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PROPERTIES OF ORGANIC MATTER IN CHOSEN SOILS FERTILIZED WITH SEWAGE SLUDGE

The properties of organic matter from Dystric Arenosols and Stagnic Luvisol fertilized with sewage sludge produced in biological-chemical treatment plants have been examined. Organic matter (fractions: post-decalcination, bitumins, fulvic acids, humic acids, humines) has been fractionated and humic acid properties (elemental composition, UV, VIS, FT IR spectra) have been determined. Organic matter from the soils has been characterized by similar per cent of carbon and nitrogen and a similar humification level in the separated fractions. The most humified and matured acids (i.e. with higher proportion of aromatic groups, lower content of aliphatic side-chains, and higher condensation of aromatic rings) have been found in Stagnic Luvisol.

1. INTRODUCTION

The soil and weather conditions in Poland do not favour the humus accumulation in the agriculturally utilized soils. A high per cent of light soils in arable land along with their aerobic character (associated with negative water balance and warmer climate) contribute to the mineralization of organic matter introduced into the soil [1], [2]. The surplus of cereals in the Polish croplands as well as insufficient organic and mineral fertilization also accompany the unfavourable organic matter balance in soils [3], [4]. Agricultural utilization of sewage sludge may become its appropriate utilization (at the rational applying of this sludge with no harm to natural environment) and can improve the negative balance of organic matter in soils [4].

The present study has been aimed at evaluating the properties of organic matter from humus horizons of the soils fertilized with sewage sludge.

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2. MATERIAL AND METHODS

The soil samples were collected in October 2007 from the humus horizons of three types of soil fertilized with sewage sludge (a year after fertilization at the rate of $15 \text{ t} \cdot \text{ha}^{-1} \text{ d.m.}$). The sludge was produced in mechanical-biological municipal wastes treatment plants in Łuków and Węgrów. The following soils were tested:

[A] Dystric Arenosols developed from water-glacial sand (Siedlce Upland); sand (%) = 85; silt (%) = 11; clay (%) = 4; organic matter (%) = 1.94; C/N = 9.1; $\text{pH}_{\text{KCl}} = 4.95$.

[B] Dystric Arenosols developed from water-glacial sand with loam underneath at the depth of 1 m (Węgrów Depression); sand (%) = 88; silt (%) = 9; clay (%) = 3; organic matter (%) = 1.73; C/N = 9.7; $\text{pH}_{\text{KCl}} = 7.00$.

[C] Stagnic Luvisol developed from loam (Łuków Plain); sand (%) = 44; silt (%) = 50; clay (%) = 6; organic matter (%) = 2.43; C/N = 10.1; $\text{pH}_{\text{KCl}} = 6.43$.

In the above soil material, organic matter fractions were subjected to sequential extraction (in 3 replications) according to Shnitzer method [5]: decalcination ($0.05 \text{ M H}_2\text{SO}_4$) → extraction of bitumens (with hexane and ethanol mixture in automated Soxtherm extractor) → extraction of humus substances (0.1 M NaOH) → separation into humic and fulvic acids as a result of acidification.

The content of organic carbon compounds in separated fractions was determined by means of oxidation-titrimetric method, while that of total nitrogen – by applying Kjeldahl method. The levels of carbon and nitrogen in bitumens were analyzed with auto-analyzer, whereas carbon and nitrogen concentrations in humic acids and humines were calculated based on the difference between both determinations.

In the separated and purified humic acids (HA) the following parameters were determined by means of Shnitzer method [5]:

- Ash content after soil combustion at $550 \text{ }^\circ\text{C}$.
- C, H, and N content in an auto-analyzer, Series II 2400 (Perkin Elmer) equipped with a thermal conductivity detector (TCD) and acetanilite as a reference material. The elemental composition (oxygen content was calculated from the difference) was compared to absolutely dry and ashless mass of the samples. The ratios (H/C, O/C, O/H, N/C) and the molecule internal oxidation ($\omega = [(2\text{O} + 3\text{N}) - \text{H}]/\text{C}$) were also calculated.
- The light absorbance (UV-VIS Lambda 25 spectrometer, Perkin Elmer) of humic acid solutions (in 0.05 M NaHCO_3) was measured at wavelengths: 280 nm (A_{280}), 400 nm (A_{400}), 465 nm (A_{465}), 600 nm (A_{600}), and 665 nm (A_{665}), and absorbance ratios $A_{2/4}$ (A_{280}/A_{465}), $A_{2/6}$ (A_{280}/A_{665}), $A_{4/6}$ (A_{465}/A_{665}) as well as $\Delta\log K = \log A_{400} - \log A_{600}$ were also calculated.
- IR spectra (FT IR), in the range of $400\text{--}4000 \text{ cm}^{-1}$, for KBr pellets were measured in Magna FT 60 Nicolet spectrometer.

3. RESULTS AND DISCUSSION

The soils selected represent the taxonomic units and properties characteristic of the arable lands in the South-Podlasie Lowland. They were found to contain low content of organic matter and C/N ratio typical of mineral arable lands (about 10) indicating good conditions for organic matter mineralization [2], [3].

