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THE IMPACT OF DIFFERENT FERTILIZATION SYSTEMS ON CONTENT, COMPOSITION, ENERGY INTENSITY OF ORGANIC MATTER IN CHERNOZEM SOIL

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Aim. To determine the regularities of the transformation of quality and quantity composition of humus, its energy intensity at long-term fertilization of soils. **Methods.** Long-term stationary experiments were conducted on chernozem soils of different granulometric compositions. The analytical work was done in the certified laboratory in accordance with the current normative documents: preliminary treatment of samples for physical and chemical analysis (DSTU ISO 11464); determination of dry substance and humidity by the mass – by the gravimetric method (DSTU ISO 11465). Mass fraction of total carbon was determined by the oxidimetric method (DSTU 4289:2004); humus group composition − by Turin's method in the modification of Ponomariova and Plotnikova (DSTU 7828:2015); low heating value of the soil and organic material − by the calorimetric method using B-08-MA set (DSTU 7866:2015); preparations of humic substances were isolated according to DSTU 7606:2014. **Results.** Long-term fertilization promotes considerable changes in the quality composition of the whole system of humic substances of chernozems of different granulometric compositions. It also has a different impact on the energy accumulation both in the soil and in humic acids (HA). **Conclusions.** The new formation of HA in typical heavy loamy chernozem with organic and mineral fertilization systems occurs due to the second and third fractions on the background of the decrease in the first and the most mobile fraction of HA. The mobility degree of the whole system of humic substances under the impact of different fertilization systems does not differ from the control considerably; the tendency towards the increase in this index was observed only for the mineral fertilization system. In the organic and mineral fertilization systems, the new formation of HA in typical weak alkali light loamy chernozem occurs due to the first and second fractions. The aggravation of HA structure and the increase in the degree of condensation was registered only for the organic fertilization system. The level of mobility of the whole system of humic substances in this soil is increased compared to the control under the impact of the organic and mineral fertilization systems. A considerable difference in the indices of energy, present in the soil and HA fractions, isolated from this soil, was determined. The maximal amount of energy is in labile forms of HA – in the range of 10.62−15.85 MJ/kg, the smallest amount – in the fractions, tightly connected to the mineral part of the soil (1.47−4.09 MJ/kg). The amount of energy is in direct relationship to the applied agrotechnical means, which is in good agreement with the data on the impact of different fertilization systems on the humic condition of soils.

Keywords: chernozems, fertilization systems, humus, humic acids, energy capacity.
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INTRODUCTION

It is known [1] that the anthropogenic impact on soil leads to the changes in chemical, physical, agrochemical, physical-chemical, and biological properties, in particular, in the amount and quality of humus. The experimental studies on humic substances are directed towards the study of the composition, structure, and functions of humic substances [1–5]. The results of the analysis of humic substances are controversial on many issues. Regardless of numerous current experimental works and theories, the issue of the role of humic sub-

stances in the processes of transformation of the main indices of soil fertility is still urgent [6–9].

Long-term experiments provide an enormous amount of information about the level of productivity and quality of the agricultural products, the status of soil fertility, the impact of different intensity of using chemization means on the main components of agroecosystems. This is the only correct way, which ensures deeper understanding of the main regularities of the agrogenic impact on each component of agroecosystems and the whole system in general [10].

Recently the energetic principle of estimating the circulation of substances and energy has been used to characterize the agricultural systems in general and some chains in particular [11]. The studies have determined that soil contains considerable stocks of active energy. The higher the humus-related energy is, the higher soil performance is. The main energy accumulator in humus is humic acids (HA); their share is about 40 % of the total amount of energy in humus [12].

The study was aimed at determining the regularities of the transformation of quantity and quality composition of humus, its energy intensity at long-term fertilization of chernozem soils.

MATERIALS AND METHODS

The work was performed in stationary experimental fields of Poltava IAIP on typical heavy loamy chernozem (established in 1964) and Myronivka Wheat Institute – on typical weak alkali light loamy chernozem (established in 1912). Soil samples were collected from the 0–20 cm soil layer on the following variants: without fertilizers (control); organic fertilization system; mineral fertilization system. Comparison variants were fallow and wild land.

