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Humus content in a podzolized chernozem after a long-term application of fertilizers in a field crop rotation

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Abstract. The article presents the results of the research into influence of a long-term (50 years) application of different fertilizer rates and fertilizer systems in the field crop rotation on the humus composition and optical parameters of humic acids of a heavy- loamy podzolized chernozem of the Right Bank Forest-Steppe of Ukraine.
It was found that application of fertilizers significantly affects the dominance of humic acids over fulvic acids in the composition of soil, which indicates humate type of soil. Chroma index of humic acids is within 3.56–3.75 depending on a fertilizer. Indicators of the optical properties of humic acids of a podzolized chernozem have a high degree of humification.

Key words: humus, humic acids, fulvic acids, optical density, fertility, podzolized chernozem, fertilizers, field crop rotation.

INTRODUCTION

Humus content in soil is the main indicator of potential soil fertility, therefore conservation, maintenance and restoration of humus are the main tasks of agriculture. The direction of transformation processes of organic matter in the soil in general characterizes the degree of quantitative changes of humus. The study of such changes caused by a long-term influence of fertilizers is especially important for the soils low in organic matter (Mazur, 2002). Podzolized chernozems refer to this type of soils and are prevailing in the Right Bank Forest-Steppe of Ukraine.

Humus level in soil covers a set of morphological features and chemical properties of humus that allows to detect specific forms and types of humus. In this case humus forms are characterized and distinguished according to morphological characteristics, and type of humus is defined as a result of detection of humic substances. The content, reserves and quality of humus belong to the most important indicators, since almost all agronomically valuable soil properties depend from their level (Nosko, 1990).

In contemporary arable farming the issue of soil fertility and efficient soil management remains one of the most urgent. Over recent years the amount of applied mineral fertilizers has decreased by 8–10 times, organic fertilizers – by 4–5 times.

Annual losses of humus under existing structure of cultivated areas in the Forest-Steppe make up 0.6–0.7 t ha^{-1} (Shedey, 2005; Tsvey, 2010). Therefore, this situation requires a comprehensive approach to improving soil fertility, and especially to the efficient use of fertilizers.

The aim of the research was to define the changes in the indexes of humus content of a podzolized chernozem under the influence of a long-term application of various fertilizer rates and fertilizer systems in a field crop rotation in order to improve their monitoring and to specify the rules and recommendations for a safe application of fertilizers.

MATERIALS AND METHODS

This research was carried out on the experimental field of Uman National University of Horticulture in the stationary experiment of the Department of Agrochemistry and Soil Science. The experiment was launched in 1964, and it is based on a 10-field crop rotation extended – in time and space (spring barley + meadow clover, meadow clover, winter wheat, sugar beet, corn, peas, winter wheat, silage corn, winter wheat, sugar beet).

The following fertilizer systems were used in the crop rotation: organic (manure 9 tons, 13.5 tons, 18 tons), mineral ($N_{45}P_{45}K_{45}$; $N_{90}P_{90}K_{90}$; $N_{135}P_{135}K_{135}$) and organic-mineral (manure 4.5 tons + $N_{22}P_{34}K_{18}$; manure 9 t + $N_{45}P_{68}K_{36}$; manure 13.5 t + $N_{67}P_{102}K_{54}$). Fertilizer rates are specified per 1 ha of crop rotation area.

Before the experiment the soil was under a long-term cultivation under field crops, hence it was a degraded, 'plowed-out' soil. Soils samples taken before the experiment (1964) had the following parameters: content of physical clay – 66.5%, base saturation – 95%, humus content – 3.31%; content of easily hydrolysable organic nitrogen (according to the Tiurin – Kononova method); mobile compounds of phosphorus and potassium (according to Chirikov method) – 122 and 135 mg kg^{-1}; pH_{KCl} – 6.2 respectively.