Table 1

Proportion of carbon and nitrogen of separated fractions in their total content in soil

Soil	In solution after decalcination	Bitumens	In solution of NaOH	In solution of fulvic acids	In solution of humic acids	Humines	Humic acids/fulvic acids
	% C fraction in C_{org}						C
A	9.03	2.36	47.4	28.2	19.2	41.2	0.68
B	12.1	3.69	38.4	23.1	15.3	45.8	0.65
C	9.59	2.95	44.3	23.6	20.7	43.1	0.88
–	% N fraction in N_{tot}						N
A	5.40	0.48	34.6	16.2	18.4	59.5	1.13
B	4.49	0.55	42.3	20.7	21.6	52.5	1.04
C	5.67	0.50	39.0	19.3	19.7	54.8	1.02

The fractional composition of organic matter is presented as the carbon percentage of particular fractions in its total content in the soil (table 1). Considerable carbon amounts were separated at the stage of soil decalcination (using 0.05 M H_2SO_4). That fraction is mainly represented by simpler organic compounds, low-molecular, loose and weakly bounded to mineral components of the soil; it is most labile and vulnerable to mineralization [1], [6]. A low carbon content in the fraction of bitumens is characteristic of agriculturally utilized mineral soils, because the biological activity and intensive mineralization in that soil do not favour the accumulation of organic compounds that can be extracted with organic solvents [6]. The amount of carbon separated by alkaline extraction (0.1 M NaOH) and detected in the fraction of humines testifies to a similar level of humification of organic matter in the soils studied. Quite apparent surplus of fulvic acid carbon (the values of carbon ratio for these fractions <1) was recorded in all the soils. It can be supposed that humic substances separated using NaOH are at the initial stage of humification, for which, in opinion of some authors [3], [7], the surplus of fulvic acids is characteristic. In Polish arable land of high agricultural culture, the surplus of humic acid fraction can be observed, which is a desirable trait of the humus, indicates its durability in the soil environment and guarantees advantageous influence on soil features [1], [2], [6].

Slightly lower amounts of the soil nitrogen were separated by means of the analytical procedures applied (table 1). Most of nitrogen that is transferred to the soil

solution during decalcination process is the mineral source of that element. Low per cent (about 0.5%) of nitrogen was found in the fraction separated using organic solvents, which confirms that bitumens constitute the sparse source of nitrogen compounds [8]. In alkaline solution, slight surplus of nitrogen in humic acids' fraction was recorded, while fulvic acids were less abundant in nitrogen.

Table 2

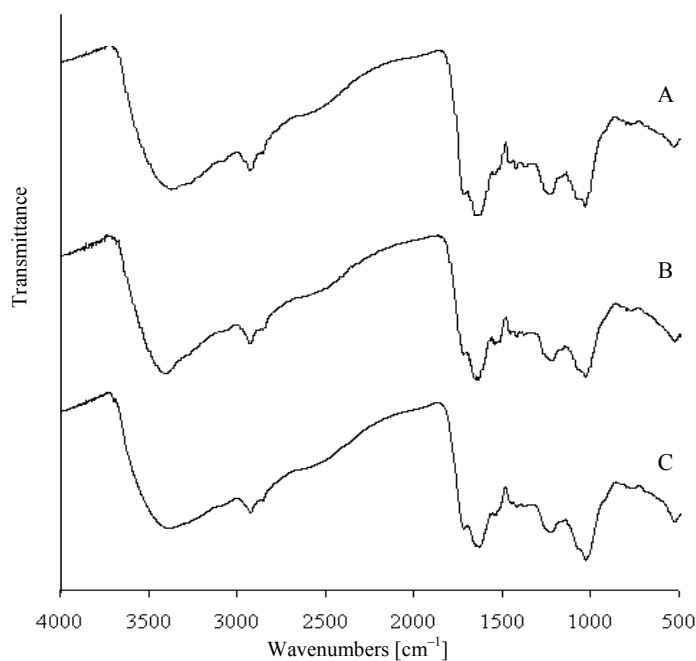
Elemental composition (atomic %) and values of spectrometric coefficients for humic acids in soils

Soil	C	H	N	O	H/C	O/C	O/H	N/C	ω	$A_{2/4}$	$A_{2/6}$	$A_{4/6}$	$\Delta\log K$
A	35.0	41.4	2.56	21.1	1.18	0.602	0.508	0.073	0.239	2.61	11.6	4.42	0.654
B	34.7	42.3	2.93	20.1	1.22	0.578	0.475	0.084	0.191	2.75	11.7	4.25	0.645
C	34.3	41.2	2.55	22.0	1.20	0.641	0.533	0.074	0.303	2.77	9.74	3.51	0.566

The similarity in organic matter properties between the soils tested was confirmed by humic acids properties (table 2). Similar elemental composition and the resulting atomic ratios were determined, first of all H/C, i.e. the elements whose quantitative inter-relations determine the "aromaticity" and "aliphaticity" of humic acids. The H/C values correspond to the aromatic rings conjugated with aliphatic chains containing up to 10 carbon atoms [9]. The values of H/C above unity may also prove that the content of aliphatic groups is higher than that of aromatic groups in humic acid molecules. The humic acids investigated had also similar values of spectrometric coefficients ($A_{2/4}$, $A_{2/6}$, $A_{4/6}$, and $\Delta\log K$). This allowed the conclusion that the acids were "matured" and presented high humification level: the acids from Stagnic Luvisol were characterized by relatively the highest humification. This was proven by lower $\Delta\log K$ and $A_{4/6}$ values, as well as by a high value of molecule internal oxidation state (ω), which is a reliable oxidation parameter taking into account the whole elemental composition [3], [7], [10].

