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QUANTITY AND QUALITY OF ORGANIC MATTER IN SOIL AFTER APPLICATION OF VARIOUS ORGANIC MATERIALS

ILOŚĆ I JAKOŚĆ MATERII ORGANICZNEJ W GLEBIE PO APLIKACJI RÓŻNYCH MATERIAŁÓW ORGANICZNYCH

Abstract: Organic carbon concentrations in soil, irrespective of the year of research increased significantly after application of organic materials for the soil fertilization in comparison with the soil from the NPK mineral treatment. The content of low molecular humus compounds extracted from soil using H_2SO_4 solution was small, regardless of the applied fertilization or year of research. However, after the third year of research a significant increase in this humus fraction content was noted in soil of all treatments where fertilization was applied. After the third year of research, carbon content in alkaline extract rose significantly in soil of all treatments where fertilization with organic materials was applied, in comparison with the soil from mineral NPK treatment. The content of humic acid carbon in soil was lower than fulvic acid carbon, which resulted in lower than one values of Cha : Cfa ratio. However, obtained results point to marked increase in both humus fractions in results of residual effect of applied fertilization. Residual effect of applied fertilization apparently increased the value of absorbance coefficient A4/6, which points to a decreased degree of condensation of humic acid molecule and greater aliphatisation.

Keywords: soil, organic matter, organic materials, sewage sludge

Introduction

Undoubtedly, organic matter determines physical, chemical and biological properties of soils [1, 2]. Soils impoverishment in organic matter is not only a problem in Poland [3]. A complex process of soil organic matter formation and its transformation is to the greatest extent shaped by the site conditions, although cultivation measures, including fertilization, are not without importance [4, 5].

In view of growing deficit of natural fertilizers, observable in Poland and worldwide, there appeared a possibility of utilising for fertilization organic waste materials as an alternative source of organic matter [6, 7]. Because of considerable yield forming value of natural and organic fertilizers and biodegradable waste materials as well as their advantageous effect on some soil properties, which have been confirmed by Polish and

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foreign scientists, there is a need to assess their effect on more complex properties of soil organic matter [8-10].

Assuming a beneficial effect of fertilization with organic materials on the content of soil organic matter, a three-year field experiment was conducted in which fertilization with farmyard manure, municipal sewage sludge and compost based on biodegradable materials was applied to improve the quantity and quality of organic matter in Stagnic Gleysol soil.

Materials and methods

Three-year investigations were conducted as a field experiment located 10 km west of Krakow (49º59'N; 19º41'E) in conditions of moderate climate. The soil from the experimental area was classified to Stagnic Gleysol soils. Table 1 shows selected soil properties before and after the experiment.

Table 1

Physical and chemical properties of the soil before and after experiment (0-20 cm layer)

Determination	**Before experiment**	**After experiment**				
		(0)	**(M)**	**(PF)**	**(SS)**	**(C)**
pH (KCl)	5.60	5.24	5.36	5.60	5.67	5.82
Organic C [g kg^{-1}]	15.3	15.7	15.5	16.5	17.3	16.8
Total N [g kg^{-1}]	1.59	1.55	1.54	1.61	1.66	1.67
Total Cu [mg kg^{-1}]	15.8	12.8	12.1	12.1	11.0	13.2
Total Zn [mg kg^{-1}]	132.8	135.3	132.1	132.1	133.8	134.0
Total Mn [mg kg^{-1}]	2230	2199	2150	2210	2221	2205
Total Cr [mg kg^{-1}]	51.6	50.2	50.9	51.2	51.4	50.1
Total Pb [mg kg^{-1}]	35.8	31.9	30.2	29.7	30.5	31.5
Total Cd [mg kg^{-1}]	0.96	0.74	0.76	0.77	0.78	0.79
Total Ni [mg kg^{-1}]	32.7	31.9	31.1	32.2	33.9	32.9
Bulk density [g cm^{-3}]	1.52	n.d.	n.d.	n.d.	n.d.	n.d.
Total porosity [cm^{3} cm^{-3}]	0.41	n.d.	n.d.	n.d.	n.d.	n.d.
Fraction < 0.02 mm [g kg^{-1}]	520	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. - not determined

The experiment was set up with randomised block method. A plot area was 30 m^2. The experimental design comprised 5 treatments in four replications: *without fertilization* (0), *mineral NPK treatment* (M) (110.0 kg N ha^{-1}, 58.6 kg P ha^{-1} and 120.0 K ha^{-1}), *pig manure* (PF) (14.30 t ha^{-1} fresh mass), *municipal sewage sludge from mechanical-biological treatment plant* (SS) (14.15 t ha^{-1} fresh mass) and *compost produced from plant and other biodegradable materials* (C) (6.46 t ha^{-1} fresh mass). Selected properties of the manure, municipal sewage sludge and compost were presented in Table 2.

