Бюллетень Почвенного института им. В.В. Докучаева. 2019. Вып. 97.
Dokuchaev Soil Bulletin, 2019, 97

UDC 631.417
DOI: 10.19047/0136-1694-2019-97-113-128

Cite this article as:
Filatova A.I., Mamontov V.G., Panova P.Yu., Molecular weight composition of humic acids in urban soils (the Northern Administarative District of Moscow city taken as an example), Dokuchaev Soil Bulletin, 2019, V. 97, pp. 113-128, DOI: 10.19047/0136-1694-2019-97-113-128

MOLECULAR WEIGHT COMPOSITION OF HUMIC ACIDS IN URBAN SOILS (THE NORTHERN ADMINISTRATIVE DISTRICT OF MOSCOW CITY TAKEN AS AN EXAMPLE)

© 2019 A. I. Filatova, V. G. Mamontov, P. Yu. Panova*

Russian State Agrarian University –
Moscow Agricultural Academy named after K.A. Timiryazev,
Russia,127550, Moscow, Timiryazevskaya str., 49
**e-mail: soillab@rgau-msha.ru*

Received 31.10.2018, *Revised* 08.11.2018, *Accepted* 28.05.2019

The article provides research results and comparative analysis of humic acids in sod-podzolic soil of the Experimental Forest of the Russian State Agrarian University (protected area) and urban soils located in the Timiryazev district of Moscow. Humic acids of the zonal sod-podzolic soil of the Experimental Forest include four fractions with varying molecular weight: the 1st fraction – ≥ 23 440 unified atomic mass units (amu), the 2nd one – 13 340 amu, the 3rd one – 5 500 amu and the 4th one – 2 460 amu. The fraction with a molecular weight of 5 500 amu and a relative content of 38 % dominates among them, while the share of low-molecular fractions (< 20 000 amu) accounts for 70 % of the total mass of humic acids. When weight-average molecular mass of humic acids is 17 530 amu, the average molecular mass of the low-molecular fractions is 9 960 amu. Humic acids of urbanozems differ in molecular weight composition from humic acids of sod-podzolic soil. In most cases it consists of 5–6, less commonly of 3, fractions with molecular weight from 1 780 to ≥ 23 440 amu. The share of medium- and high-molecular fractions fluctuates from 31–37 % to 47–50 % of the total mass of humic acids. The characteristic feature of humic acids of urbanozems is the presence in their composition of low-molecular fractions with such molecular weights, which are not found in humic acids of sod-podzolic soil. Thus, humic acids of urbanozems are characterized by higher weight-average molecular mass ranging from 17 680 to 19 980 amu, as well as by higher weight-average molecular mass of the low-molecular fractions which vary from 10 680 to 13 650 amu.

Keywords: sod-podzolic soil, urbanozem, humic acids, fraction, molecular weight, weight-average molecular mass.

INTRODUCTION

In the study of soil organic substance gel chromatography method has become widely used, it has recommended itself as a reliable and fast way to fractionate and determine molecular masses of humic substances in the study of their formation processes, migration and transformation. With its help a significant amount of valuable scientific information on the characteristics of various soil organic substance has been obtained. In particular, it became possible to establish well the polydispersity of humic acids, i.e. the presence of molecules with different molecular weights among them (Khan, Friesen, 1972; Goh, Williams, 1979; Aleksandrova, 1980; Orlov, 1990; Piccolo, Conte, 2000), provided that a molecular mass (MM) of humic acids (HA) have a very wide range (Tan, Giddens, 1972; Kolesnikov, 1978; Orlov, 1990; Popov, 2004), and the fractions themselves differ in composition and properties.

With a decrease in MM in HA, as it was shown, the content of H and N decreases, the amount of O, carboxyl groups, the degree of oxidation and the fraction of cyclic structures in their composition increase (Swift, Posner, 1972; Tan, Giddens, 1972; Aleksandrova, 1980; Goh, Williams, 1982; Lishtvan et al., 2012). A decrease in the molecular weight of HA is accompanied by an increase in their age (Chichagova, Tarasova, 1992) and the concentration of paramagnetic centers (Strigutskii et al., 1992). The HA high-polymeric fraction are enriched in fatty acids, polysaccharose and polypeptides; the concentration of photosensitizer chromophores is much lower in them, and therefore, the absorption intensity in the UV and the visible spectrum parts is lower (Rishard et al., 2008).