The analytical work was done in the certified laboratory in accordance with the current normative documents: preliminary treatment of samples for physical and chemical analysis (DSTU ISO 11464); determination of dry substance and humidity by the mass – by the gravimetric method (DSTU ISO 11465); mass fraction of total carbon was determined by the oxidimetric method (DSTU 4289:2004); fraction and group composition of humus − by Turin's method in the modification of Ponomariova and Plotnikova (DSTU 7828:2015); low

Table 1. The impact of long-term fertilization in field crop rotations on the group and fraction composition of humus

Index	Typical heavy loamy chernozem					Typical weak alkali light loamy chernozem			
	Control	Manure	NPK	Fallows	Wild land	Control	Manure	NPK	Wild land
C_{total}, %	2.71	2.76	2.92	2.83	3.89	2.11	2.29	2.05	3.08
Humus, %	4.67	4.76	5.03	4.88	6.71	3.64	3.95	3.53	5.31
C_{HA}, % to C_{total}	36.2	52.2	47.6	37.5	43.8	29.8	33.2	36.6	25.3
Humification degree	High	Very high		High	Very high	Average	High		Average
C_{FA}, % to C_{total}	28.4	15.9	18.5	21.9	14.0	40.2	24.5	38.5	32.8
C_{HA}/C_{FA}	1.27	3.27	2.57	1.71	3.13	1.74	1.36	0.95	0.77
Type of humus	FH	H		FH	H	FH		HF	
$C_{HA}1$, % to C_{total}	3.7	1.5	1.7	1.1	5.3	1.8	2.6	6.3	3.9
C_{HA}, % to C_{total}	15.5	26.8	31.5	27.9	20.4	25.0	27.9	27.3	17.9
$C_{FA}1$, % to C_{total}	6.6	8.4	9.3	7.0	3.6	11.4	10.9	4.6	11.0
$C_{FA}2$, % to C_{total}	8.1	1.8	2.1	7.4	9.7	15.6	7.9	19.0	12.0
$C_{HA}1/C_{FA}1$	0.83	0.24	0.24	0.25	1.50	0.17	0.24	0.43	0.35
$C_{HA}2/C_{FA}2$	1.91	14.80	15.33	3.76	2.09	1.61	3.56	1.44	1.48
SMDhs	0.19	0.17	0.20	0.10	0.18	0.23	0.31	0.39	0.35

Note. FH – fulvic-humic type of humus, H – humic type of humus, HF – humic-fulvic type of humus, SMDhs – system mobility degree of the whole system of humic substances.

heating value of the soil and organic material − by the calorimetric method using B-08-MA set (DSTU 7866:2015); preparations of humic substances were isolated according to DSTU 7606:2014: the extraction took place due to consecutive treatment of soil samples with the solution of sulfuric acid, molar concentration $c(1/2H_2SO_4)$ = 0.1 mol/cubic decimeter (decalcification) with further isolation of HA using potassium hydroxide and their precipitation, the purification by centrifugation and drying under the flow of warm air and breaking. Humus condition was estimated by the system of indices, suggested by Orlov *et al.* [13]. To characterize the intensity of humification process on different stages, the indices of the quantitative ratio of humic acids of fractions 1 and 2 to the corresponding fractions of fulvic acids (FA) were used; $C_{HA}1/C_{FA}1$ – to evaluate the intensity of the process of new formation of humic acids and the formation of their mobile forms; $C_{HA}2/C_{FA}2$ – to evaluate the intensity of polymerization of humic structures and formation of humates [4]. The mobility degree of the system of humic substances (SMDhs) was determined by the ratio of the sum of mobile fractions (HA1 + FA1) to the sum of stable fractions (HA2 + HA3 + FA2 + FA3) of humic substances.

RESULTS AND DISCUSSION

It was determined that the long-term application of fertilizers causes the differentiation of soil fertility by the level of humus content and qualitative changes of the organic matter (Table 1). While the long-term introduction of mineral fertilizers led to increase of humus content by 7.7 % in typical heavy loamy chernozem, the introduction of organic fertilizers had a somewhat lesser positive effect (increase by 1.8 % only). As of the moment of samples collection, humus content on the fallow was at the level of 4.88 % and on the wild land – 6.71 %.

