

Comparison of the effect of various long-term fertilization systems on the content and fractional composition of humic compounds in Lessive soil

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Abstract: A field experiment was established in 1972 on Luvisol. Three types of fertilizers – cattle manure (CM), cattle slurry (CS) and mineral fertilizers were used. CS was applied in the following doses: I – balanced with CM in terms of the amount of introduced total nitrogen and II – balanced with CM in terms of the amount of introduced total organic carbon (C_{tot}). 39 years after the experiment was established, half of each experimental plot was limed and since then the experiment was carried in two series – non-limed and limed soils. The paper presents the results of soil analyses 41 years after the experiment was started. It was found that each fertilization system increased the C_{tot} content in soil in relation to the unfertilized control plot. The increase of C_{tot} fluctuated between 0.35–6.22 g/kg of dry matter. In both series, the highest C_{tot} content was observed in the soil fertilized with CM and CM + PK. Limed compared to non-limed soil contained nearly 25% more carbon of humic acids than fulvic acids and nearly 20% lower content of low molecular humic bonds. Liming considerably widened the humic acids carbon:fulvic acids carbon ($C_{\text{HA}}:C_{\text{FA}}$) ratio of the fertilized soils, up to 1.32–1.87, while the corresponding objects of the non-limed series showed the $C_{\text{HA}}:C_{\text{FA}}$ ratio between 0.75–0.97.

Keywords: organic fertilizers; mineralization; absorbance; decomposition; macronutrient; soil organic matter

Increasingly often, the agricultural production space management involves measures aimed at the protection of soil organic matter (SOM). In the EU countries, this issue is regarded as a priority, which was expressed in the proposal for the Directive of the European Parliament and of the Council establishing a framework for the protection of soil. Decreasing content of SOM in soils and the risks associated with its mineralization, besides lowering the productivity of soils (Seremesic et al. 2017), have environmental significance, leading to high emissions of carbon dioxide from soils (Jäger et al. 2011, Šimková et al. 2014).

The formation of SOM is supported by fertilization, in particular with organic fertilizers originating from animal production. The effect of slurry depends on its chemical composition, dry matter content, the time of application and the dose. It is therefore necessary to monitor the effects of the use of slurry,

in particular where it has been applied for several years during the time of experiment on the same field. The SOM balance in soils fertilized with slurry is determined by the dose applied and, where it is balanced in terms of the amount of carbon introduced with the commonly used dose of manure, its humus-forming value may equal 90–97% in relation to manure (Sądej and Namiotko 2011).

In terms of the fertility of soils and the assessment of soil degradation, not only SOM but also the quality of the humic compounds being formed is important (Doni et al. 2014). As regards manure, an increase is observed in both the loosely and tightly bound fractions of the soil humus (Yan et al. 2007). The regular use of manure increases the content of the fraction of humic acids carbon (C_{HA}), especially the fraction bound with calcium ($C_{\text{HA-Ca}}$), fulvic acids carbon (C_{FA}) and the humin fraction (Lapa et al.

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2011). It also widens the $C_{HA}:C_{FA}$ ratio, increases the aliphatisation of C_{HA} in the soil, raises their susceptibility to oxidation, and reduces the average molecular weight as compared with the properties of C_{HA} in soils not fertilized with manure. C_{HA} in soils fertilized only with mineral fertilizers, as compared with C_{HA} in soils fertilized with manure, are characterized by a greater share of aromatic structures, lower susceptibility to oxidation and higher absorbance values at a wavelength of 465 nm.

Researcher's opinions about the effects of slurry on the quality of humic compounds are not unambiguous. According to Lithourgidis et al. (2007), the use of slurry leads to the formation of labile humus fractions, which is associated with a high rate of decomposition of this fertilizer in the soil, while Dębska (2004) and Sądej and Namiotko (2011) claim that slurry fertilization resulted in an increase in the content of C_{HA} and humins. Moreover, SOM in soils fertilized with slurry, as compared to soils unfertilized and fertilized with NPK, is characterized by a higher $C_{HA}:C_{FA}$ ratio.

The aim of this study was to determine the effect of long-term fertilization with organic and mineral fertilizers and combined organic and mineral fertilization on the quantitative and qualitative changes of soil organic matter.

