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HUMUS CONTENT AND HUMUS FRACTIONS AFTER LONG-TERM SYSTEMIC MINERAL AND ORGANIC-MINERAL FERTILIZATION ON MOLLIC FLUVISOLS

N. SIMEONOVA* S. TODOROVA

Agricultural University, Plovdiv, Bulgaria
***e-mail: neli_art@abv.bg**

Abstract: The present work studies the effect of long-term systemic mineral and organic-mineral fertilization on the humus amount, humus type and humus fractions on Mollic fluvisols in Plovdiv region. Fertilizer norms are 1) $N_{75}P_{30}K_{20}$; 2) $N_{25}P_{15}K_0$ + organic; 3) $N_{50}P_0K_{20}$ and 4) Standard. It was found that long-term systemic mineral and organic-mineral fertilization (forty-seven years) has a stabilized effect on humus content in studied soils. The systemic fertilization lead to a slight decrease of soil humus amount, although the fertilization was excluded since three years. The humus type – was not influenced from the long-term fertilization.

Key Words: Humus, Humic acids, Fulvic acids, Humus type, Fertilization

1. INTRODUCTION

In the composition of soils organic compounds are imparted quite a specific role because the accumulation of humus is exclusively related to the soil formation process. Therefore, the humus content and humus composition are among the most important diagnostic features that reflect the nature and the line of modern soil formation process. Although the biological metabolism of substances in arable soils, especially those without mineral fertilization, has been impaired, the direct dependence of humus quality on natural soil formation process of the respective soil difference is increasing. This is more clearly visible in soils developing under grassy vegetation and accumulative relief than in forest soils, which were formed in the conditions of broken ground and under trees or tree-and-grass vegetation.

Humus appears to be the source of many nutrients for plants, a regulator of physicochemical and biological properties of the soil, which determine the water-aerial and nutritional regime of plants in all natural areas.

The concept of soil humus has been formed over a long period of time, starting with Bercelius in the 19th century (Williams, Sprengel, Mulder, Kostichov, etc.). During the 20th century the study of the nature of humus substances in the soil and the way of their formation was so deep that lead to the formation of special schools humus studies such as the Russian school (Tyurin, Kononova, Aleksandrova, Ponomareva, Orlov, etc.), the German school (Scheffer, Schahtschabel, Flaig, etc.) and the French one (Duchaufour, Jaquin, Andreux, Bruckert, Montrosier, Vedy, etc.).

Orlov efficiently uses the studied humus fractions to determine criteria for qualitative description some of which have to be parameterized in accordance with the range of their registered values for the respective climatic zone or its periphery by the inherent particular traits of local soils. Some of the most symptomatic among these criteria are the humus type (the ratio of humic acids quantity to fulvic acids quantity C_{ha}/C_{fa}) and the mineralization index (C/N). The biological activity of the medium, which leads to the formation of humus itself, is described by the pH of the medium, the alkali saturation of organic-mineral colloids and the efficient activity index expressed by the ratio N_{min}/N_{total}.

It has been long known that in arable soils, treatments and most of all of fertilization, affect the humus quality one of the indicators of which is its saturation with nitrogen.

These changes have not been systematically traced in our country and therefore in the local literature there is only fragmentary information mainly related to trials conducted in separate research stations. However, the traced changes are almost always accounted for based on different mineral fertilization systems. The effect on the acid-alkali, organic-mineral and oxidation-reduction systems of the soil after suspension of long-time fertilization is almost absent from the studied literature.

For these reasons we set ourselves the objective to study the humus conditions of mollic fluvisols that have been subject to long-term fertilization experiment in the conditions of crop-rotation and the fertilization of which has been suspended in 2006.

- To achieve the objective, we had to solve the following problems:
- To determine the present humus condition;
- To reveal the changes in humus quality by comparison;
- To follow the rate of mineralization as source of nutrients and to outline the predominant stimulating factor (chemical conditions for insoluble-immobilized humus components, water-aerial regime and the related moisture and temperature of air at ground level, and the specificity of the cultivars grown on this field.

