40%), and in some samples a very high (ΣCH and ΣCF >40%) degree of humification (Table 2). Consequently, the content of humins was the highest in the soils in the SOM accumulation stage, and systematically decreased as SOM transformation progressed. The soils in the SOM accumulation stage contained more than 90% humin fraction in TOC, whereas drained soils contained less than 70% (Table 2). Humin content was positively correlated with TN (Table 3, Figure 1a) and TOC

content (Table 3). Although the clay content was low in the studied soils, a strong positive correlation between humin content and clay content was also observed (Table 3, Figure 1b). The lowest ΣCHCF:humins ratio was observed in the soils in the SOM accumulation stage (Table 2). Drainage of soils caused a significant increase in this ratio, almost 7-fold in the surface horizons of muck soils and 11-fold in muck-like soils.

The above data were confirmed by the results of organic matter's susceptibility to oxidation (Tables 3 and 4). The organic carbon fraction content, which is not susceptible to oxidation (C<sub>NL</sub>), was positively correlated with the humin content (Table 3, Figure 1c) and other humus fractions (Table 3). The C<sub>NL</sub> fraction content also had a significant positive correlation with TOC content (Table 3). The C<sub>L</sub> fraction content was the highest in muck soils (Table 4).

TOC and non-labile carbon (C<sub>NL</sub>) content decreased as SOM transformation progressed (Table 4). The lability of carbon (L) increased 2-fold in muck soils. In muck-like soils L was lower. The CPI and LI were higher in muck soils than in muck-like soils, as



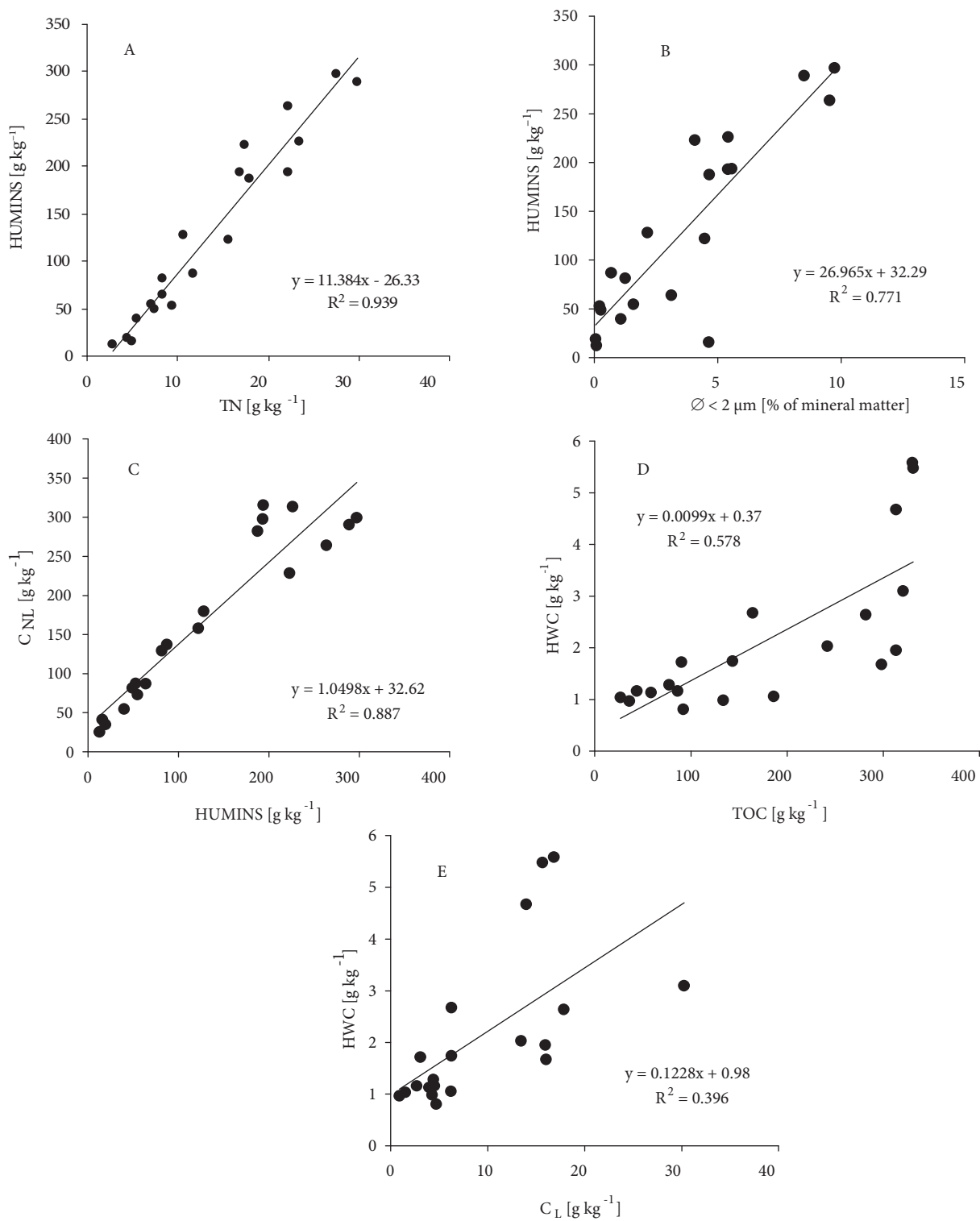


Figure 1. Linear regression of some soil properties.