Long-term fertilization promoted considerable changes in the quality composition of the whole system of humic substances. The 3-fold decrease in the content of "free" humic acids (HA1) compared to the control with no fertilizers was noted for organic and mineral fertilization systems. The content of this fraction of humic acids in the wild land turned out to be 1.3-fold higher than that for the control. The introduction of both organic and mineral fertilizers promoted the increase in the content of humic acids, connected with calcium (HA2), in humus. The content of this fraction in humus of the wild land soil was at the level of the control; the amount of HA2 fraction increased twice, compared to the control, in fallow humus.

The content of tightly bound HA (HA3) in humus decreased after the introduction of mineral fertilizers in the fallow down to the "low" level by the scale of Orlov *et al.* [13]. The application of organic and mineral fertilization systems promoted the increase in the degree of humification for the organic substance of the soil, the change in humus type for the humic one (in the control and fallow the humus type is fulvic-humic). The $C_{HA}2/C_{FA}2$ ratio is the reflection of the second stage of humification, which is remarkable for the aggravation of HA structure and the increase in the condensation degree [4]; it expands considerably in typical chernozem with organic and mineral fertilization systems. The $C_{HA}1/C_{FA}1$ ratio reflects the first stage of humification or the process of new formation of HA. The new formation of HA in typical heavy loamy chernozem with organic and mineral fertilization systems occurs due to the second and third fractions on the background of the decrease in the first, the most mobile fraction of HA. The mobility degree of the whole system of humic substances in this type of chernozem under the impact of studied fertilization systems did not differ from the control considerably; the tendency towards the increase in this index was observed only for the mineral fertilization system.

After long-term application of the organic fertilization system on typical weak alkali light loamy chernozem, some advantage was registered for the humus content (the increase by 8 %) compared to the control; the content of humus decreased by 3 % for the mineral fertilization system. In the wild land (the comparison variant) the content of total humus in the soil was at the level of 5.3 % (1.5-fold higher than that for the control).

The content of the mobile fraction of HA (HA1) after the introduction of mineral fertilizers increased 2.7-fold compared to the control; after the addition of organic fertilizers – 1.2-fold, and on the wild land – 3.6-fold. There were no significant changes observed regarding the content of fractions HA2 and HA3 for different fertilization systems, but the content of humins in the wild land and the soil after the introduction of manure increased 1.4-fold compared to the control. In all the experiment variants there was a narrowing in the $C_{HA}:C_{FA}$ ratio, the type of humus for the organic fertilization system was fulvic-humic (similar to the control), and with the mineral fertilization system the type of humus changed for humic-fulvic (similar to the wild land). The aggravation of HA structure and the

increase in the degree of condensation in typical weak alkali light loamy chernozem was registered only for the organic fertilization system. In the organic and mineral fertilization systems, the new formation of HA in this soil occurs due to the first and second fractions. The degree of mobility of the whole system of humic substances in this soil increased compared to the control under the impact of the organic and mineral fertilization systems.

According to the results of direct calorimetric determination of the soil and preparatively isolated humic acids, there was basic information, obtained about the quantitative indices of their energy capacity (Table 2).

The organic fertilization system in typical heavy loamy chernozem promoted the maximal accumulation of energy in the soil (the increase by 0.11 MJ/kg) compared to the control without any fertilizers (0.96 MJ/kg) and the mineral fertilization system (1.03 MJ/kg). Less energy was accumulated in typical light loamy chernozem with the organic and mineral fertilization systems, compared to the control. With the mineral fertilization system, more energy was accumulated in the first HA fraction in the soils, different in their granulometric composition, compared to the control and the organic fertilization system. A larger amount of energy in the second HA fraction was accumulated with the organic fertilization system in typical heavy loamy chernozem. Less energy was accumulated in the second fraction of HA in typical light loamy chernozem compared to the control without any fertilizers. With the organic fertilization system in typical heavy loamy chernozem, humic acids, bound to the clay fraction and stable sesquioxides (HA3), accumulated more energy than these fractions in the soil of the control variant and after the introduction of mineral fertilizers. HA3 fraction accumulated 2.5 times more energy in typical light loamy chernozem in case of the mineral fertilization system, and 1.8 times more energy in the organic system, compared to the control.