2. MATERIAL AND METHODS

2.1. Methods Used To Determine The Quantity and Composition of Humus

As mentioned before, the stages and mechanisms of humus formation (especially the formation of humic acids) have long been in the focus of researchers. Initially, the humic substances were studied mainly through analysis. This period is characterized by the works of I.V. Tyurin (1937), M.M. Kononova (1951, 1963), and S. Wachsman (1937). Nowadays it marks its development as one of the methods of studying soil genesis by going deep into the mechanisms of formation of specific organic matters in soils.

Tyurin's method (1931, 1936) is one of the modifications of the volumetric method for determination of the organic carbon in the soil by oxidation with $K_2Cr_2O_7$ in strong acid medium until formation of CO_2 according to the equation:

$$2\ K_2Cr_2O_7 + 8\ H_2SO_4 = 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2 \qquad (1)$$

$$3C + 3O_2 = 3CO_2 \qquad (2)$$

The quantity of oxygen used for oxidation of the organic carbon is determined by the difference between the quantity of dichromate taken for oxidation and the quantity remaining unused after oxidation. This is done by titration with Sol & Moor salt solution and phenylantranyl acid as indicator.

The oxidation of the organic matter achieved following the described methods accounts for about 90% of the values obtained according to Gustafson's method of dry oxidation. The use of silver sulphate as accelerator increases the scope of oxidation to 95%. The method ensures good reproducibility of the results; it is fast, does not require any special equipment and at present is generally adopted, especially in mass analyses. The course of analysis requires higher attention to be paid to oxidation temperature, which should not exceed 180 °C. Therefore, the matter is heated for a longer time (45 min) at 120 °C. A different and older version is the description of Tyurin's method in the publications by Belchikova (1965) and the guidelines by Arinushkina (1970).

According to the modified method of Orlov and Grindel (1967), the soil organic matter is oxidized entirely according to Tyurin's method with solution of $K_2Cr_2O_7$ in H_2SO_4 but the quantity of chromic acid used for oxidation is read by spectrophotometry rather than by the volumetric method. Detailed description of this method is given in the mentioned publications by Orlov and Grindel and in *Practice in humus biochemistry* (1969). This method is especially convenient for determining small quantities of organic carbon (such as water extracts or soil solutions). It has also been described in an article by K.V. Dyakonova in the collection *Organic matter in virgin and arable soil* published by Nauka, Moscow, in 1972. The total nitrogen in the soil is determined mainly by Keldal's method. The incomplete oxidation of the cyclic forms of nitrogen in the composition of humic substances does not affect the results of analysis because they are in very small quantities.

To determine with high precision the nitrogen content in soils with high content of nitrates is used Jodlbauer's method, which differs from Keldal's method by the fact that burning (or mineralization) is achieved using phenol sulphuric acid instead of sulphuric acid.

The specialised research units related to the Russian science school highly appreciate Tyurin's method for determination of total nitrogen (N_{total}) that they deem even more precise that Keldal's method but more appropriate for soils containing less mineral forms of nitrogen. Later was launched a similar method of Anstett A. (1956).

The humus fractions content is determined with satisfactory precision by the method of M. Kononova and N. Belchikova using $Na_4P_2O_7$ as described in the monograph Organic matter in virgin and arable soils (1962). However, much more precise idea about the group and fraction humus content is obtained by the method of Ponomareva-Plotnikova but the finding of sub-fractions increases the probability to affect the native nature of the obtained products.

3. RESULTS AND DISCUSSION

The studied mollic fluvisols formed on alluvial deposits features very well formed humus accumulation horizon with claying in the zone of soil-forming materials.