These and other materials (Okolelova, Baranovskaya, 1987; Mamontov et al., 2009; Karpukhin et al., 2010) allowed us to expand significantly our understanding of formation and functioning of the soil organic part and the peculiarities of its transformation under the influence of natural and anthropogenic factors. However, they were obtained in the study of virgin soils and soils of agrocoenosis, while the information on the peculiarities of the molecular weight HA composition of urban soils is virtually absent. At the same time, such information is, of course, necessary to obtain whole and objective picture of the characteristics of the organic substances in urbanozems as the most important factor determining their stable state and effective functioning.

MATERIALS AND METHODS

The objects of our research were urban coenoses soils of the Northern Administrative District of Moscow: sod-podzolic soil of the Experimental Forest (protected area), the urbanozems of Dubki Park, lawns of Timiryazevskaya Street, interbuilding territory along Timiryazevskaya Street (IBT), Koptevsky boulevard, mini-park in Bolshaya Academicheskaya Street.

It was previously established that urbanozems significantly differ from zonal sod-podzolic soil both in labile, dynamic properties and in fundamental, relatively stable indicators. In contrast to acidic, unsaturated with bases sod-podzolic soil, urbanozems are characterized by a neutral or slightly alkaline PH, a higher content of humus, exchangeable Ca and Mg and a wider ratio of Ca: Mg in the humus layer, free carbonates presence; their profile may be not differentiated by granulometric and total composition. Compared to zonal sod-podzolic soil, urbanozems contain less total SiO_2, TiO_2 and often Na_2O, more Al_2O_3, Fe_2O_3, MgO, CaO (Mamontov et al., 2016).

To obtain the specimens the humic acids were extracted with 0.1 n. NaOH solution to the maximum extraction after preliminary decalcification of the soil according to the generally accepted technique (Orlov, Grishina, 1981). Sephadex G-50 was used to fractionate HA. The concentration of HA added on column was 4 mg/ml; 0.1 n NAOH solution served as a solvent, 0.015 M phosphate buffer with pH 7.5 – as an eluent, the sampling choice was carried out through 2 ml, the optical density was measured at KFK-3-01 at the wavelength of 315 nm. Blue dextran was used to determine a free volume; MM fractions of HA were found by the empirical formula (Osterman, 1985).

RESULTS AND DISCUSSION

Fractionation of the studied soils HA on Sephadex G-50 helped reveal the heterogeneity of their molecular mass composition (Fig. 1).

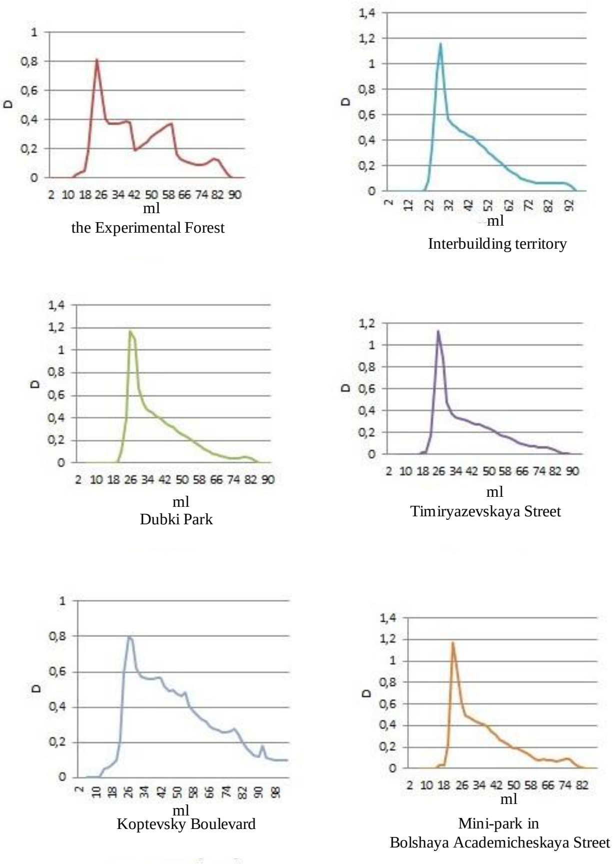

Fig. 1. Gel-filtration chromatograms of humic acids in urban soils.