The field was limed before the experiment outset. The measure was applied according to hydrolytic acidity (962.0 kg CaO ha^{-1}). In the spring of the following year, after completing essential cultivation measures, manure, sewage sludge and compost were spread evenly on the plots surface and then ploughed. Two weeks later supplementary mineral fertilizers were applied and ploughed with the soil by means of cultivator + harrow aggregate. The nitrogen dose supplied with organic materials was 110.0 kg N ha^{-1}. Phosphorus and potassium were supplemented with mineral fertilizers to an equal level, introduced with fertilization on all treatments (except the control), (phosphorus to

58.6 kg P ha^{-1} as single superphosphate and potassium to 120.0 kg K ha^{-1} as 60% potassium salt). In the second and third year of the research, identical element doses as in the first year were applied, but solely as mineral fertilizers, in order to supplement nutrients (nitrogen, phosphorus and potassium).

Table 2

Physical and chemical properties of the organic materials

Determination	Pig FYM (PF)	Sewage sludge (SS)	Compost (C)
Total N [g kg^{-1} d.m.][b]	34.0	26.2	38.9
P [g kg^{-1} d.m.]	12.8	8.2	5.8
K [g kg^{-1} d.m.]	21.8	1.9	29.9
S [g kg^{-1} d.m.]	4.76	9.66	3.61
Cu [mg kg^{-1} d.m.]	156	103	33
Zn [mg kg^{-1} d.m.]	284	1146	194
Mn [mg kg^{-1} d.m.]	355	194	280
Cr [mg kg^{-1} d.m.]	2.8	23.4	15.0
Pb [mg kg^{-1} d.m.]	1.2	55.7	9.3
Cd [mg kg^{-1} d.m.]	0.80	3.97	1.42
Ni [mg kg^{-1} d.m.]	10.1	21.1	10.4
EC [mS cm^{-1}] [a]	2.89	1.69	2.62
pH (H_2O)	8.23	6.23	7.31
Organic matter [g kg^{-1} d.m.]	831	414	531
Water content [g kg^{-1} f.m.][c]	774	703	563
Ash [g kg^{-1} d.m.]	169	586	469

[a] EC = electrical conductivity; [b] data are based on 105°C dry matter weight; [c] f.m. = fresh matter

The test plant was spring wheat, "Jagna" cv. Plant density was 485 pcs. per 1 m^2. Chemical measures were applied during vegetation period to protect the plantation against weeds. The length of wheat vegetation period in the individual years depended on the weather conditions. Wheat was harvested at full grain maturity. In order to determine grain yield, wheat was harvested from the area of 4 m^2, separately from each plot.

Sewage sludge used for the experiment originated from municipal mechanical-biological treatment plant situated in the Malopolska Region, the sewage sludge was stabilized. Compost was produced from plants and other biodegradable wastes, according to MUT-Kyberferm technology, at a composting plant located in Krakow. The proportions of individual waste in biomass for composting were: 25% grass, 20% wood pellets, 20% leaves, 10% market waste, 5% tobacco waste and 20% coffee production waste. Pig manure was stored on manure plate for 6 months.

The soil material was collected each year after the plant vegetation ended. Samples of soil material were collected from each plot separately. Collected material was dried in the open air, ground in a porcelain mortar and then sifted through a sieve with Ø 1 cm. In material prepared in this way, organic carbon was assessed by oxidative-titrating method. Content of humus compounds was extracted from soil by means of 0.05 mol dm^{-3} H_2SO_4 solution and a mixture of 0.1 mol dm^{-3} $Na_4P_2O_7$ solution + 0.1 mol dm^{-3} NaOH. Carbon of humic acids (Cha) was isolated in the extract of sodium pyrophosphate and sodium base, whereas carbon of fulvic acids (Cfa) was calculated from the difference between the amount of carbon in the extract and the amount of humic acid carbon (Cha) contained in the extract. The extraction residue - non-hydrolysing carbon was computed from the difference between organic carbon content (C_{org}) and the amount of carbon in the extract. In appropriately prepared solutions of humic acids, light absorbance was measured at the wavelength 465 and 665 nm and colour ratio was (A4/6) was computed.