The data from Table 1 (during fertilization) and Table 2 (after suspension of fertilization) show that the humus content in the horizon under the surface decreases in all cases except the portion with combined organic-mineral fertilization where an increase of the humus content in the layer under the surface is registered. In the version with increased preceding nitric fertilization and reduced phosphoric fertilization compared to the present version with excluded phosphoric fertilization we recorded significant increase in the humus content and the total nitrogen on both depths. In comparison, according to statistical data, in unexploited (virgin) mollic fluvisols the humus content in the surface horizon was around 5% and in our formerly fertilized versions it is in the range of 3 to 4% in versions with excluded phosphoric fertilization.

The total nitrogen content decreases with depth to the exception of the version with organic-mineral fertilization and especially in crop-rotation of maize after alfalfa. The group and fraction humus content in Table 3 and Table 4 shows the following values of the essential indices.

The aggressive fulvic acid content is insignificant in all versions (3 to 15%). The total content of all humic acids is relatively low. This corresponds to the quantity of unhydrolyzable remainder (humin) with 71-80% in wheat-after-maize version and 67-90% in the maize-after-alfalfa version. The humic acids content is not big either: 13-22% in the versions with wheat after maize and 13-17% in the version with maize after alfalfa. The quantity of fulvic acids is even smaller – between 3 and 10% - in the version maize after alfalfa. It should be note here that in the version maize after alfalfa without fertilization the quantity of hydrolyzable organic carbon is very low while the quantity of the remainder that can not be hydrolyzed, humin, is very high.

Table 1. Total carbon content (%), humus (%), total nitrogen (%) and percentage distribution of extracted fractions to the content of total carbon

Variants	Total C %	Humus %	Total nitrogen %	Humic acids	Fulvic acids	Total	Humin
1. Standart (control)	1.43	2.47	0.164	28.2	6.6	34.8	65.2
2. NPK	1.64	2.48	0.193	25.5	2.6	28.1	71.8
3. NPK + organic fertilizer	1.79	3.09	0.210	27.3	2.4	29.7	57.7
4. NPK with reduced phosphorus	1.37	2.36	0.180	28.9	27.3	56.2	49.8

This corresponds to slightly increased value of the C/N ratio as a sign of slower mineralization. On the other hand, the produced mineral nitrogen is in important quantity, especially its ammonium form. Significant are also the quantities of nitric nitrogen, especially in the sub-superficial horizon of the same version. The humus type is from fulvic-humic to humic. Humic acids in all versions are entirely combined to calcium and show very high optic density – $Q_{4/6} < 4$. This is a sign of high level of condensation of the aromatic nuclei but it is less pronounced in the version maize after alfalfa. In the version the quantity of total and mineral nitrogen is less, i.e. reduced is also the quantity of nitrogen combine with cyclic structures of aromatic nuclei or they have undergone a stage of slow mineralization producing NH_4^+ and NO_3^- forms. We have observed a tendency of clear influence of the order of crops in the crop rotation on the balance mineralization-humification and from there on the humus composition. However, this tendency shall be interpreted after longer studies. The observed tendency consists in slower rate of mineralization of the humus in the version maize after alfalfa, which we believe is due to the favoured nitric nutrition of the plants resulting from symbiotic nitrogen-fixing tuber bacteria in the alfalfa. Furthermore, the suspension of mineral fertilization for four years has caused overall reduction of the rate of mineralization of the soil organic matter reflected in the slightly increased values of humus and nitrogen content (Table 1 and Table 2). In the same time, the presence in the medium of 2-3% active calcium leads to development of the assimilation of the most condensed organic matter by the calcium.

This sequestration of humus has lead to significant increase of humin in the versions with excluded phorphoric fertilization and with combined organic-mineral fertilization during the previous period (Table 1 and Table 4). However, this tendency is not observed in the version with moderate nitric fertilization. This attracts our attention to the influence of active calcium on the rate of mineralization and humification. It is probably due to the increased mineral nitrogen content that the level of humin has remained unchanged while the content of humic and even more of fulvic acids has increased. Hence, the reduction of active calcium stimulated by mineral fertilization has lead to acceleration of the processes of biodegradation of the stable humus components such as humin and probably also of the sources of vegetal origin. Evidences of this are the established higher values of the index of efficient activity of biodegradation N_{min}/N_{tot} in the version with moderate nitric fertilization as well as in the version with organic-mineral fertilization.