In the soil samples the carbon content was determined by the method of I.V. Tiurin in the modification of the *Central Research Institute* of *Agrochemical* Maintenance of Agriculture (Orlov, 1992), its factional and group composition – by the method of I.V. Tiurin in the modification of V.V. Ponomareva & T.A. Plotnikova (1980). Optical density of sodium humate solutions was determined by photocolorimeter with a set of light filters at the wavelengths of 430, 465 and 665 nμ. Concentration of the 1st and 2nd fractions of humic acids (HA-1 + HA-2) was calculated by the Bouguer-Lambert-Beer general formula. Chroma index of humic acids was determined according to the ratio of optical density of sodium humate solutions at a wavelength 465 nμ to a corresponding value at the wave length 665 nμ. To characterize soil humus we include humification index according to the recommendation of D.S. Orlov in the system of indexes of humus content in soil.

To evaluate the accuracy of experimental data we used confidence interval derived via mathematical statistics program of application software Statistica 6.0

RESULTS AND DISCUSSION

The research results showed that a long-term systematic use of soil in agricultural production led to to the reduction in humus content compared to the figures at the time when the experiment was launched (Table 1).

Table 1. The content of humus in a podzolized chernozem after a long-term (50 years) application of fertilizers in field crop rotation, %

Variant of experiment	Layer of soil, cm				
	0–20	20–40	40–60	60–80	80–100
Before the experiment	3.31 ± 0.13	3.00 ± 0.21	2.74 ± 0.12	1.98 ± 0.15	1.58 ± 0.09
Without fertilizers (control)	2.73 ± 0.22	2.43 ± 0.22	2.19 ± 0.19	1.90 ± 0.14	1.56 ± 0.06
$N_{45}P_{45}K_{45}$	2.76 ± 0.15	2.65 ± 0.22	2.39 ± 0.14	1.93 ± 0.16	1.56 ± 0.07
$N_{90}P_{90}K_{90}$	2.80 ± 0.15	2.61 ± 0.20	2.38 ± 0.12	1.94 ± 0.16	1.54 ± 0.09
$N_{135}P_{135}K_{135}$	2.84 ± 0.16	2.69 ± 0.20	2.36 ± 0.17	1.93 ± 0.10	1.58 ± 0.05
Manure 9 t	2.88 ± 0.10	2.73 ± 0.16	2.40 ± 0.13	1.94 ± 0.13	1.58 ± 0.07
Manure 13,5 t	3.03 ± 0.17	2.80 ± 0.11	2.39 ± 0.12	1.95 ± 0.16	1.59 ± 0.07
Manure 18 t	3.24 ± 0.11	2.95 ± 0.15	2.51 ± 0.14	1.98 ± 0.09	1.55 ± 0.11
Manure 4.5 t + $N_{23}P_{34}K_{18}$	3.16 ± 0.15	2.91 ± 0.13	2.63 ± 0.17	1.98 ± 0.08	1.55 ± 0.09
Manure 9 t + $N_{45}P_{68}K_{36}$	3.34 ± 0.17	3.03 ± 0.12	2.79 ± 0.15	1.98 ± 0.06	1.58 ± 0.05
Manure 13.5 t + $N_{68}P_{101}K_{54}$	3.39 ± 0.17	3.14 ± 0.13	2.89 ± 0.18	1.99 ± 0.08	1.56 ± 0.07

At the same time fertilization systems, that had been studied, influenced the content of humus in different ways. Thus, under mineral system in the layer of 0–20 cm of soil the humus content reduced by 0.47–0.55 abs.% compared with its content at the time when the experiment was launched, however, when we compare it with control, we observe inessential increase (by 0.03–0.11 abs.%), that is, within experimental error. Other scientists observed a similar impact of mineral fertilizers on the humus content in the soil (Brock et al., 2013; Kõlli & Tamm, 2013; Kõlli et al., 2015).