The results were verified statistically using two-way ANOVA (factors: fertilization and years of experiment) in totally randomised design, using f-Fisher. The significance of differences between arithmetic means were verified on the basis of homogenous groups determined by Duncan test at the significance level $\alpha < 0.05$. All statistical computations were made using Statistica PL packet.

Results and discussion

Applied fertilization did not cause any significant changes in organic carbon content in soil, after the first year of the experiment (Table 3). After the third year of the research an increased organic carbon content was registered in the soil of organic material treatments in comparison with C content after the first year of the experiment, however a marked difference was visible in the soil on the treatment where municipal sewage sludge (SS) was added. In the soil of the treatment where mineral NPK fertilization was applied (M) and on the non-fertilized treatment, organic carbon content diminished in comparison with the concentration assessed in the soil sampled in the first year.

Table 3

The content of organic C and C extracted H_2SO_4 and $Na_4P_2O_7$+NaOH [g kg^{-1} d.m. ± SD]

Objects	After 1st year	After 3rd year	Mean
	Organic C		
No fertilization (0)	$17.0^{bc} \pm 1.08$	$15.7^{abc} \pm 1.53$	16.3±1.47
Mineral fertilization NPK (M)	$15.7^{abc} \pm 0.85$	$15.5^{abc} \pm 1.42$	15.5±1.18
Pig FYM (PF)	$15.6^{abc} \pm 0.29$	$16.5^{abc} \pm 1.28$	16.1±1.06
Sewage sludge (SS)	$15.0^{ab} \pm 0.43$	$17.3^{c} \pm 1.64$	16.2±1.67
Compost (C)	$14.8^{a} \pm 0.30$	$16.8^{abc} \pm 0.67$	15.8±1.12
	C extracted H_2SO_4		
No fertilization (0)	$0.45^{b} \pm 0.05$	$0.51^{cde} \pm 0.04$	0.48±0.06
Mineral fertilization NPK (M)	$0.44^{b} \pm 0.04$	$0.54^{de} \pm 0.03$	0.49±0.06
Pig FYM (PF)	$0.36^{a} \pm 0.03$	$0.46^{bc} \pm 0.06$	0.41±0.07
Sewage sludge (SS)	$0.50^{bcd} \pm 0.01$	$0.57^{e} \pm 0.01$	0.54±0.03
Compost (C)	$0.50^{bcd} \pm 0.01$	$0.53^{de} \pm 0.02$	0.52±0.02
	C extracted $Na_4P_2O_7$+NaOH		
No fertilization (0)	$5.97^{d} \pm 0.09$	$6.05^{d} \pm 0.28$	6.01±0.21
Mineral fertilization NPK (M)	$5.76^{cd} \pm 0.28$	$5.96^{d} \pm 0.24$	5.86±0.28
Pig FYM (PF)	$4.92^{a} \pm 0.26$	$5.55^{bc} \pm 0.25$	5.24±0.41
Sewage sludge (SS)	$5.22^{ab} \pm 0.08$	$5.74^{bc} \pm 0.18$	5.48±0.29
Compost (C)	$5.21^{ab} \pm 0.08$	$5.69^{bc} \pm 0.22$	5.48±0.29

Means marked by the same letters did not differ significantly at $\alpha < 0.05$ according to the Duncan test; factors fertilization × year

Organic carbon concentration, most important from the point of view of physical, chemical and biological properties of soil, did not increase markedly after the application of organic materials as fertilizers, as compared with the soil from the treatment where mineral NPK fertilization was used, which might have been due to the properties of applied organic materials, their dose or biochemical processes occurring in soil after application of these materials [11, 12]. On the basis of available literature a beneficial effect of fertilization with organic materials on organic carbon content in soil may be inferred. However, the range of changes of this element content is conditioned mainly by the dose of applied organic materials [13]. On the basis of results obtained by the Author it is difficult to unanimously demonstrate significantly better effect of any of the applied organic materials on organic carbon content.