Table 4. Labile ( $C_L$ ) and non-labile ( $C_{NL}$ ) carbon and indices for the soils studied (only for soil samples at a depth of 0-20 cm).

Soils	n	$C_L$	$C_{NL}$	TOC	L	CPI	LI	CMI	HWC
		g kg <sup>-1</sup>							g kg <sup>-1</sup>
Accumulation stage (reference)	4	29.96	259.42	289.38	0.115	–	–	100.00	3.11
Muck soils	4	51.84	190.39	242.23	0.272	0.837	2.37	198.37	3.87
Muck-like soils	6	9.19	46.58	55.77	0.197	0.193	1.71	33.00	1.44

n – number of samples;  $C_L$ ,  $C_{NL}$ , and TOC are mean values of analyzed samples; L (Lability of carbon) =  $C_L/C_{NL}$ ; CPI (Carbon Pool Index) =  $TOC_{sample}/TOC_{reference}$ ; LI (Lability Index) =  $L_{sample}/L_{reference}$ ; CMI (Carbon Management Index) =  $CPI \times LI \times 100$

a result of lower TOC and labile carbon content. In muck soils an increase in CMI was observed. Intense transformation of SOM in the case of muck-like soils resulted in a considerable decrease in CMI, when compared with the reference soils.

The quantity of HWC in TOC increased in drained soils, as compared to the reference soil samples (Table 2); however, these changes were observed only in surface horizons. In subsurface mucks the HWC content approximated most closely the content of HWC in untransformed soils. Hot-water extractable carbon content was positively correlated with TOC and TN (Table 3, Figure 1d). A strong positive correlation was observed between HWC content and oxidizable carbon fraction content ( $C_L$ ) (Figure 1e).

## Discussion

The process of organic matter transformation initiated by dewatering leads to the mineralization of organic carbon compounds, the release of CO<sub>2</sub> to ambient air, and a drop in TOC content. Situated at higher altitudes in the landscape, muck-like soils are subjected to more pronounced lowering of the groundwater level and greater aeration, which in turn intensifies organic matter mineralization and leads to a substantial decrease in TOC content. This process should be regarded as very negative, as it decreases the sequestration of carbon in the soil. It should also be noted that the C:N ratio in the investigated soils was lower than in low-moor peats (Okruszko 1993). Generally, in low-moor peats the C:N ratio is about 20, whereas in high-moor peats it can be as high as

55. The organic matter of the studied soils was well decomposed in the accumulation stage. Drainage caused further transformation of organic matter and changes in the C:N ratio. Low pH is associated with the activation of mobile humus compounds, a decrease in the adsorbing capacity of soil (CEC in Table 1), and leaching of alkaline cations. This is especially evident in muck-like soils.

The chemical fractionation used in the present study is a technique suitable for the study of SOM composition (Duchaufour 1983) and has been widely used in recent years (Fernandez et al. 2001; Sánchez-Marañón et al. 2002; Zancada et al. 2003). It facilitates extraction of humus compounds based on their solubility. Drainage of organic soils caused an increase in the solubility of humus compounds. Consequently, in drained muck soils, the CH content and CF content was higher than in the reference soils. The potential lability of carbon also increased. An increase is particularly noted in the 'free' least bound humic fraction (CH I). Additionally, as it was observed by Orlov (1998), increased biological activity that occurred in the surface of the soil probably promoted formation of alkali-soluble humic substances; therefore, the labile forms content in SOM increased.

Considering the CH:CF ratio, organic soils differ from mineral soils (which are more thoroughly investigated). In sandy podzolic soils (Podzols), the CH:CF ratio is usually below 1.0, while in fertile Chernozems it exceeds 1.0 and is often as high as 2.0-2.5 (Kononova 1966; Stevenson 1994). In organic soils, this ratio is indicative of the maturity and

stability of SOM. A CH:CF ratio about or below 1.0 indicates a significant supply of plant debris, as fulvic acids are the first product of the humification process. Higher fulvic acid content is also a measure of the content of the soluble fraction of TOC. Fresh plant debris is continuously transported to soils in the SOM accumulation stage; therefore, the CH:CF ratio is lower than in the case of mucks. Generally, a CH:CF ratio in excess of 1.0 is beneficial, indicating that organic matter is stable and mature, and that permanent bonds with the mineral soil phase dominate over mobile formations, which are easily transported inside the soil profile (Kononova 1966). Yet, with regard to organic soils, a CH:CF ratio above 3.0 is not beneficial, as it is indicative of aged organic matter and the absence of fresh plant debris (Okruszko 1993). It should be noted that the soils examined in the present study had such a high CH:CF ratio (Table 2). On the other hand, in muck-like soils, considered to be 'degraded organic soils', the considered ratio is low. This indicates that muck-like soils can have the beneficial character of SOM, and that CH prevails over CF; however, other aspects of these soils—low TOC and CMI—indicate a lack of or low carbon sequestration capacity, which suggests that drainage is negative.