Application of semi decomposed manure contributed to the conservation of the humus content in the soil at the level of 2.88–3.24%. In this case the content of humus depended on the rate of its application and was higher with increasing application rates. That is, in the variant of experiment with a high rate of manure (18 tons ha^{-1}) humus content equaled the index value at the time when the experiment began (3.31%). It proves that organic fertilizers are a source of energetic material for soil microorganisms that contribute to enhancing the process of humus formation. Combined application of organic and mineral fertilizers was the most significant among the variants that were studied in the experiment and contributed to the formation and accumulation of humus in the soil.

In the 0–20 cm layer of soil under the first level of organic-mineral fertilizer system the humus content made up 3.16%, which is by 0.43% more than in the control variant. The concept of qualitative composition of humus is wider and includes both the ratio between the amount of carbon in the different fractions within two groups (humic and fulvic acids), and the amount of carbon of insoluble residue. All above mentioned compounds form the humus of the soil. While studying humus level of the soil it is very important to investigate fraction-group composition of humus (Table 2).

Table 2. Fractional-group composition of humus (layer 0–20 cm) of podzolized chernozem after a long-term (50 years) fertilizers application in field crop rotation

Variant of experiment	C_{total}, %	Humic acids (HA): HA–1	HA–2	HA–3	Amount	Fulvic acids (FA): FA–1a	FA–1	FA–2	FA–3	Amount	$C_{ha}+C_{fa}$	Humin	$C_{ha} : C_{fa}$
		in % from C_{total}											
Without fertilizers (control)	1.58	6.4	18.1	9.9	34.4	2.4	4.7	6.6	3.5	17.2	51.6	48.4	2.00
$N_{45}P_{45}K_{45}$	1.60	5.7	19.6	9.7	35.0	1.9	4.4	6.9	3.7	16.9	51.9	48.1	2.07
$N_{90}P_{90}K_{90}$	1.62	5.5	20.7	10.4	36.6	2.0	4.5	7.0	3.3	16.8	53.4	46.6	2.18
$N_{135}P_{135}K_{135}$	1.65	6.0	21.6	10.8	38.4	1.9	4.3	7.4	3.1	16.7	55.1	44.9	2.30
Manure 9 t	1.67	5.4	21.9	9.6	36.9	2.6	3.9	6.9	3.3	16.7	53.6	46.4	2.21
Manure 13.5 t	1.76	5.8	22.8	10.9	39.5	2.4	3.5	7.0	3.1	16.0	55.5	44.5	2.47
Manure 18 t	1.88	5.8	23.9	11.6	41.3	1.7	3.2	6.8	3.2	14.9	56.2	43.8	2.77
Manure 4.5 t + $N_{23}P_{34}K_{18}$	1.83	5.9	22.9	10.3	39.1	1.9	3.9	6.3	3.4	15.5	54.6	45.4	2.52
Manure 9 t + $N_{45}P_{68}K_{36}$	1.94	6.1	24.7	11.4	42.2	1.5	3.5	6.1	3.0	14.1	56.3	43.7	2.99
Manure 13.5 t + $N_{68}P_{101}K_{54}$	1.97	6.6	25.4	11.6	43.6	1.5	3.2	6.1	3.0	13.8	57.4	42.6	3.16

Research showed that fractional-group composition of humus changed depending on the particularities of fertilizer application judging by the change in fractions of humic (HA) and fulvic acids (FA) in the humus content, they differed significantly after a long-term application of various fertilizer rates and systems in field crop rotation.

The result of the research into the group composition of humus of podzolized chernozem showed that fertilizers had a significant impact on the content of humic and fulvic acid groups in humus. So, the application of $N_{45}P_{68}K_{36}$ with 9 t ha^{-1} of manure led to the increase in humic acids in the soil layer of 0–20 cm to 42.2%, which is by 2% higher compared to the variant with the application of 18 tons of manure per 1 ha of crop rotation area and the variant $N_{90}P_{90}K_{90}$ – by 15% respectively.