The content of low-molecular humus compounds extracted from soil with 0.05 mol·dm^{-3} solution of H_2SO_4, which are attributed a similarity to fulvic acids, was small, irrespective of applied fertilization and years of the experiment (Table 3) [14]. However, it should be noted that after the third year of the research a marked increase in this humus fraction in soil was registered, except the soil from the treatment without fertilization.

Soil organic matter is composed of components being at various phases of decomposition and of large molecular compounds with specific properties. The most mobile fraction of organic matter may combine carbohydrates, proteins and their derivatives, low molecular fractions of humic acids and many other simple organic compounds. The content of this fraction of organic matter in agricultural soils is conditioned by agrotechnological measures but the main factor determining its content is the kind and quality of organic material supplied to the soil. In some authors' opinions supplying to the soil fresh organic materials increases the amount of soluble organic matter [15]. In the presented investigations application of the analysed organic materials did not cause any major changes in the content of organic compounds extracted from the soil with sulphuric acid solution. It may result from the properties of applied materials, particularly the degree of their stabilization. According to Debska [15], quantitative assessment of soluble organic material is a complex process and depends on many factors, in the first place connected with the extraction procedure. The quantity of soluble carbon determined in the extract depends among others on: the kind of extractant, extraction time, sample moisture, the ratio of sample weight to the extractant volume and method of carbon assessment in the extracts.

The content of carbon extracted with a 0.1 mol dm^{-3} mixture of $Na_4P_2O_7$ and NaOH after the first year of the experiment was significantly diversified due to applied fertilization (Table 3). Like in case of humus compounds extracted with sulphuric acid, the highest content of carbon in the alkaline extract was assessed in the soil from pig manure treatment (PF). After the third year of research, the amount of carbon in alkaline extract raised significantly in the soil of all treatments where fertilization with organic materials was conducted. Also Lina et al [16] assessed higher content of alkaline soluble organic carbon fraction after application to the soil of among others sewage from food industry, abundant in organic matter. Moreover, the quoted authors stated that sewage abundant in organic matter maybe used for a temporary increase in organic carbon content in soil.

Under conditions of sustainable agriculture, one of the main elements of preserving soil fertility is supplementing nutrients, which are absorbed with the plant yield and supplying organic matter which affects physical, chemical and biological soil properties and whose resources were considerably diminished [17]. Maintaining an adequate humus level in soil requires fertilization with materials abundant in organic matter, soil liming and supply of equivalent nutrients, such as nitrogen, phosphorus or potassium, which are absorbed with plant yield [18]. Finding a way to improve organic substance balance was forced also by growing deficiency in production of the basic natural fertilizer - manure. Supplying to the soil considerable amount of organic substance should result in increased content of organic carbon. Research conducted so far demonstrated diversified dynamics of the transformations of organic substance supplied to the soil conditioned by fractional composition of humic substances and properties of humic acids [19]. In the Author's own investigations the content of humic acid carbon was smaller than the content of fulvic acid carbon, irrespective of the applied fertilization, however obtained results indicate a considerable increase in both humus fractions in result of the residual effect of applied fertilization (Table 4). Also, the results of research conducted by Perez-Lomas et al [19] point to increased content of humic acid carbon after supply to the soil of sewage sludge composted with wooden waste supplement. As the above mentioned authors report, the increase in this humus fraction content was lower in comparison with fulvic acid carbon content. According to the authors quoted above, the temperature is an important factor modifying the rate of mineralization or organic matter supplied to the soil.

Table 4

The content of C humic, C fulvic acids and C non-hydrolysing [g kg^{-1} d.m. ± SD]