MATERIAL AND METHODS

Site and experimental set-up. The field experiment was established in 1972 at the Agricultural Experimental Station in Bałcyny (Poland), owned by the University of Warmia and Mazury in Olsztyn. According to the World Reference Base for Soil Resources (IUSS Working Group WRB 2014), investigated soil belonged to the Luvisols type, subtype Albic Luvisols. A randomized block design

was applied in six replications, and an area of each experimental plot was 40 m².

Three fertilization systems were compared: organic – cattle manure (CM) and cattle slurry (CS), mineral (NPK) and combined organic (CM and CS) + mineral (PK). In each year, CS was applied in two doses: I – equivalent to CM in terms of the amount of total nitrogen introduced into the soil, and II – equivalent to CM in terms of the amount of organic carbon introduced into the soil. The supplementary mineral fertilization with phosphorus (P) and potassium (K) on the plots fertilized with CS and CM was applied in an amount equivalent to ½ of the dose of these components introduced on the plot fertilized exclusively with NPK. The chemical composition of organic fertilizers is presented in Table 1. Average annual doses of CS and CM are collated in Table 2.

The fertilizers were applied in the spring, prior to sowing spring cereals or planting root crops, and in the autumn, prior to sowing oilseed rape and winter cereals. In 2010, ½ of the area of the plots was limed using carbonate lime in a dose 3.5 t CaO/ha. Since then, the experiment was carried out in two series: non-limed soil (NLS) and limed soil (LS).

In the years 1972–1987, the crop rotation consisted of the following plants species: potato, spring barley + undersown red clover with grasses, red clover with grasses, winter oilseed rape, winter wheat, winter rye as a catch crop, maize, spring barley and winter wheat. In 1988, red clover with grasses was removed from the crop rotation system and since that time a 7-year cycle of rotation was used.

Soil sampling and chemical analyses. Primary soil samples were taken from the layer 0–25 cm of soil after the plants harvest. The extraction of humic compounds was performed by the Kononova-Belchikowa method (Kononova 1966), using the following solutions: H₂SO₄ at a concentration of 0.05 mol/dm³

Table 1. Chemical composition of organic fertilizers (% fresh matter)

Component	Cattle manure	Cattle slurry
Dry matter	23.06	8.22
Total organic carbon	8.53	3.12
Total organic nitrogen	0.49	0.31
P	0.17	0.12
K	0.43	0.32
Mg	0.09	0.05
Ca	0.14	0.10

Table 2. Fertilizers rates applied in the experiments per year

Object	Yearly means for 41 years			
	organic fertilizer (t/ha)	mineral fertilizer (kg/ha)		
		N	P	K
Cattle manure	21.0	–	–	–
Cattle slurry I	38.0	–	–	–
Cattle slurry II	64.8	–	–	–
Supplemented PK fertilization	–	–	17.6	50.5

(fraction Ia); a mixture of 0.1 mol/dm³ sodium pyrophosphate – Na₄P₂O₇ + 0.1 mol/dm³ NaOH (1:1 v/v) (fraction I), and NaOH at a concentration of 0.1 mol/dm³ (fraction II). The extraction of humic acids (HA) in fraction I was performed using a 0.1 mol/dm³ NaOH solution, after the samples had been decalcified twice with 0.2 mol/dm³ HCl (Schnitzer and Skinner 1968). The content of C_{FA} in fraction I was calculated from the difference between the amount of C extracted using the mixture of Na₄P₂O₇ + NaOH, and the amount of C_{HA}. The content of C_{HA} bound with calcium (C_{HA-Ca}) was calculated from the difference between the amount of C_{HA} separated using a mixture of 0.1 mol/dm³ Na₄P₂O₇ + 0.1 mol/dm³ NaOH, including the ones that were free, calcium-bound and bound to non-silicate R₂O₃ forms, and the amount of C_{HA} separated through the multiple treatment of the soil with 0.1 mol/dm³ NaOH. The content of C referred to as post-extraction residue, non-hydrolyzing C (C_{nh}), was calculated from the difference between the content of C_{tot} in the soil and the amount thereof extracted using a mixture of Na₄P₂O₇ + NaOH (fraction I). Total organic carbon (C_{tot}) and the content of C in particular fractions of humic compounds was determined using an oxidation-reduction method in a mixture of 0.066 mol/dm³ K₂Cr₂O₇ and 9.0 mol/dm³ H₂SO₄.

