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Carbon and nitrogen fractions in drained organic soils

Frakcje węgla i azotu w odwodnionych glebach organicznych

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Abstract

Pedological studies were carried out in the upper course of the Liviec River involving laboratory analyses of three profiles of hemic muck organic soil. The objective was to evaluate the basic properties (pH, crude ash content and carbon and nitrogen content) and to determine the speciation of carbon and nitrogen based on the sequential extraction with a neutral reagent (0.25M KCl) and two-stage acid hydrolysis at different concentrations of hydrogen ions (0.25M H_2SO_4 and 2.5M H_2SO_4).

The muck horizons, in relation to the peat horizons, had a higher content of ash and a lower concentration of carbon and lower carbontonitrogen ratios. The reduction of acidity in the examined soil had a significant impact on a higher proportion of mineral nitrogen forms. The moorshing process caused by desiccation of the examined soil contributed to an increase in the proportion of soluble organic matter forms (extracted with 0.25M KCl) and easily hydrolysing organic forms (extracted with hydrolysis in 0.25M H_2SO_4).

Streszczenie

Badania gleboznawcze prowadzono w dolinie górnego biegu rzeki Liwiec. Badaniami laboratoryjnymi objęto trzy profile gleb organicznych hemowo-murszowych. Celem ich była ocena podstawowych właściwości (pH, zawartość popiołu surowego oraz C i N), a także określenie specjacji węgla i azotu, na podstawie sekwencyjnej ekstrakcji odczynnikiem obojętnym (0,25M KCl) oraz dwuetapową hydrolizą kwaśną, przy różnym stężeniu jonów wodorowych (0,25M H_2SO_4 i 2,5M H_2SO_4).

Poziomy murszowe, w stosunku do torfowych, charakteryzowały się większą zawartością popiołu, mniejszą węgla i niższymi wartościami stosunku węgla do azotu. Zmniejszenie zakwaszania badanych gleb istotnie wpływało na większy udział mineralnych form azotu. Proces murszenia spowodowany odwodnieniem badanych gleb, przyczynił się do zwiększenia udziału rozpuszczalnych form materii organicznej (wyekstrahowanych 0,25M KCl) oraz organicznych form łatwo hydrolizujących (wydzielonych hydrolizą w 0,25M H_2SO_4).

1. INTRODUCTION

Total or partial anaerobic conditions generated by high levels of ground waters on hydrogenic habitats are a prerequisite for peat accumulation (an incomplete degradation of organic matter in peat forming plants). It is estimated that approximately 90% of peatbogs on non-forested areas have been drained in Poland [Dembek et al. 2000]. The drainage was mainly due to anthropogenic causes, land improvement and hydraulic engineering activities (including river control) as well as industrial investments [Ilnicki 2002, Piaścik and Gotkiewicz 2004, Jurczuk 2011, Ostrowski and Dembek 2012]. Drainage inhibits the accumulation of organic matter and introduces the decline phase in the soil on peatbogs, during which the mineralisation of organic matter under aerobic conditions and its negative balance predominate. The simultaneous moorshing process, which is characterised by intensive biological, physical and chemical transformations of the parent peat, results in the formation of muck organic soil [Okruszko 1993, Systematyka gleb Polski 2011]. The consequences of organic matter mineralisation during the moorshing process (the release of nutrients and gas emissions) extend outside the soil environment and contribute to an intensification of global phenomena such as greenhouse effects and water eutrophication [Sapek 2010, Łachacz 2012].

The organic matter transformations during the moorshing process are naturally associated with carbon and nitrogen speciation. Because of the high concentrations of biogenic elements, especially carbon and nitrogen, the organic soil types constitute an important reservoir of these elements and formastage of their biogeochemical cycles in the environment [Okruszko 1993, Sokołowska et al. 2005, Kalembasa and Becher 2009, 2010]. Studies on the nature of carbon and nitrogen transformations in organic soils are important in the context of consequences of organic matter mineralisation and a current issue in the process of their restoration.

The objective of the studies was to determine carbon and nitrogen speciation in the organic soil exposed to the moorshing process based on a sequential analysis with a neutral reagent and two-stage acid hydrolysis at different concentrations of hydrogen ions.