Moreover, environmental factors ought to be mentioned, as drained soils can retain less water and cannot protect against floods. Although the volume of fresh organic matter inflow in these soils was similar to that observed in the muck soils, as all the drained soils were covered by grassland vegetation, they contained less SOM and were subject to intense transformation of complex humus compounds into simpler forms.

In addition to specific humus compounds (humic acids, fulvic acids, and humins), organic matter also comprises non-specific compounds (carbohydrates, amino acids, lignin, tannins, and others) that may not be extractable and are contained in humins (Simpson et al. 2007). In contrast to specific humus compounds, some non-specific humus compounds are susceptible to rapid microbial decomposition (Stevenson 1994). Therefore, the decrease in the humin content in the progressive stages of SOM transformation was determined by its conversion into simpler forms in the present study. The content of humic compounds

in TOC is also defined by the degree of humification, expressed as the sum of humic and fulvic acids in TOC (Kononova 1966). With the progression of humification in organic soils, nitrogen is accumulated in the complex humic compounds in the humin fraction (Okruszko 1993). In the soils in the SOM accumulation stage, the process of organic matter humification was slow and involved primary humification, referred to as the degree of decomposition in peats. In drained soils, the humification process involved primary humification during organic matter accumulation and secondary humification, which took place beginning with the start of the muck-forming process. As such, the degree of humification of muck and muck-like soils was much higher than in soils in the SOM accumulation stage.

According to Benites et al. (2000), the  $\Sigma$ CHCF:humins ratio provides information on soil genesis. It indicates where carbon is accumulated in the soil profile and identifies the soil zones where carbon is translocated. In the present study the increases in this ratio observed in drained soils confirm the above discussion. The process of SOM transformation increased the solubility of humus compounds. The content of humic and fulvic acid fractions increased, and the decomposition of mainly non-specific humus compounds caused a decrease in the humin fraction.

The high  $C_L$  fraction content in the soils in the SOM accumulation stage was affected by the supply of fresh plant debris. A decline in the content of humin and the  $C_{NL}$  fraction in the progressive stages of SOM transformation was the result of organic matter transformation and conversion of organic compounds into simpler forms. When organic soil is drained the oxidation processes are rapid and transformation of complex organic compounds may occur. Soil organisms contribute to a decrease or increase in humus lability, depending on their enzymes (Wolters 2000). The initiation of the muck-forming process led to a certain increase in  $C_L$  content and a drop in  $C_{NL}$  content (Table 4), indicating that complex humus compounds that make up  $C_{NL}$  were transformed into simpler compounds, forming  $C_L$  in drained soils. A greater increase in carbon lability in surface horizons than in sub-surface horizons was

caused by more intense organic matter transformation in the surface layers. The reference soils were marked by a high percentage of complex, untransformed organic compounds (humins and  $C_{NL}$ ). The strong relationship between  $C_{NL}$  and the humin fractions shows that  $C_{NL}$  consisted of the carbon fraction that was stabilized due to chemical or physical association within the soil mineral matrix (Conteh et al. 1999).

The initiation of the muck-forming process caused intense microbiological changes in SOM. Firstly, easily decomposable components of organic matter were mineralized (lower TOC), and then more resistant organic compounds were transformed into less complex compounds, leading to an increase in labile carbon content ( $C_L$ ) and lability (L). The drop in the discussed values in the muck-like soils was due to a lower TOC content—the result of advanced SOM mineralization and the initiation of acidification and leaching processes. It was supposed that the content of the labile carbon fraction is largely determined by the land use system (Blair et al. 1995) and, consequently, by the processes taking place in the soil. The CMI accounts for both quantitative ( $C_L$ ,  $C_{NL}$ , TOC) and qualitative (LI, CPI) values. As more carbon is lost from a soil, it becomes more difficult to rehabilitate such soil and the CPI is a measure of this (Blair et al. 1995). In our muck-like formations this index implies that the soil was depleted of total carbon and that reclamation would be difficult. In the muck soils the CPI was higher and the changes in total carbon were

less intense than in muck-like soil. The process of organic matter transformation increased the CMI at the initial stage, while intense and prolonged SOM transformation, as well as soil drying, led to a drop in the CMI. A CMI below 100 indicates negative processes in the soil.

HWC is a measure of labile C (Sparling et al. 1998). In the present study it generally increased with TOC; however, when the portion of HWC in TOC is taken into consideration, subsurface mucks and untransformed soils were the most similar, suggesting that the intensity of the microbial processes was similar. More intensive microbial activity occurred in the mucks and muck-like formations.

Drainage of organic soils causes mineralization of SOM and the release of a greenhouse gas— $CO_2$ —to the atmosphere. As a consequence, the role of SOM in immobilization of biogens is lost, and the environment and crops may become polluted. Following drainage, organic soils cease being geochemical barriers for water in agricultural land.

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