CONCLUSIONS

Long-term fertilization promotes considerable changes in the quality composition of the whole sys-

Table 2. The energy capacity of soils and preparations of humic acids

Variant	Extraction method	Typical heavy loamy chernozem	Typical light loamy chernozem
		low heating value, MJ/kg	
Control	Fraction 1 – HA1	12.29	12.24
Manure	Extraction agent o.2 n	10.62	11.44
NPK	NaOH	15.85	12.88
	LSD_{05}	0.86	0.19
Control	Fraction 2 – HA2	10.46	5.92
Manure	Extraction agent 0.1 n	15.12	3.82
NPK	NaOH, after soil decalcification	10.65	2.85
	LSD_{05}	0.96	0.08
Control	Fraction 3 – HA3	2.91	1.47
Manure	Extraction agent 0.2 n	4.09	2.69
NPK	NaOH, after 7 h of heating on boiling water bath	3.13	3.71
	LSD_{05}	0.08	0.10
Control	Initial soil	0.96	0.90
Manure		1.07	0.89
NPK		1.03	0.74
	LSD_{05}	0.01	0.01

tem of humic substances of chernozems of different granulometric compositions. The new formation of HA in typical heavy loamy chernozem with organic and mineral fertilization systems occurs due to the second and third fractions on the background of the decrease in the first, the most mobile fraction of HA. The mobility degree of the whole system of humic substances under the impact of different fertilization systems does not differ from the control variant considerably; the tendency towards the increase in this index was observed only for the mineral fertilization system. The aggravation of the structure of humic acids and the increase in the degree of condensation in typical weak alkali light loamy chernozem was registered only for the organic fertilization system. In the organic and mineral fertilization systems, the new formation of HA in this soil occurs due to the first and second fractions. The level of mobility of the whole system of humic substances in this soil is increased compared to the control without any fertilizers under the impact of the organic and mineral fertilization systems.

A considerable difference in the indices of energy, present in the soil and the fractions of humic acids, isolated from this soil, was determined. The maximal amount of energy was registered in labile forms of humic acids – from 10.62 to 15.85 MJ/kg, the smallest amount – in the fractions, tightly connected to the mineral part of the soil (1.47 – 4.09 MJ/kg). The amount of energy is in direct relationship to the applied fertilizers, which is in good agreement with the data on the impact of different fertilization systems on the humic condition of soils.

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Вміст, склад, енергоємність органічної речовини та їхні зміни у чорноземах під впливом різних систем удобрення

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Мета. Встановити закономірності трансформації кількісного та якісного складу гумусу, його енергоємності за тривалого удобрення ґрунтів. **Методи.** Здійснено тривалі стаціонарні досліди на чорноземних ґрунтах різного гранулометричного складу. Аналітичні роботи – в атестованій лабораторії за діючими нормативними документами: попереднє оброблення зразків для фізико-хімічного аналізу (ДСТУ ISO 11464); визначення сухої речовини і вологості за масою − гравіметричним методом (ДСТУ ISO 11465); масову частку загального вуглецю визначали оксидиметрично (ДСТУ 4289:2004); груповий склад гумусу − за методом Тюріна у модифікації Пономарьової та Плотнікової (ДСТУ 7828:2015); питому теплоту згоряння ґрунтового і органічного матеріалу − калориметричним методом на установці В-08-МА (ДСТУ 7866:2015); препарати гумусових речовин виділяли за ДСТУ 7606:2014. **Результати.** Тривале удобрення сприяє істотним змінам якісного складу усієї системи гумусових речовин чорноземів різного гранулометричного складу. Органічна і мінеральна системи удобрення на чорноземах різного гранулометрічного складу по-різному впливають на накопичення енергії як у ґрунті, так і в гумінових кислотах (ГК). **Висновки.** За органічної та мінеральної систем удобрення в чорноземі типовому важкосуглинковому новоутворення ГК відбувається за рахунок другої і третьої фракції на тлі зниження першої найрухливішої фракції ГК. Ступінь рухливості всієї системи гумусових речовин під впливом різних систем удобрення істотно не відрізняється від контролю, лише за мінеральної системи удобрення спостерігали тенденцію до підвищення цього показника. За органічної та мінеральної систем удобрення в чорноземі типовому слабовилугуваному легкосуглинковому новоутворення ГК відбувається за рахунок