The properties of HA were also assessed based on their optical density. To this end, solutions of HA in a concentration of 0.02% in 0.1 mol/dm³ NaOH were prepared, in which the measurement of absorbance was performed using a flow injection spectrophotometer in a 1 cm path length quartz cuvette. Absorbance was measured using visible light waves with lengths $\lambda = 464$ nm (A₄), and $\lambda = 664$ nm (A₆). Based on the determined absorbance values, coefficients A_{4/6} were calculated (Chen et al. 1977).

The content of total nitrogen (N_{tot}) was determined with the Kjeldahl method. A distillation unit Büchi K-355 was employed for the distillation of nitrogen.

Statistical analysis. The results underwent statistical processing according to the two-way analysis of variance at the level of significance $P \leq 0.05$, using the statistical calculation software of Statistica v. 10.0 (StatSoft, Tulsa, USA). The lowest significant differences (*LSD*) between the analyzed values were determined with the two-dimensional Duncan's test. Power of the correlation between soil chemical properties, expressed by the Pearson's correlation coefficient (R^2) was calculated in MS Excel 2010 (Microsoft, Redmond, USA).

RESULTS AND DISCUSSION

The content of C_{tot}, N_{tot} and C:N ratio. In both series of the experiment, NLS and LS, the highest C_{tot} value was noted in the soil fertilized with CM along with mineral fertilization (PK) (Figure 1). This positive effect of the combined mineral and organic fertilization on the C_{tot} content is confirmed by Fließbach et al. (2007) and Moharana et al. (2012). Although the same amounts of C_{tot} were introduced in CM and CS II, the fertilization with CM of the soil in the NLS series resulted in an increase in the content of C_{tot} by over 15%, and for LS by as much as 34% compared with the soil fertilized with CS II. The results prove that the use of higher doses of CS is not justified as it does not result in a significant increase in the content of C_{tot} compared with lower doses of this fertilizer, calculated on the basis of the amount of N_{tot} introduced to the soil. Similar conclusions are also drawn by Lithourgidis et al. (2007) and Dębska (2004).

After 41 years of the application of NPK, the content of C_{tot} in the NLS was similar to its content in the soil of the control plot (CP) and the plot fertilized with CS I. This seems to confirm the opinion, often found in the literature, that mineral fertilization has a weak effect on the content of humus in soil (Banger et al. 2009).

In the objects fertilized with slurry and NPK, liming tended to reduce the content of C_{tot}, while in soil of the CM fertilized object, liming increased the C_{tot} content compared to NLS.

Another consequence of the fertilization is an increase of the soil richness in nitrogen, which, as compared with the non-fertilized soils, may range from almost 5% to over 50% (Černý et al. 2008, Sądaj and Przekwas 2008, Banger et al. 2009, Sądaj et al. 2016). Statistical analysis showed no significant differences between the content of N_{tot} in the arable layer of the soil fertilized with CS applied in both doses and the content of N_{tot} in the soil fertilized with NPK.

The liming treatment only slightly modified the contents of C_{tot} and N_{tot} in the soil (Figure 1). No effects of the combined action of liming and fertilization on the content of these components in the soil were shown, either, which confirms the empirical results obtained by Szymańska et al. (2008). On the other hand, a significant relationship between C_{tot}:N_{tot} ratio was found in the present study (Figure 2, Table 3).