2. MATERIALS AND METHODS

The field studies were carried out on the most important peatbog area in Wysoczyzna Siedlecka (the Siedlecka Highland) in the upper course of the Liwiec River (Fig. 1). These wetlands are located on a flood terrace and are mainly fluviogenous and soligenous. They are composed of magnocaricetum peat, rush peat and alder peat [Dembek et al. 2000, Dembek 2000]. The studies were conducted on three profiles of hemic muck soil from the first flood terrace (Fig. 1) formed from magnocaricetum and rush peat

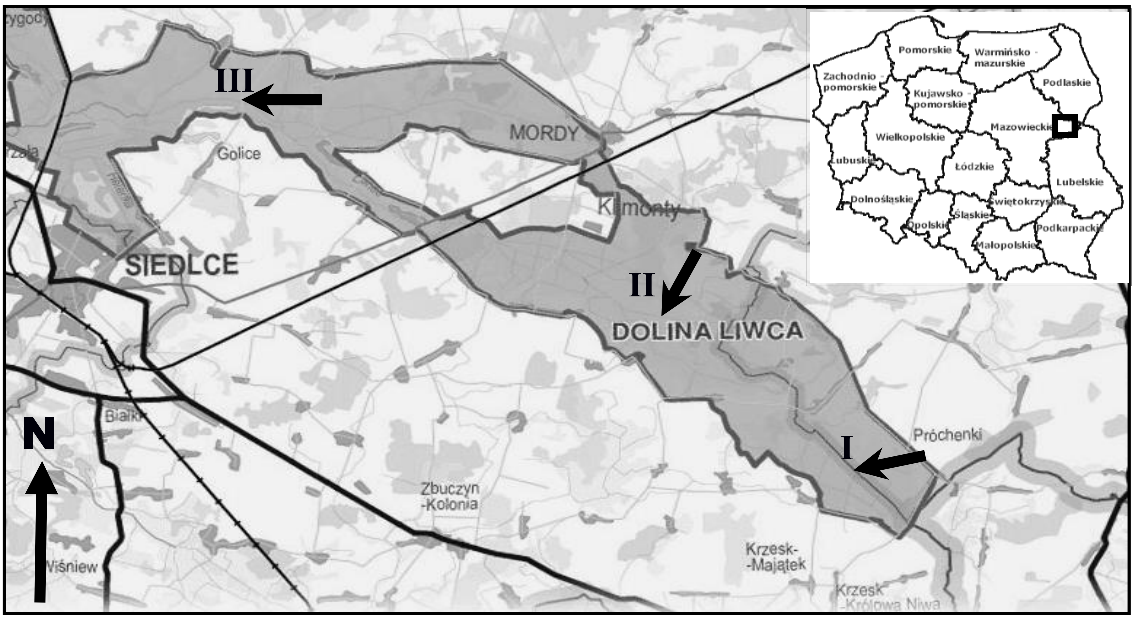

Fig. 1. Locations of soil pits.

with the following sequence of genetic horizons: M1-M2-Oe1-Oe2 [Systematyka gleb Polski 2011]. Ground water was located at the level of 85–95 m. The collected samples (n = 12) were dried (at 40°C), comminuted and sieved through a 2mm sieve. The content of ash was measured by weighing after combustion in a muffle furnace (at 500°C). Total carbon (TC) and total nitrogen (TN) were determined on a Series II 2400 auto-analyser (Perkin Elmer, TCD) with acetanilide as the standard material.

The sequential extraction (in three repetitions) of carbon and nitrogen compounds (Table 1) was carried out according to the method described by Kalembasa [1995] with the following extraction solutions (m/v = 1/25):

- 0.25M KCl, extraction at room temperature for 3 hours;
- 0.25M H_2SO_4, hydrolysis at boiling temperature of the mixture under a water reflux condenser for 3 hours; and
- 2.5M H_2SO_4 (as specified above).

After the extraction and hydrolysis procedures, the solution was clarified with centrifugation (4000 rpm) and filtering through a cellulose filter. The content of carbon and nitrogen in the solutions was determined with the oxidative-titrating method [Kalembasa 1991] and Kjeldahl's method [Kalembasa 1995], respectively.

The statistical calculations were performed with STATISTICA 10 PL software (Statsoft, Tulsa, USA). The following descriptive statistics were used: arithmetic mean, minimum value, maximum value, standard deviation and variation coefficient. The relations between the selected characteristics were expressed with the simple correlation coefficient (r).

3. RESULTS AND DISCUSSION

The presence of hemic muck organic soil with well-developed muck horizons (sod – M1 and sub-sod – M2) was reported on the examined area [Systematyka gleb Polski 2011]. The selected morphological parameters and properties of the examined soil are presented in Table 2.