According to KUMADA [10] humic acids in Dystric Arenosols should be classified as the B-type, while those from Stagnic Luvisol – as the A-type. Lower $A_{4/6}$ values of humic acids from Stagnic Luvisol may suggest that they have more condensed aromatic rings, higher molecular weight, a higher number of carbon atoms in aromatic bindings and lower in aliphatic ones and are potentially less mobile in the soil profile [11]. The humic acids studied were represented by typical FT IR spectra with bands of about (in cm^{-1}) 3400, 2900, 1700, 1600, 1400, 1200, and 1000 (figure 1) which is consistent with literature data [1], [12]. In humic acids of podzolic soil, slightly lower band intensity within 2960–2920 range was found, which was the measure of aliphaticity (stretching vibrations of C–H in methyl– CH_3 and methylene = CH_2 groups). This confirmed the suggestions based on UV VIS spectrometry that the proportion of aliphatic groups in these acids is low. In that soil, slightly poorly developed absorption bands at the wave numbers of about 1720 cm^{-1} (carbonyl groups C=O in acids and ketones as well as ali-

phatic and aromatic aldehydes) and $1620\text{--}1650\text{ cm}^{-1}$ ($\text{C}=\text{O}$, NH in 1st-order amides and $\text{C}=\text{C}$ in aromatic rings) were observed. A weak band at about 1540 and 1510 cm^{-1} , indicating the presence of aromatic structures, was found in the humic acids – the most fully developed band was detected for the humic acids of B-type soil. The interpretation of those spectra is not completely consistent with the UV VIS results. However, the possibility of overlaying the adjacent absorption bands should be taken into account. Poorly intensive absorption was observed in the range from 1460 to 1380 cm^{-1} (C-H bindings of aliphatic $-\text{CH}_3$ and $=\text{CH}_2$ groups in alkanes and cyclo-alkanes, $\text{C}=\text{O}$ of carboxylic acids, C-O of phenols, OCH_3 groups of lignins). Apparent absorption (the most intensive in the A-type soil) was found in humic acids at maximum of about 1230 cm^{-1} , which confirms the occurrence of C-O in phenols, carboxylic acids, or esters. Intensive bands at the maximum near 1000 cm^{-1} , characteristic of aliphatic side-chains and lignin in aromatic rings, were also recorded. In general, the presented FT IR spectra confirmed the similarity of chemical nature of the humic acids studied.



FT IR spectra for humic acids in soils studied

4. CONCLUSIONS

1. Organic matter from the humus horizons in Dystric Arenosols and Stagnic Luvisol fertilized with sewage sludge was characterized by similar carbon and nitrogen

per cent in the fraction after decalcination, bitumens, fulvic acids, humic acids, and humines.

2. The value of C/N ratio in the soils studied testifies to the favourable conditions for organic matter mineralization. Significant proportion of the fraction after decalcination and the fraction of fulvic acids indicates a potential opportunity for organic compounds to migrate inside the soil profile.

3. Humic acids in the soils tested proved to be “matured” and highly humified. The most humified humic acids (i.e. with a higher number of aromatic groups, lower content of aliphatic side-chains, and higher condensation of aromatic rings) were found in Stagnic Luvisol.

4. Sewage sludge should be utilized as a fertilizer because it contains organic matter and nutrients which are re-introduced into the cycle of elements in the natural environment.

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WŁAŚCIWOŚCI MATERII ORGANICZNEJ GLEB NAWOŻONYCH OSADAMI ŚCIEKOWYMI

Badano właściwości materii organicznej gleb rdzawych i gleby płowej nawożonych osadami ściekowymi z biologiczno-chemicznych oczyszczalni ścieków. Przeprowadzono frakcjonowanie materii orga-

nicznej (frakcja po dekalcytacji oraz frakcje bituminów, kwasów fulwowych, kwasów huminowych i humin) oraz badano właściwości kwasów huminowych (skład pierwiastkowy, UV, VIS, FT IR). Materia organiczna badanych gleb charakteryzowała się podobnym udziałem węgla i azotu w wyróżnionych frakcjach i podobnym stopniem humifikacji. Silniej zhumifikowane i dojrzałe kwasy huminowe (o większym udziale ugrupowań aromatycznych, mniejszym udziale bocznych łańcuchów alifatycznych, większej kondensacji jąder aromatycznych) stwierdzono w glebie płowej.