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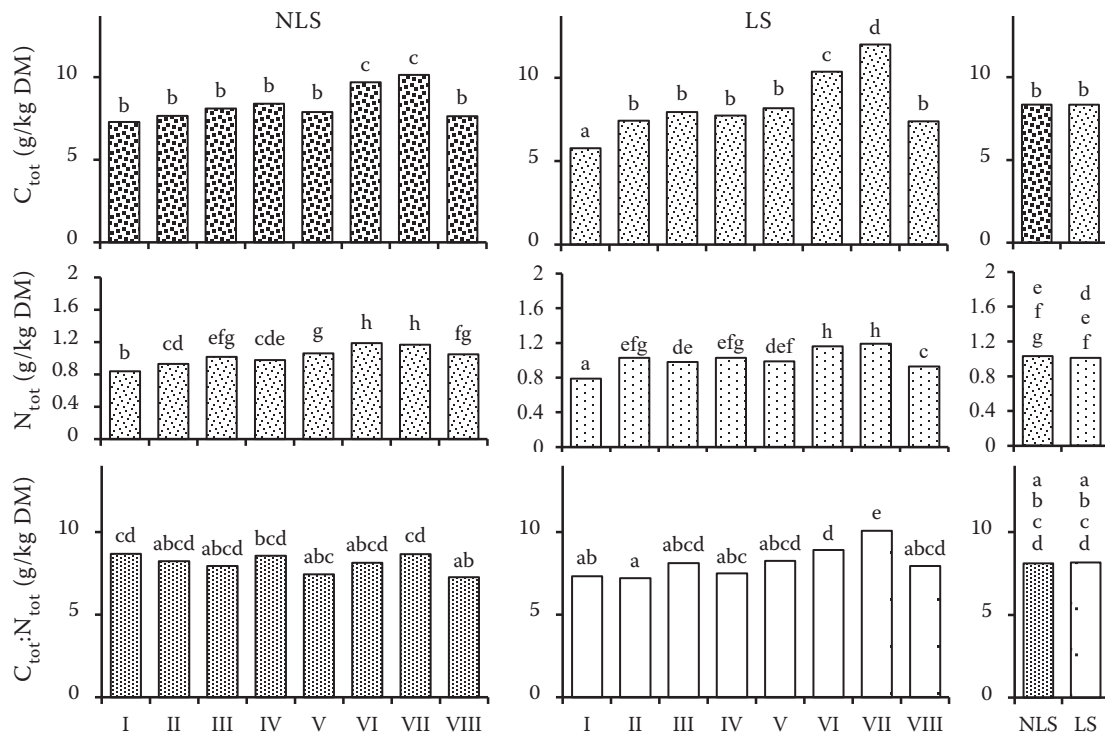


Figure 1. Effect of different fertilization systems on total organic carbon (C_{tot}), total organic nitrogen (N_{tot}) content and $C_{tot}:N_{tot}$ ratio in soil. Different letters above the bars denote significant differences between fertilization systems at $P = 0.05$ level. I – control plot (CP); II – CS I (cattle slurry); III – CS I + PK; IV – CS II; V – CS II + PK; VI – CM (cattle manure); VII – CM + PK; VIII – NPK; NLS – non-limed soil; LS – limed soil; DM – dry matter

Fractional composition of humic substances in the soil. The studies of Diacono and Montemurro

(2010) showed that the effect of mineral and organic fertilizers on the composition of formed humic sub-