The advancement of the moorshing process was assessed as medium (Mt II), which was indicated by the characteristics of the muck horizons and their extent in the profile up to 25 cm [Okruszko 1993, Ilnicki 2002]. The differentiation of the morphological parameters of the examined soil due to the moorshing process was confirmed with the results of the laboratory analyses with the muck horizons having a significantly higher content of ash (2–3 times

Table 1. Forms of elements and methods of their extraction

Extraction reagent	Form of element (operational) and method of extraction	
	Carbon	Nitrogen
0.25M KCl	Not determined	N_{MIN} nitrogen in mineral compounds ($N\text{-}NH_4$ + $N\text{-}NO_x$), distillation from the extract after alkalisation (MgO) and reduction (with Devard's mixture); N_{KCL}, determined in the extract after mineralisation of the solution; N_{OR} – soluble organic nitrogen, $N_{OR} = N_{KCl} - N_{MIN}$
0.25M H_2SO_4	$C_{OŁH}$ – easily hydrolysing organic carbon	$N_{OŁH}$ – easily hydrolysing organic nitrogen measured after hydrolysis and mineralisation of the solution
2.5M H_2SO_4	C_{OTH}– difficult to hydrolyse organic carbon	N_{OTH} – difficult to hydrolyse organic nitrogen measured after hydrolysis and mineralisation of the solution
Post-extraction residues	C_{ONH} – non-hydrolysing organic carbon, $C_{ONH} = TC - (C_{OR}+C_{OŁH}+C_{OTH})$	N_{ONH} – non-hydrolysing organic nitrogen, $N_{ONH} = TN - (N_{KCl}+N_{OŁH}+N_{OTH})$

Table 2. Selected properties of the examined soil profiles

Profile, genetic horizon, depth	Characteristics of genetic horizons [Systematyka gleb Polski 2011]	pH_{KCl}	Crude ash	TC	TN	TC:TN
			% of DM			
Profile I						
M1 (0–10 cm)	Muck, fine crumb structure	6.31	28.2	36.8	3.19	11.5
M2 (10–25 cm)	Muck, medium crumb structure	6.30	30.5	37.7	3.11	12.1
Oe1(25–50 cm)	Magnocaricetum peat, haemic (R2)	6.17	14.9	48.3	3.19	15.2
Oe2 (50–85 cm)	Rush peat, haemic (R2)	5.98	10.2	51.8	3.25	15.9
Profile II						
M1 (0–8 cm)	Muck, fine crumb structure	5.53	27.3	35.9	2.88	12.5
M2 (8–22 cm)	Muck, medium crumb structure	5.92	28.6	36.6	2.87	12.7
Oe1 (22–50cm)	Rush peat, haemic (R2)	5.96	9.94	49.5	3.11	15.9
Oe2 (50–95 cm)	Rush peat, haemic (R2)	5.77	10.5	49.8	3.19	15.6
Profile III						
M1 (0–10 cm)	Muck, very fine crumb structure	6.28	23.1	39.9	3.51	11.4
M2 (10–25 cm)	Muck, fine crumb structure	5.98	28.3	39.4	3.39	11.6
Oe1 (25–55 cm)	Magnocaricetum peat, haemic (R2)	5.97	14.3	48.3	3.04	15.9
Oe2 (55–90 cm)	Rush peat, haemic (R2)	5.96	14.5	50.4	3.08	16.4

higher), significantly lower content of carbon and lower TC:TN ratios than the peat horizons. The concentration of nitrogen was less variable within profiles. The reported properties are typical of drained organic soil where anaerobic conditions in the roof prompt mineralisation of the organic matter and a release of carbon in a completely oxidised form (CO_2) into the atmosphere. The content of nitrogen oscillates around the "initial" level (i.e. before the protective action of water ceased) or it may be secondarily accumulated (concentrated) in the muck horizons. On the background of transformations of biogenic elements, the carbontonitrogen ratio becomes narrowed in the muck mass in comparison with the parent peat. The TC:TN values (11.4–16.4) determined for the examined soil horizons are typical of eutrophic soil on low-moor peatlands. They may indicate their over-desiccation as well as biological activity and a large degree of organic matter transformation caused by mineralisation and humification processes [Okruszko 1993, Ilnicki 2002, Kalembasa and Becher 2009, 2010].