The amount of humic acids in all variants of the experiment of field crop rotation in the layer 0–20 cm varied within 34.4–43.6% of the total carbon content in the soil (C_{total}). This indicates a high degree of humification of organic substances (Borisova et al., 2005). The content of humic acids in the soil in a field crop rotation under mineral, organic and organic-mineral fertilizer systems compared to unfertilized plots was higher by 2–12%, 7–20% and by 14–27% respectively.

The fraction of fulvic acids, depending on the variant of the experiment was within 13.8–17.2% of the total carbon content in the soil. Under mineral fertilizer system fulvic acid amount decreased by 2–3%, under organic – by 2–13%, and under organic-mineral – by 10–20 % compared with unfertilized plots. It indicates that organic fertilizers, either alone or in combination with mineral fertilizers are an important factor in increasing the overall content of humus in the soil, as well as humic acid groups (Graefe & Beylich, 2006; Kõlli, Graefe & Tamm, 2015; Andreetta et al., 2016; Bödeker et al., 2016; Paterson et al., 2016; Baskaran et al., 2017).

Depending on the variant of the experiment the fractional composition of humic acids in the soil layer of 0–20 cm shows that fraction of humic acids bound with calcium (HA–2) prevails and makes up 18.1–25.4% of the amount of C_{total}. Fraction of free humic acids and bound with mobile sesquioxide (HA–1) makes up the smallest part – 5.4–6.6% in the content of organic carbohydrate. Fraction of humic acids bound with clay minerals and stable sesquioxide (HA–3) falls in between in the composition of fulvic acids and made up 9.6–11.6%.

In the composition of fulvic acids prevails the fraction bound with HA–2 (FA–2) and makes up 6.1–7.4% of the total content of organic carbon. Whereas corresponding parts of fractions of free fulvic acids and bound with mobile sesquioxides (FA–1a), bound with HA–1 (FA–1) and bound with HA–3 (FA–3) make up 1.5–2.6%; 3.2–4.7 and 3.0–3.7 % respectively.

The part of insoluble residue (humin) decreased compared with unfertilized plots depending on fertilizer rates by 1–7% under mineral, by 4–9% – under organic and by 6–12% – under organic-mineral fertilizer systems.

A long-term use of fertilizers in a field crop rotation greatly influenced the increase of humic acids in the humus content over fulvic acids, and led to the expansion of ratio C_{ha}: C_{fa}. Therefore, the ratio of carbon of humic and fulvic acids in the 0–20 cm layer of soil in field crop rotation was within 2.07 to 3.16 depending on the particular fertilizing. Accordingly, there was a humate type of humus in all variants of the experiment. Comparing the ratio of C_{ha}: C_{fa} in the soil under various fertilizer systems in a field crop rotation, we can conclude that the application of organic fertilizers and their combinations with mineral fertilizers contributes more to the accumulation of humic acid groups than– fulvic acids and changes the type of humus into humate direction.

Besides fractional-group composition of humus, the study of changes in the optical properties of humic acids under different soil fertilizing is also an important indicator of soil formation. The research carried out by (Kononova, 1972) proved that the data on the optical density of humic acids bound with calcium (HA–2) is essential to determine the patterns of change in the extinction coefficient (E). These acids are the most optically dense as compared with other fractions of humic acids in podzolized soils.

A study of the optical density of the HA–2 in the 0–20 cm layer of podzolized chernozem showed (Table 3) that the extinction coefficient at the wavelength of 430 nμ was 22.14–24.83, at 465 nμ – 16.72–19.35 and at 665 nμ – 4.70–5.86, depending on the rates and systems of fertilizer application. In the experiment with unfertilized plots the optical density coefficient was 21.67, 16.45 and 3.66 respectively, which indicates the saturation of the HA–2 with aliphatic chains and the relatively young nature of their molecules.

Under application of mineral fertilizers in field crop rotation degree of condensation of HA–2 increased compared to unfertilized plots at the wavelength of 430 nμ by 7–11%, at 465 nμ – by 8–12% and at 665 nμ – by 28–31% respectively, indicating mineralization of HA–2 due to the decrease of aliphatic hydrocarbon chains in their structure.