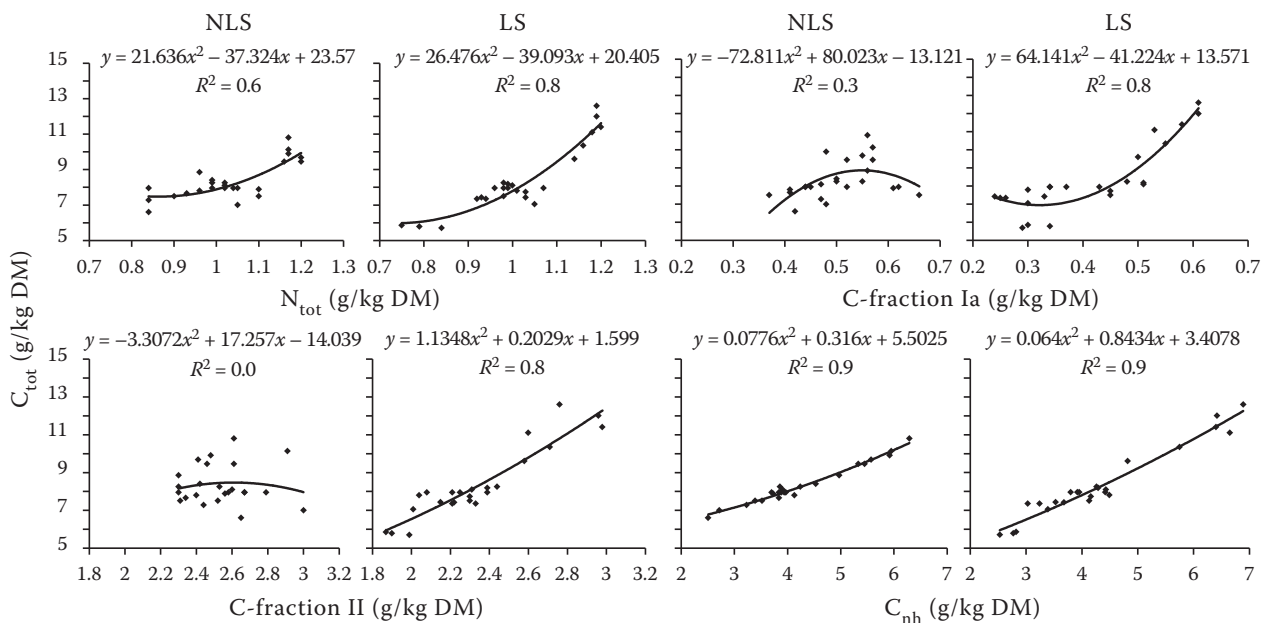


Figure 2. Relationships between total organic carbon (C_{tot}) content and total organic nitrogen (N_{tot}), C-fraction Ia, C-fraction II, and non-hydrolyzing carbon (C_{nh}) fractions extracted from soil. NLS – non-limed soil; LS – limed soil; DM – dry matter

Table 3. Pearson's simple correlation coefficients between soil chemical properties after 41 years of differentiated fertilization systems and soil liming

Variable	11	10	9	8	7	6	5	4	3	2	1	
Non-limed soil												
1 C _{tot}	0.44	0.99**	0.01	-0.42*	0.45*	-0.29	0.25	0.38	0.46*	0.75**	-	
2 N _{tot}	0.45**	0.71**	0.28	-0.65**	0.66**	-0.44	0.36	0.56**	-0.23	-		
3 C _{tot} :N _{tot}	0.04	0.50*	-0.37	0.27	-0.24	0.17	-0.12	-0.17	-			
4 Fraction Ia	0.51*	0.34	-0.01	-0.17	0.24	0.00	0.31	-				
5 C extracted	-0.05	0.08	0.57**	-0.14	0.57**	0.26	-					
6 C _{HA}	-0.22	-0.35	0.23	0.91**	-0.65**	-						
7 C _{FA}	0.15	0.36	0.26	-0.88**	-							
8 C _{HA} :C _{FA}	-0.28	-0.41*	-0.01	-								
9 Fraction II	-0.40*	-0.10	-									
10 C _{nh}	0.46*	-										
11 C _{HA-Ca}	-											
Limed soil												
1 C _{tot}	0.91**	0.97**	0.93**	0.74**	0.49*	0.96**	0.91**	0.83**	0.92**	0.91**	-	
2 N _{tot}	0.81**	0.91**	0.86**	0.69**	0.38	0.84**	0.78**	0.76**	0.68**	-		
3 C _{tot} :N _{tot}	0.88**	0.88**	0.84**	0.66**	0.51*	0.92**	0.88**	0.76**	-			
4 Fraction Ia	0.67**	0.87**	0.85**	0.80**	0.12	0.79**	0.65**	-				
5 C extracted	0.96**	0.79**	0.87**	0.53**	0.76**	0.96**	-					
6 C _{HA}	0.96**	0.89**	0.93**	0.75**	0.53**	-						
7 C _{FA}	0.62**	0.30	0.45*	-0.15	-							
8 C _{HA} :C _{FA}	0.65**	0.80**	0.74**	-								
9 Fraction II	0.87**	0.89**	-									
10 C _{nh}	0.82**	-										
11 C _{HA-Ca}	-											

*correlation coefficient r significant for $\alpha = 0.05$; **correlation coefficient r significant for $\alpha = 0.01$ ($n = 24$). C_{tot} – total organic carbon; N_{tot} – total organic nitrogen; C_{HA} – humic acids carbon; C_{FA} – fulvic acids carbon; C_{nh} – non-hydrolyzing carbon; C_{HA-Ca} – carbon of humic acids bounded with calcium

stances is different. Long-term mineral fertilization led to an increase in the content of humic compounds in the most mobile bounds at the expense of the fraction more tightly bound with the mineral part of soil (Schulz et al. 2002). In addition, exclusive mineral fertilization led to a decrease in the content of C_{HA}, in particular their labile fractions, the consequence of which is the deteriorated quality of humus of soil aggregates. In this scope, organic fertilizers act differently, as they can serve as substrate for renewing humic compounds. Most often, these fertilizers have a positive effect on the quality of SOM, among others through a significant increase in the share of C_{HA} in the fractional composition of organic matter (Watanabe et al. 2007, Yanardağ et al. 2015). Such dependencies are also confirmed by the results of

our study, in which CM compared to other types of fertilizers significantly contributed to the increase in C_{HA} (Table 4).