The measurement of pH (in a 1M KCl solution) demonstrated a low diversification of this parameter both between the examined soil profiles and within the individual horizons of the soil profiles. The recorded values (from 5.53 to 6.31) for these horizons, according to the recommendations by Okruszko [1993] for the organic soil, allow for the horizons to be classified as moderately acidic. However, our studies have not confirmed the view reported in the literature on the lower acidity of peat in relation to muck, which is mainly due to eluviation of alkaline cations deep into the soil profile [Okruszko 1993, Ilnicki 2002, Piaścik and Gotkiewicz 2004, Bogacz 2005].

The differentiation of profile soil properties under the influence of the moorshing process was also evidenced by carbon and nitrogen speciation. It is presented as the proportion of these elements in the sequenced fractions in relation to their total content (Tables 3 and 4).

The proportion of hydrolysing carbon (extracted with the two-stage acid hydrolysis) in the individual soil horizons ranged from 19.3% to 36.9% of its total content and was significantly higher in the muck horizons than in the peat horizons. The process of moorshing contributed mainly to an increase in the proportion of carbon in the easily hydrolyzing forms ($C_{OŁH}$ – extracted with 0.25M H_2SO_4) whose proportion in the muck horizons was approximately two times higher than in the peat horizons. For carbon in the difficult-to-hydrolyse forms (C_{OTH}), the differences between the muck and peat horizons were significantly smaller.

The extraction with 0.25M KCl of the individual soil horizons yielded nitrogen in the mineral (N_{MIN}) and soluble organic (N_{OR}) forms. The proportion of nitrogen in the mineral forms was very variable and ranged from 0.55% to 2.32%, being slightly higher in the muck horizons. The soluble organic nitrogen fractions (N_{OR}) constituted a significantly higher (approximately two times) proportion in the muck horizons as compared to the peat horizons. The potential mobility of organic and mineral nitrogen forms that were prone to extraction with a potassium chloride solution had an additional impact on the differentiation of this element in the soil profile. In other studies on shallow organic soil, Kalembasa and Becher [2009] found that the proportion of soluble organic nitrogen constituted from 0.21% to 0.98% of its total content.

Table 3. Proportion (%) of organic carbon fractions in the muck and peat horizons of the examined organic soil profiles

Statistic	C-hydrolysed			C_{ONH}
	Σ	$C_{OŁH}$	C_{OTH}	
Muck horizons (M)				
Mean	33.8	22.0	11.8	66.2
Range	31.1–36.9	18.7–25.4	9.54–14.0	63.1–68.9
Standard deviation	1.92	2.78	1.59	1.92
Variability coefficient (%)	5.67	12.6	13.4	2.90
Peat horizons (Oe)				
Mean	21.0	11.4	9.61	79.0
Range	19.3–25.1	9.77–15.6	9.12–10.1	74.9–80.7
Standard deviation	2.08	2.19	0.331	2.08
Variability coefficient (%)	9.92	19.2	3.45	2.64

Table 4. Proportion (%) of nitrogen fractions in the muck and peat horizons of the examined organic soil profiles

Miara statystyczna	N_{MIN}	N_{OR}	N - hydrolysed			N_{ONH}
			Σ	$N_{OŁH}$	N_{OTH}	
Muck horizons (M)						
Mean	1.44	1.42	69.8	36.8	33.0	27.3
Range	0.71–2.32	1.02–1.71	65.5–74.7	30.9–41.7	27.2–40.0	22.9–31.8
Standard deviation	0.63	0.29	3.67	3.78	4.64	3.71
Variability coefficient (%)	43.9	20.8	5.26	10.3	14.1	13.6
Peat horizons (Oe)						
Mean	1.04	0.740	53.7	20.3	33.4	44.5
Range	0.55–1.61	0.56–0.94	48.6–57.5	17.0–26.6	28.2–38.2	40.8–49.4
Standard deviation	0.38	0.16	3.30	3.74	3.62	3.21
Variability coefficient (%)	36.2	21.8	6.15	18.4	10.8	7.22