першої і другої фракцій. Ускладнення структури ГК і зростання ступеня конденсованості зафіксовано лише за органічної системи удобрення. Рівень рухливості всієї системи гумусових речовин у цьому ґрунті під впливом органічної і мінеральної систем удобрення підвищувався порівняно з контролем. Встановлено значну різницю у показниках енергії, яка міститься у ґрунті та у фракціях ГК, екстрагованих з цього ґрунту. Максимальна кількість енергії знаходиться у лабільних формах ГК – у межах 10,62−15,85 МДж/кг, найменша − у фракціях, міцно зв'язаних з мінеральною частиною ґрунту (1,47−4,09 МДж/кг). Кількість енергії прямо залежить від застосованих агротехнічних прийомів, що повністю узгоджується з даними щодо впливу різних систем удобрення на гумусовий стан ґрунтів.

Ключові слова: чорноземи, системи удобрення, гумус, гумінові кислоти, енергоємність.

Содержание, состав, энергоемкость и их изменения в черноземах под влиянием разных систем удобрения

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Цель. Установить закономерности трансформации количественного и качественного состава гумуса, его энергоемкости при длительном удобрении почв. **Методы.** Осуществлены длительные стационарные опыты на черноземных почвах различного гранулометрического состава. Аналитические работы − в аттестованной лаборатории с действующими нормативными документами: предварительная обработка образцов для физико-химического анализа (ДСТУ ISO 11464); определение сухого вещества и влажности по массе − гравиметрическим методом (ДСТУ ISO 11465); массовую долю общего углерода определяли оксидиметрически (ДСТУ 4289: 2004); фракционно-групповой состав гумуса − по методу Тюрина в модификации Пономаревой и Плотниковой (ДСТУ 7828:2015); удельную теплоту сгорания почвенного и органического материала − калориметрическим методом на установке В-08-МА (ДСТУ 7866:2015); препараты гумусовых веществ выделяли по ДСТУ 7606:2014. **Результаты.** Длительное внесение удобрений способствует существенным изменениям качественного состава всей системы гумусовых веществ черноземов разного гранулометрического состава. Органическая и минеральная системы удобрения на черноземах разного гранулометрического состава по-разному влияют на накопление энергии как в почве, так и в гуминовых кислотах (ГК). **Выводы.** При органической и минеральной системах удобрения в черноземе типичном тяжелосуглинистом новообразование ГК происходит за счет второй и третьей фракций на фоне снижения первой самой подвижной фракции ГК. Степень подвижности всей системы гумусовых веществ под влиянием различных систем удобрения существенно не отличается от контроля, только при минеральной системе удобрения наблюдается тенденция к повышению этого показателя. При органической и минеральной системах удобрения в черноземе типичном слабовыщелоченом легкосуглинистом новообразование ГК происходит за счет первой и второй фракций. Усложнение структуры ГК и рост степени конденсированности зафиксированы только при органической системе удобрения. Уровень подвижности всей системы гумусовых веществ в этой почве под влиянием органической и минеральной систем удобрения повышался по сравнению с контролем. Установлено значительную разницу в показателях энергии, содержащейся в почве и во фракциях ГК, экстрагированных из этого грунта. Максимальное количество энергии находится в лабильных формах ГК − в пределах 10,62−15,85 МДж/кг, наименьшее − во фракциях, прочно связанных с минеральной частью почвы (1,47−4,09 МДж/кг). Количество энергии напрямую зависит от применяемых агротехнических приемов, что полностью согласуется с данными о влиянии различных систем удобрения на гумусное состояние почв.

Ключевые слова: черноземы, системы удобрения, гумус, гуминовые кислоты, энергоемкость.

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