In the NLS series, most low-molecular humic bonds (fraction Ia) were noted in the soil from CS II and CM objects.

The main components of humus that determine its properties in the soil are humic acids, whose characteristics are modified by the type of fertilization applied (Watanabe et al. 2007, Kawasaki et al. 2015). In the present study, the fertilization in the NLS series had no effect on the content of free humic compounds bound with the non-silicate forms of iron and aluminum, and bound with calcium (fraction I). In the humic bonds of this fraction, the fulvic acids (FA) content was higher than the HA content, which

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Table 4. Effect of different fertilization systems on fractional composition of humus compounds (g/kg dry matter)

Fertilization	Fraction Ia	Fraction I				Fraction II	$C_{\text{HA-Ca}}$	C_{nh}
		C-extracted	C_{HA}	C_{FA}	$C_{\text{HA}}:C_{\text{FA}}$			
Non-limed soil								
CP	0.44	4.07	2.29	1.78	1.29	2.56	0.97	3.21
CS I	0.40	3.82	1.73	2.09	0.83	2.35	1.27	3.83
CS I + PK	0.47	4.23	1.87	2.36	0.79	2.60	1.43	3.87
CS II	0.56	3.91	1.93	1.98	0.97	2.34	1.55	4.49
CS II + PK	0.61	4.09	1.95	2.14	0.91	2.46	1.50	4.12
CM	0.52	4.03	1.73	2.30	0.75	2.50	1.41	5.65
CM + PK	0.57	4.27	1.96	2.31	0.83	2.66	1.41	5.86
NPK	0.48	4.18	1.98	2.20	0.90	2.82	1.08	3.45
Mean	0.51	4.08	1.93	2.15	0.91	2.54	1.33	4.31
Limed soil								
CP	0.30	3.07	1.74	1.33	1.31	1.92	0.99	2.71
CS I	0.32	3.57	2.08	1.49	1.40	2.09	1.27	3.85
CS I + PK	0.35	4.06	2.31	1.75	1.32	2.18	1.46	3.89
CS II	0.44	3.49	2.03	1.46	1.39	2.33	1.20	4.24
CS II + PK	0.50	3.85	2.38	1.47	1.62	2.38	1.41	4.33
CM	0.53	4.61	2.96	1.65	1.79	2.63	1.60	5.74
CM + PK	0.60	5.43	3.54	1.89	1.87	2.90	1.92	6.57
NPK	0.25	4.11	2.21	1.90	1.16	2.23	1.39	3.27
Mean	0.41	4.02	2.41	1.62	1.48	2.33	1.41	4.33
Mean for non-limed and limed soil:	0.46	4.05	2.17	1.88	1.20	2.44	1.37	4.32
fertilization	0.035	0.196	0.117	0.196	0.164	0.129	0.124	0.515
$LSD_{0.05}$ liming	0.017	ns	0.059	0.098	0.082	0.065	0.062	ns
interaction	0.049	0.277	0.166	ns	0.232	0.183	0.176	ns

ns – not significant; CP – control plot; CS – cattle slurry; CM – cattle manure; LSD – least significant difference; C_{HA} – humic acids carbon; C_{FA} – fulvic acids carbon; C_{nh} – non-hydrolyzing carbon; $C_{\text{HA-Ca}}$ – carbon of humic acids bounded with calcium

was observed in all fertilization plots. The average content of FA was the highest in the soil fertilized with CM, which indicates that the long-term fertilization with CM only without liming, does not have a positive effect on the humification process. The reason for the accumulation of FA may be incomplete humification of SOM, leading to the formation of polyphenols, quinones, etc., which may polymerize to form FA. The application of CS and CM resulted in reduction in the content of carbon in the humic bonds of fraction II as compared with the CP soil and the soil fertilized with NPK. The content of C_{nh} and the share of this fraction in C_{tot} was the highest in the soil fertilized with CM and CM + PK. C_{nh} was also significantly positively correlated with the content of C_{tot} (Figure 2).