Organic compounds extracted with a neutral salt solution (KCl) represent the so-called dissolved organic matter that may contain amino acids, amino sugars, protein and low-molecular humic acid fractions [Kalbitz and Geyer 2002, Paul and Williams 2005]. Free amino acid forms are rapidly degraded and constitute the most important source of mineral nitrogen [Paul and Clark 2000].
The proportion of hydrolysing nitrogen, similar to carbon, was higher in the muck horizons than in the peat horizons, whereas the process of moorshing contributed to an increase in the proportion of this element only in the easily hydrolyzing organic forms ($N_{OŁH}$).
In numerous studies on the transformation of organic matter in peat soil that occurs after its drainage, it has been demonstrated that the process of moorshing transforms peat by increasing a potential availability of nitrogen, i.e. by increasing the quantity of nitrogen in organic complexes prone to mineralisation. Throughout this process, the proportion of these nitrogen forms declines, until the pool of nitrogen available to plants becomes depleted [Okruszko 1993 , Maciak 1993, Piaścik and Gotkiewicz 2004].
In general, studies on the organic compounds of soil nitrogen consist of their hydrolysis with mineral acids or bases and the quality analysis of hydrolysates [Sowdenet al. 1977, Schulten and Schnitzer 1998 , Gonet 2003]. With acid hydrolysis, nitrogen in the humic substances and the microbial proteins passes into the solution [Kalembasa 1995]. Sowden et al. [1977] reported that in different soil types, the proportion of hydrolyzing nitrogen was 84%–89% of its total content (after hydrolysis in 6M HCl) including: 33%–42% of amino acid nitrogen, 4.5%–7.4% of amino sugar nitrogen and 18%–32% of ammonia nitrogen. The studies by Maciak [1988, 1993, 1995] and by Maciak and Gotkiewicz [1983] demonstrated that a diverse proportion of nitrogen hydrolysed in 6M HCl and depended on the type of peat and degree of its decomposition as well as the method of its utilisation, yet most often in a decreasing proportion with the depth of sampling.
As shown by the correlation coefficient (Table 5), the proportion of hydrolysing carbon and nitrogen forms (except for N_{OTH}) and soluble organic nitrogen is closely related to the moorshing process. Significant positive correlations were found between the proportion of extracted forms of these elements and the content of crude ash, i.e. the parameter that is assumed to increase with moorshing process [Okruszko 1993, Ilnicki 2002]. In addition, a reduction in the content of dry matter (expressed as TC), which is typical of the moorshing process, and the narrowing of the carbon to nitrogen ratio (and possibly a higher biological activity) favour an increase in the proportion of carbon and nitrogen in the hydrolysing forms although they cause a decrease in the non-hydrolysing forms. The highest values of correlation coefficients were determined for the properties of the examined soil profile that were variable in the moorshing process (ash content, TC and TC:TN) and for the proportion of carbon and nitrogen in the easily-hydrolysing forms ($C_{ŁH}$ and $N_{ŁH}$). It was statistically proven that a reduction in acidity had a significant positive impact on the proportion of nitrogen in the mineral forms.

4. CONCLUSIONS

In the valley of the upper course of the Liwiec River, on the first flood terrace, organic haemic muck soil at an intermediate stage of moorshing was found and was formed on rush and magnocaricetum peats with a depth of up to 100 cm. The presented studies indicate a significant degree of eutrophy of the examined soil profiles, substantial oxygenation of the superficial soil horizons, a

Table 5. Linear correlation coefficients between the properties of the examined soil profiles and selected carbon and nitrogen fractions

Parameter	pH_{KCl}	Crude ash	TC	TN	TC:TN
$C_{OŁH}$	0.227	0.864	-0.921	0.062	-0.929
C_{OTH}	0.427	0.781	-0.709	-0.024	-0.690
$C_{OŁH}+C_{OTH}$	0.294	0.927	-0.959	0.048	-0.962
C_{ONH}	-0.294	-0.927	0.959	-0.048	0.962
N_{MIN}	0.859	0.417	-0.343	0.488	-0.508
N_{OR}	0.052	0.867	-0.921	-0.417	-0.760
$N_{OŁH}$	0.221	0.861	-0.909	0.146	-0.949
N_{OTH}	-0.407	-0.023	-0.005	-0.644	0.212
$N_{OŁH}+N_{OTH}$	0.049	0.878	-0.940	-0.133	-0.886
N_{ONH}	-0.097	-0.892	0.949	0.117	0.900

Critical values: (n=12): 0.564 (α = 0.05); 0.746 (α = 0.01) high degree of organic matter transformation and a relatively high biological activity reflected in the predominance of organic matter mineralisation and the decline of these organic residues. The evident consequence of the moorshing process is a higher proportion of carbon and nitrogen in the soluble organic matter forms (extracted with 0.25M KCl) and in the easily hydrolyzing organic forms (extracted with hydrolysis in 0.25M H_2SO_4) with a lower proportion in the non-hydrolysing organic forms. Lower acidification of the examined soil profiles exerts a significant impact on a higher proportion of nitrogen in the mineral forms.

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