Objects	**After 1st year**	**After 3rd year**	**Mean**
	C humic acid		
No fertilization (0)	2.38^{d}±0.17	2.33^{cd}±0.09	2.35±0.14
Mineral fertilization NPK (M)	2.01^{abc}±0.21	2.14^{bcd}±0.11	2.08±0.18
Pig FYM (PF)	1.78^{a}±0.27	1.96^{ab}±0.15	1.87±0.23
Sewage sludge (SS)	1.90^{ab}±0.29	2.09^{abcd}±0.15	1.99±0.25
Compost (C)	2.13^{bcd}±0.17	2.20^{bcd}±0.08	2.16±0.14
	C fulvic acid		
No fertilization (0)	3.59^{bc}±0.08	3.72^{bc}±0.24	3.66±0.19
Mineral fertilization NPK (M)	3.75^{bc}±0.14	3.81^{c}±0.24	3.78±0.20
Pig FYM (PF)	3.14^{a}±0.40	3.59^{bc}±0.27	3.37±0.41
Sewage sludge (SS)	3.33^{ab}±0.22	3.65^{ab}±0.16	3.49±0.25
Compost (C)	3.08^{a}±0.18	3.49^{abc}±0.15	3.28±026
	C non-hydrolysing		
No fertilization (0)	11.03^{c}±1.01	10.19^{abc}±0.45	10.61±0.89
Mineral fertilization NPK (M)	9.92^{ab}±0.69	9.63^{a}±0.49	9.78±0.62
Pig FYM (PF)	10.66^{bc}±0.37	10.24^{abc}±0.29	10.56±0.35
Sewage sludge (SS)	9.79^{ab}±0.40	9.82^{ab}±0.31	9.81±0.36
Compost (C)	9.58^{a}±0.27	9.81^{ab}±0.18	9.70±0.26

Means marked by the same letters did not differ significantly at $\alpha < 0.05$ according to the Duncan test; factors fertilization × year

It has been generally assumed that humus with a higher value of Cha:Cfa ratio is characteristic for more fertile soils. Evaluation of humus compounds on the basis of this index revealed that the applied fertilization, despite increasing the content of both humic and fulvic acid carbon, in fact did not cause any major changes in this parameter value (Table 5). Zukowska et al [20] obtained similar results. According to Rivero et al [4] significant changes in the value of discussed parameter might have been caused by bigger doses of the applied organic materials. It should be also noted that under conditions of the discussed experiment a monoculture cultivation of wheat was conducted, which might have significantly affected the value of Cha:Cfa ratio. It should be emphasized that beside the kind of applied organic materials and their doses also the crop rotation had a significant influence on the content of humic and fulvic carbon acids fraction and in result on Cha:Cfa value. Strictly speaking, the kind of post-harvest residue has a most important influence on the qualitative parameters of soil organic matter and on their amount.

Table 5

Ratio Cha : Cfa and A4/6

Objects	After 1st year	After 3rd year	Mean
	Cha : Cfa		
No fertilization (0)	0.66^{ab}±0.06	0.63^{ab}±0.03	0.65±0.05
Mineral fertilization NPK (M)	0.54^{a}±0.05	0.56^{ab}±0.05	0.55±0.05
Pig FYM (PF)	0.58^{ab}±0.15	0.56^{ab}±0.08	0.57±0.12
Sewage sludge (SS)	0.58^{ab}±0.12	0.58^{ab}±0.06	0.58±0.09
Compost (C)	0.70^{b}±0.09	0.64^{ab}±0.03	0.67±0.07
	A4/6		
No fertilization (0)	5.20^{a} ±0.06	5.58^{bc}±0.07	5.39±0.20
Mineral fertilization NPK (M)	5.09^{a}±0.11	5.55^{bc}±0.02	5.23±0.24
Pig FYM (PF)	5.13^{a}±0.16	5.56^{b}±0.12	5.29±0.26
Sewage sludge (SS)	5.45^{b}±0.07	5.66^{bc}±0.08	5.56±0.13
Compost (C)	5.56^{bc}±0.13	5.75^{c}±0.12	5.66±0.16

Means marked by the same letters did not differ significantly at $\alpha < 0.05$ according to the Duncan test; factors fertilization × year

Applied fertilization, particularly with organic materials caused a significant increase in non-hydrolysing carbon content (Table 4). Also Zukowska et al [20] reported a significant increase in this fraction of soil humus in effect of fertilization with sewage sludge, attributing it to the supply of not fully humified organic substance to the soil. This observation was confirmed by the investigations of Filipek-Mazur et al [9].