In the LS series, changes in the structure of the fraction of humic compounds were more pronounced than in the NLS series (Table 4). The average content of carbon of fraction Ia and fraction I were lower than in NLS. The lowest content of fraction Ia was noted in the soil fertilized with NPK. A higher relationship between the average content of fraction Ia and C_{tot} was demonstrated for the LS than for NLS (Figure 2).

In the LS series within fraction I bonds, C_{HA} dominated over C_{FA} and the highest content the former was found in the plots fertilized with CM. The content of C_{HA} in LS was significantly positively correlated with the content of N_{tot} , C_{tot} and the content of carbon of fraction I bonds (Table 3). As a consequence of the above changes, the $C_{\text{HA}}:C_{\text{FA}}$ ratio in LS increased as compared with NLS, with the widest ratio noted in the

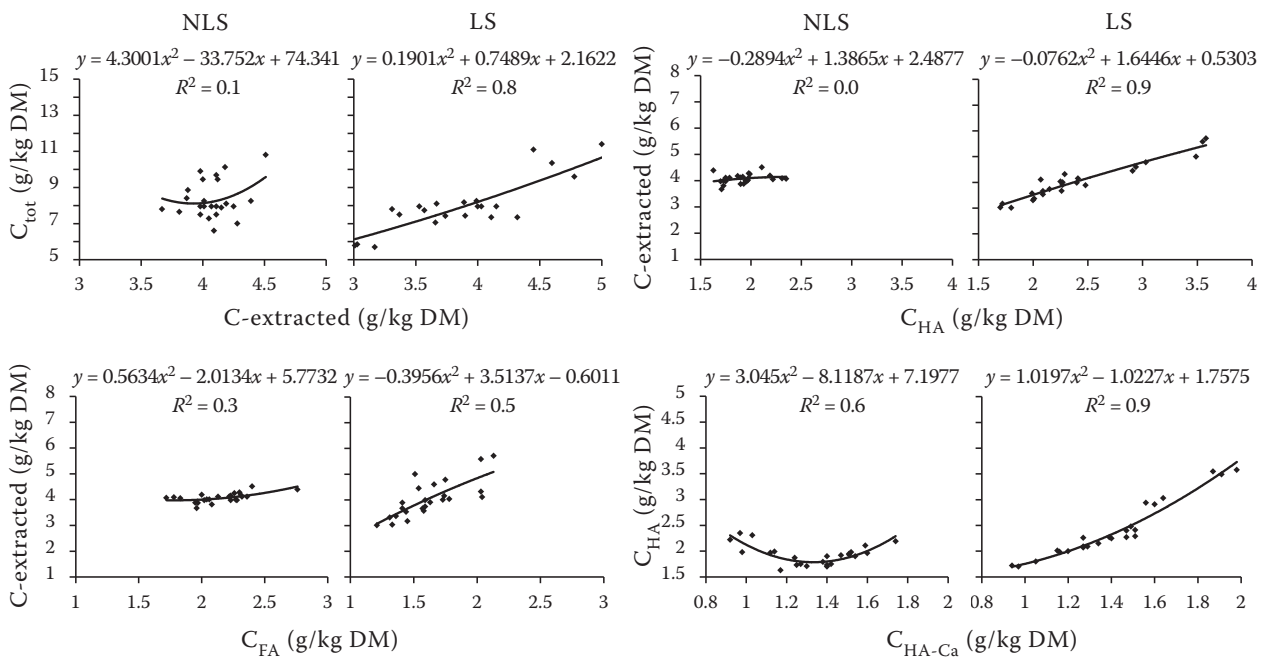


Figure 3. Relationships between total organic carbon (C_{tot}) content and C-extracted, C-extracted and humic acids carbon (C_{HA}), C-extracted and fulvic acids carbon (C_{FA}), C_{HA} and carbon of humic acids bounded with calcium (C_{HA-Ca}) fractions extracted from soil. NLS – non-limed soil; LS – limed soil; DM – dry matter

plots where CM was applied (Table 4). The obtained results indicate that humus of the limed soil fertilized with CM was characterized by a higher value of the $C_{HA}:C_{FA}$ ratio, and the C_{HA} achieved higher values of the absorbance coefficients than in the soil fertilized with CS and NPK. The results confirm the data provided in the literature (Szymańska et al. 2008).