4. CONCLUSION

The long-time mineral fertilization of mollic fluvisols has not changed the type of humus – carbonated mul. After suspension of the fertilization for four years, the effect of active calcium has increased. The abundance of unhydrolyzable remainder (humin) is significantly increased in the version with excluded phorphoric fertilization and the version with organic-mineral fertilization.

Table 2. General characteristic

Variants		$CaCO_3$ %	Active calcium %	Ca^{2+}+ Mg^{2+} meq/100g	pH (H_2O)	pH (KCl)	Salts g/100g	NH_4^+ mg/kg	NO_3^- mg/kg	Organic nitrogen %	Total C %	Humus %	$N_{min.}/N_{t.}$
wheat after corn	1..St. 0-30	1.92	1,75	22.45	7.51	6.98	0.057	18.67	21.00	0.183	1.4985	2.5834	0.02
	2..St.30-40	2.34	1,75	21.40	7.62	7.14	0.047	24.27	14.93	0.167	1.2870	2.2187	0.02
	3. N 0-30	1.36	1.00	26.65	7.67	7.12	0.041	36.60	31.73	0.186	1.5226	2.6250	0.04
	4. N 30-40	1.85	1,75	24.25	7.67	7.09	0.041	29.40	30.80	0.191	1.4425	2.4868	0.03
	5.Org. 0-30	2.10	1,75	21.65	7.61	7.13	0.046	39.20	36.40	0.194	1.5270	2.6326	0.04
	6.Org 30-40	1.99	1,75	20.65	7.66	7.15	0.043	25.20	29.40	0.194	2.1450	3.6979	0.03
	7.-P 0-30	1.69	1,25	27.45	7.73	7.20	0.039	25.20	30.80	0.208	2,4812	4,2775	0.03
	8.-P 30-40	1.23	1,25	25.80	7.67	7.21	0.042	16.80	26.60	0.170	2,1862	3,7690	0.02
corn after lucerne	9.St. 0-30	5.74	3.00	21.35	7.78	7.41	0.047	30.80	15.40	0.159	1,8834	3,2469	0.03
	10.St 30-40	5.92	3.00	19.85	7.87	7.53	0.048	29.40	32.20	0.141	1,9446	3,3525	0.04
	11.N 0-30	5.83	3,25	15.25	7.88	7.51	0.045	35.00	25.20	0.159	1.2388	2,1357	0.04
	12.N 30-40	5.57	3,25	23.30	7.88	7.57	0.045	16.80	28.00	0.126	0,8735	1,5059	0.04
	13.Org. 0-30	6.56	3,25	21.25	7.83	7.53	0.050	25.20	19.60	0.127	1,0631	1,8328	0.04
	14.Org 30-40	6.59	3,25	19.05	7.85	7.60	0.045	36.40	28.00	0.170	1,1188	1,9287	0.04
	15.-P 0-30	5.76	3,50	20.25	7.88	7.56	0.046	26.60	21.00	0.210	1,3888	2,3943	0.02
	16.-P 30-40	5.70	3,25	19.00	7.85	7.55	0.048	21.00	26.60	0.167	1,1174	1,9263	0.03