Application of organic fertilizers in the field crop rotation provided accelerated mineralization of aliphatic hydrocarbon chains of HA–2, which is proved by the increase in degree of condensation of HA–2 by 8–13%, 11–16% and 30–38% respectively. Under organic-mineral fertilizer system there was an increase in the depth of humification.

Table 3. Coefficients of the optical density of humic acids HA – 2 fraction (layer 0–20 cm) of podzolized chernozem after a long – term (50 years) usage of fertilizers in field crop rotation

Variant of experiment	Wavelength, nμ			E_{465}/E_{665}	$E_4^{0,001}$
	E_{430}	E_{465}	E_{665}		
Without fertilizers (control)	21.67 ± 0.79	16.45 ± 1.62	3.66 ± 0.21	4.49	0.122
$N_{45}P_{45}K_{45}$	23.14 ± 1.09	17.72 ± 1.68	4.70 ± 0.24	3.56	0.124
$N_{90}P_{90}K_{90}$	23.49 ± 1.82	18.12 ± 1.19	4.74 ± 0.24	3.61	0.128
$N_{135}P_{135}K_{135}$	24.03 ± 1.69	18.39 ± 1.33	4.78 ± 0.17	3.64	0.133
Manure 9 t	23.37 ± 1.14	18.28 ± 1.18	4.77 ± 0.25	3.62	0.128
Manure 13,5 t	23.81 ± 1.27	18.71 ± 1.61	4.83 ± 0.22	3.67	0.132
Manure 18 t	24.45 ± 1.72	19.02 ± 1.43	5.06 ± 0.27	3.56	0.137
Manure 4.5 t + $N_{23}P_{34}K_{18}$	23.73 ± 1.20	18.42 ± 0.68	4.78 ± 0.22	3.64	0.129
Manure 9 t + $N_{45}P_{68}K_{36}$	24.52 ± 2.27	19.17 ± 0.98	4.84 ± 0.25	3.75	0.135
Manure 13.5 t + $N_{68}P_{101}K_{54}$	25.83 ± 2.73	20.35 ± 1.29	5.26 ± 0.25	3.68	0.138

This ensured the maximum value of the optical density of HA–2. The highest level of optical density was at wavelengths 430, 465 and 665 nμ and made up 25.83, 20.35 and 5.26 respectively in the variant, when 13.5 tons of manure was applied per 1 ha of the area under crop rotation.

To compare the characteristics of the optical properties of humic acids it is common to use the ratio of the extinction coefficients at the wavelengths of 465 nμ and 665 nμ (chroma index). Chroma index is not dependent on the carbon concentration in the solution, so it is characteristic value for humic acids of different soils.

The lower the ratio is, the greater participation of concentrated aromatic nucleus and, consequently, less – of aliphatic side chains was in the construction of molecules of humic substances (Boguta et al., 2016). Calculations showed that chroma index was higher in the variant with unfertilized plots and made up 4.49, which means a better structuring of humic acids. In variants of the experiment with the application of fertilizers in the field crop rotation chroma index was within 3.56–3.75, which is typical for a podzolized chernozem and indicates a high optical density due to predominance of black humic acids bound with calcium in its composition. (DiDonato et al., 2016; Kimura et al., 2017; Jin et al. 2018).

Coefficients of the Bouguer-Lambert-Beer equation are widely used (E-value at a wavelength of 465 nμ, solution concentration of 0.001% and a cuvet length of 1 cm – $E_4^{0.001}$) to characterize humic acids. Orlov et al. (1996) gives a mean value $E_4^{0.001}$ of humic acids for chernozems within 0.113–0.131, in the variants under investigation the value of this parameter in the layer of 0–20 cm made up 0.112–0.138, which allows us to refer this soil to a podzolized chernozem.

According to the recommendation of Orlov the humification indicator, that takes into account the amount of humic acids as well as their quantity, was included into the system of parameters defining humus level in soils.