The content of the C_{HA-Ca} fraction in LS was different from that in NLS. In LS, the application of CM, CS I as well as CM + PK and CS I + PK contributed to an increase in the content of C_{HA-Ca} , as compared with NLS (Table 4). This relationship was reverse in the soil treated with CS II, where the content of C_{HA-Ca} was smaller by an average of 16% than in NLS.

Studies by other authors (Yanardağ et al. 2015) indicate that the application of both organic fertilizers (FYM and SL) brings about similar effects in relation to the content of both C_{tot} and C_{HA} and C_{FA} in soil. Liming increased the significance of correlations between most of the analyzed carbon fractions and the content of C_{tot} , which was not found for NLS (Tables 3 and 4).

One of the properties characterizing the internal structure of HA is optical density, which depends on the ratio of C contained in the aromatic nucleus to the C in side radicals (Kononova 1966, Chen et al. 1977). The value of $A_{4/6}$ in soil from particular experimental plots ranged from 4.08 to 6.20 (Figure 4).

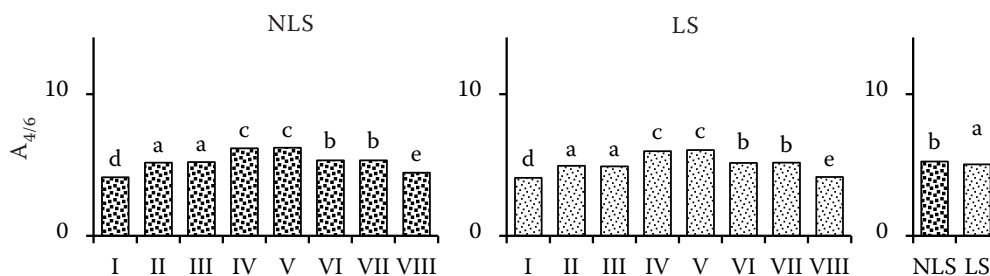


Figure 4. Values of absorbance $A_{4/6}$ ratios for humic acids (HA) solutions calculated on the basis of their optical properties. Different letters above the bars denote significant differences between fertilization systems at $P = 0.05$ level. I – control plot (CP); II – CS I (cattle slurry); III – CS I + PK; IV – CS II; V – CS II + PK; VI – CM (cattle manure); VII – CM + PK; VIII – NPK; NLS – non-limed soil; LS – limed soil

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Higher values of the absorbance quotient were found in NLS than in LS, which indicates more intensive humification of organic matter and greater losses of SOM from the NLS plots. The qualitative parameters of humic substances were also subject to changes as a result of the application of various fertilization systems. It is assumed that humic acids, being chemically 'younger', are characterized by lower optical density than 'mature' acids, which results from the stronger condensation of the aromatic nucleus in 'mature' HA, and the predominance of side chains in younger acids. In both series of the experiment, the value of the A4/6 ratio increased following the application of CS II fertilization, which is confirmed by the increase in the molecular weight of the humic substances formed in this variant. HA isolated from the soil material sampled from the plots fertilized with CM and CS I were characterized by lower values of A4/6.

Long-term fertilization systems contributed significantly to the increase in the content of total organic carbon and total nitrogen in the soil. Following the fertilization with cattle slurry and mineral fertilizers, the increase in the content of these components was smaller than after the fertilization with cattle manure. In both series (NLS and LS), the content of the C mobile fractions and their share in C_{tot} were higher after fertilization with CS II and CM than CS I and NPK. Liming of the soil resulted in an increase in the $C_{\text{HA}}:C_{\text{FA}}$ ratio as compared with the non-limed soil, and contributed to the decrease in the share of low-molecular humic bonds in the soil. Humus of the limed soil fertilized with CM was characterized by a higher value of the $C_{\text{HA}}:C_{\text{FA}}$ ratio, and the C_{HA} achieved higher values of the absorbance coefficients than in the soil fertilized with CS and NPK. In the non-limed soil, within the fertilized plots, C_{FA} dominated over C_{HA} . A higher percentage of C_{HA} in the content of C_{tot} was found in the soil fertilized with CS and NPK than in the soil fertilized with CM. The largest share in the identified fractions of humus consisted of humins. A larger amount of this fraction of humus was found in the soil fertilized with organic fertilizers than in the soil fertilized with mineral fertilizers.

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