Table 3. Group and fraction humus content

Variants		Total C, %	Extract with 0,1n H_2SO_4	Extract with mix of 0,1 M $Na_4P_2O_7$ и 0,1 n NaOH			Gray humic acids	Humin	$C_{H.A.}/C_{F.A.}$	Извлек с 0,1 n NaOH		$Q_{4/6}$	Org. N, %	C / N
				Total	Humic acids	Fulvic acids				Bounded with R_2O_3	Bounded with Ca^{2+}			
wheat after corn	1.St. 0-30	1.4985	0.0542	0.3973	0.3380	0.0593	0.0806	1.1012	5.70	-	100	3.6	0.1834	8.2
	2.St. 30-40	1.2870	0.0454	0.2951	0.2051	0.0900	0.0663	0.9919	2.28	-	100	3.5	0.1673	7.8
	3.N 0-30	1.5226	0.0509	0.4342	0.3431	0.0911	0.0568	1.1795	3.77	-	100	3.5	0.1860	8.2
	4.N 30-40	1.4425	0.0438	0.3730	0.2353	0.1377	0.0758	1.0695	1.71	-	100	3.2	0.1914	7.5
	5.Org. 0-30	1.5270	0.0468	0.2717	0.3125	0.0595	0.0853	1.1550	5.25	-	100	3.3	0.1941	7.7
	6.Org 30-40	2.2020	0.0441	0.3923	0.2965	0.0958	0.1091	1.8097	3.09	-	100	2.9	0.1941	11.3
	7.-P 0-30	2.5897	0.0511	0.4891	0.3400	0.1491	0.1092	0.2106	2.28	-	100	3.5	0.2075	12.5
	8.-P 30-40	2.3002	0.0462	0.4551	0.2934	0.1617	0.1399	1.8451	1.81	-	100	3.4	0.1700	13.5
corn after lucerne	9.St. 0-30	1.9594	0.0249	0.2327	0.1852	0.0992	0.0460	1.6750	1.87	-	100	3.3	0.1593	12.3
	10.St 30-40	2.0194	0.0228	0.1978	0.0960	0.1018	0.0614	1.8216	0.94	-	100	3.9	0.1405	14.4
	11.N 0-30	1.2469	0.0309	0.2984	0.1527	0.1457	0.0972	1.7210	1.05	-	100	3.6	0.1593	7.8
	12.N 30-40	0.8815	0.0288	0.2501	0.1222	0.1279	0.0742	0.6314	0.96	-	100	3.7	0.1245	7.1
	13.Org 0-30	1.0710	0.0261	0.3496	0.1854	0.1642	0.0819	0.7214	1.13	-	100	3.8	0.1271	8.4
	14.Org 30-40	1.1266	0.0295	0.3115	0.1512	0.1603	0.1049	0.8151	0.94	-	100	3.8	0.1700	6.6
	15.-P 0-30	1.3968	0.0281	0.3666	0.1818	0.1848	0.0972	1.0302	0.98	-	100	3.7	0.2101	6.6
	16.-P 30-40	1.1251	0.0254	0.3115	0.1795	0.1320	0.0819	0.8136	1.36	-	100	3.8	0.1673	6.7

Table 4. Percentage distribution of extracted fractions to the content of total carbon

Variants		Humic acids	Fulvic acids	Total	Gray humic acids	Humin
wheat after corn	1. St. 0-30	22.56	3.96	26.52	23.85	73.49
	2. St.30-40	15.94	6.99	22.93	32.33	77.07
	3. N 0-30	22.53	5.98	28.51	16.55	71.49
	4. N 30-40	16.31	9.55	25.86	32.21	74.14
	5.Org. 0-30	20.46	3.90	24.36	27.30	75.64
	6.Org 30-40	13.47	4.35	17.82	36.80	82.18
	7.-P 0-30	13.13	5.76	18.89	32.12	81.11
	8.-P 30-40	12.76	7.03	19.79	47.68	80.21
corn after lucerne	9.St. 0-30	9.45	5.06	14.51	19.82	85.49
	10.St 30-40	4.75	5.04	9.79	63.96	90.21
	11.N 0-30	12.25	11.68	23.93	63.65	76.07
	12.N 30-40	13.86	14.51	28.37	60.72	71.63
	13.Org. 0-30	17.31	15.33	32.64	44.17	67.36
	14.Org 30-40	13.42	14.23	27.65	69.38	72.35
	15.-P 0-30	13.02	13.23	26.25	53.47	73.75
	16.-P 30-40	15.95	11.73	27.68	45.63	72.32

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