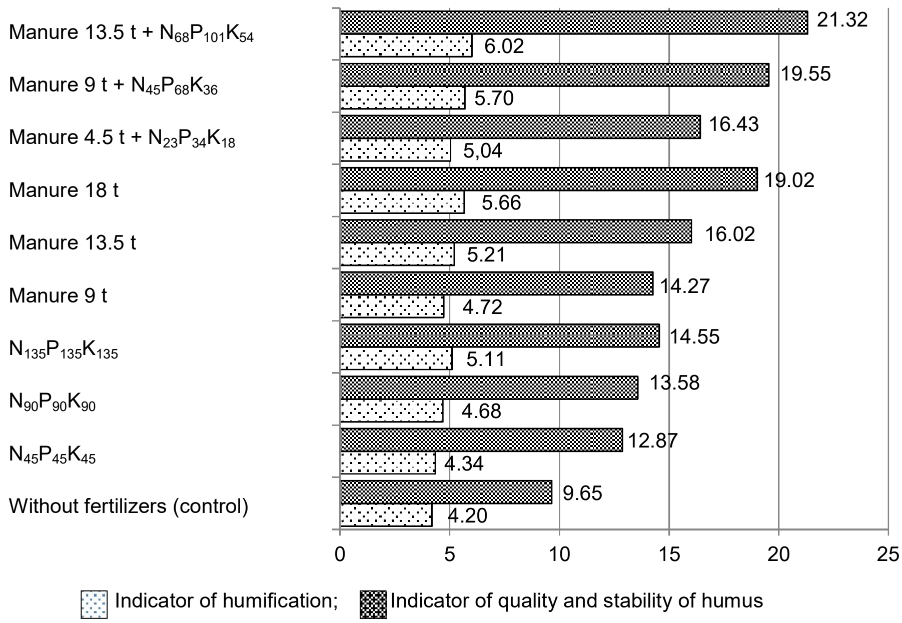

Figure 1. Indicators of the optical properties of humic acids of HA – 2 fraction of podzolized chernozem after a long-term (50 years) usage of fertilizers in field crop rotation.

According to this indicator the soil of studied variants under mineral, organic and organic-mineral fertilizer systems had a high degree of humification (4.34–6.02), that indicates that it is a podzolized chernozem (see Fig. 1). A slight decrease in the index of humification was observed in the soil plots without a long-term fertilizing and made up 4.20, which was by 10% less than in the experimental variant $N_{90}P_{90}K_{90}$ and by 26% in the variant with Manure 18 tons and Manure 9 tons + $N_{45}P_{68}K_{36}$.

One of the important criteria of the optical properties of humic acids is the indicator of the quality and stability of humus proposed by Fernández-Romero et al. (2016) and Melnik & Kowalczuk (2018).

The highest index of quality and stability of humus was 21.32 in the variant when 13.5tons of manure and $N_{68}P_{101}K_{54}$ were applied. The value of this index showed the signs of improving the humus content in soil.

CONCLUSIONS

1. Fractional-group composition of humus of a podzolized chernozem after a long-term (50 years) application of different rates of fertilizers and fertilizer systems in crop rotation is characterized by the predominance of humic acids over fulvic acids and this leads to an expansion of the ratio C_{ha}: C_{fa}, which indicates humate type of soil. The fraction of humic acids bound with calcium (HA–2) makes up 18.1–25.4% of C_{total} and prevails in the fraction of humic acids. The fraction of fulvic acids bound with HA–2 (FA–2) makes up 6.1–7.4% of $C_{total\ and}$ prevails in the fraction of fulvis acids.

2. These data indicate that podzolized chernozem after a long-term systematic application of fertilizers had a high optical density of humic acids which is characteristic for the soils of a chernozem type. Chroma index is characteristic for a podzolized

chernozem (3.56–3.75), and indicates a high optical density due to the predominance of black humic acids bound with calcium in its composition.

3. In terms of the optical properties of humic acids podzolized chernozem had a high degree of humification, which provides high and stable indicators of humus content in soil.

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