Computed absorbance coefficient A4/6 of humic acid solutions did not reveal any major changes between soils from individual treatments (Table 5). Residual effect of applied fertilization clearly increased this parameter value. Increasing value of absorbance ratio 4/6 may evidence a marked decrease in the degree of humic acids particles or greater aliphatisation and higher number of functional groups [4]. Also Pedra et al [21], using compost produced from municipal wastes and anaerobically stabilized sludge for fertilization, demonstrated an increase in the value of absorbance coefficient A4/6, associating the changes of the discussed parameter with diminishing the condensation degree of humic acid particles and greater aliphatisation. Results of research published by Aranda et al [22] indicate greater changes of organic matter quality concerning aromatization of humic acids. According to Zukowska et al [20] only fertilization with sewage sludge dosed 600 $Mg \cdot ha^{-1}$ affected a significant decrease in the dimension and degree of humic acid particles condensation. According to Debska [19], one of the indices used for an assessment of the degree of organic materials humification process advancement and the characteristics of formed humus substances, may be the value of absorbance ratio A4/6. At the early stages of formation, humic acids generally with smaller molecular mass and lower degree of aromatic structures condensation, are characterized by higher values of A4/6 ratio. Optical properties of soil humic acids may change not only under the influence of soil forming processes or fertilization but also organic matter may originating from postharvest residue may affect their properties. the same plant was cultivated each year in the discussed experiment, therefore the value of A4/6 ratio was basically shaped by the applied fertilization, although it cannot be assumed that the amount of postharvest residue was identical in each year of the experiment.

Conclusions

1. Irrespective of the year of research, organic carbon concentrations in soil did not increase significantly after the application of organic materials as fertilizers in comparison with the value assessed in the soil of treatment where mineral NPK fertilization was applied.
2. The content of low-molecular humus compounds extracted from the soil by H_2SO_4 solution was small, independently of applied fertilization and year of the experiment. However, it should be noticed that after the third year of research, a significant increase in this humus fraction was registered in the soil of all fertilized treatments.
3. After the first year of the experiment the highest concentrations of carbon in alkaline extract were assessed in the soil of the treatment where manure was used. Carbon content in alkaline extract (after the third year of the research) increased significantly in soil of all treatments in comparison with the content assessed in the soil receiving mineral fertilization.
4. The content of humic acid carbon was lower than fulvic acid carbon, which resulted in lower than one values of Cha : Cfa ratio. Research results obtained after the third year of the experiment point to a considerable increase in both humus fractions content in result of a residual effect of the applied fertilization.
5. Absorbance coefficient A4/6 of humic acid solutions did not reveal any major changes between the soil of individual treatments. Residual effect of the applied fertilization increased visibly this parameter value.

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ILOŚĆ I JAKOŚĆ MATERII ORGANICZNEJ W GLEBIE PO APLIKACJI RÓŻNYCH MATERIAŁÓW ORGANICZNYCH

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Abstrakt: Zawartość węgla organicznego w glebie, niezależnie od roku badań, znacznie zwiększyła się po zastosowaniu do nawożenia gleby materiałów organicznych, w porównaniu do gleby z obiektu, w którym zastosowano nawożenie mineralne NPK. Zawartość niskocząsteczkowych związków próchnicznych wyekstrahowanych z gleby roztworem H_2SO_4 była niewielka bez względu na zastosowane nawożenie oraz rok badań. Niemniej, po trzecim roku badań stwierdzono istotne zwiększenie zawartości tej frakcji próchnicy w glebie wszystkich obiektów, w których zastosowano nawożenie. Po trzecim roku badań zawartość węgla w ekstrakcie alkalicznym istotnie zwiększyła się w glebie wszystkich obiektów, w których zastosowano nawożenie materiałami organicznymi, w porównaniu do zawartości w glebie z obiektu, w którym zastosowano nawożenie mineralne NPK. Zawartość węgla kwasów huminowych w glebie była mniejsza od zawartości węgla kwasów fulwowych, co skutkowało mniejszymi od jedności wartościami ilorazu Ckh:Ckf. Uzyskane wyniki wskazują jednak na znaczące zwiększenie obu frakcji próchnicy w wyniku następczego działania zastosowanego nawożenia. Efektem następczym zastosowanego nawożenia było zwiększenie współczynnika absorbancji A4/6, co wskazuje na zmniejszenie stopnia skondensowania cząsteczki kwasów huminowych oraz większą alifatyzację.

Słowa kluczowe: gleba, materia organiczna, materiały organiczne, osady ściekowe