Four fractions are clearly distinguished on the HA gel-filtration chromatogram of the sod-podzolic soil located in the regions of different MM, and there are six fractions on the gel chromatogram of the HA of Koptevsky Boulevard urbanozem. The first and the last fractions in the area of high and low MMs were more or less clearly distinguished on the HA gel-filtration chromatograms of other urbanozems, and between them there is a vast area assigned to fraction 2 where it did not occur any distinct separation into fractions. The eluents belonging to this area of gel-filtration chromatograms were collected, evaporated, each to a volume of 2 ml, and passed over through a gel column. As a result of this the HA in some urban soils could be divided into a number of fractions (Fig. 2).

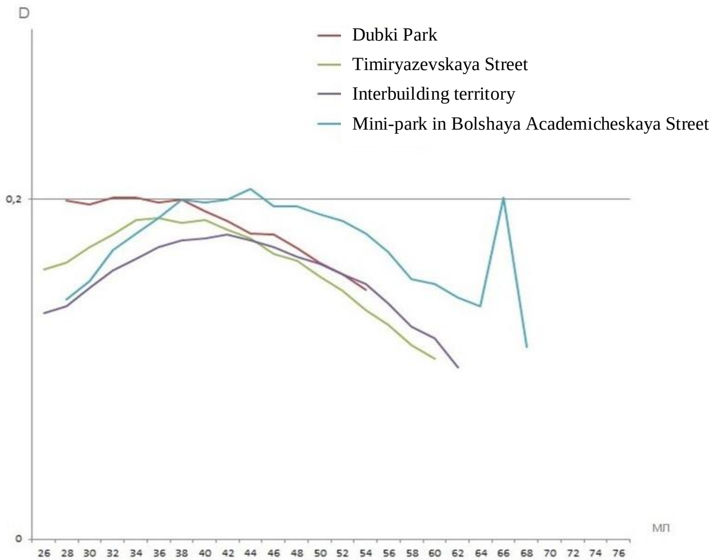

Fig. 2. Gel-filtration chromatograms of the 2nd fraction of humic acids in urban soils.

Three fractions were found in the HA of the urbanozems in Dubki Park and the lawn of Timiryazevskaya Street, and four fractions – in the HA of the urbanozem in the mini-park in Bolshaya Akademicheskaya Street, while the HA of the urbanozem of the interbuilding territory were not divided into fractions.

The assessment results for molecular weight composition of the HA in the studied soils are presented in Table 1.

Table 1. Molecular weight composition of humic acids in urban soils

Object, soil	**Fraction number**	**Fraction MM, amu**	**Relative fraction content, %**	**Weight-average HA MM, amu**	**Weight-average MM of low-molecular fractions, amu**
Experimental Forest, sod-podzolic soil	1	≥ 23 440	30	17 530	9 960
	2	13 340	24		
	3	5 500	38		
	4	2 460	8		
Interbuilding territory along Timiryazevskaya Street, urbanozem	1	≥ 23 440	40	18 500	11 200
	2	11 350	55		
	3	2 090	5		
Dubki Park, urbanozem	1	≥ 23 440	50	19 980	13 650
	2	16 980	14		
	3	13 340	17		
	4	9 660	18		
	5	2 880	1		
Timiryazevskaya Street, urbanozem	1	≥ 23 440	47	19 560	12 890
	2	14 450	18		
	3	12 300	29		
	4	4 320	2		
	5	3 390	4		
Koptevsky Boulevard, urbanozem	1	≥ 23 440	31	17 680	10 990
	2	14 450	19		
	3	10 470	10		
	4	8 220	25		
	5	3 130	10		
	6	1 780	5		
Mini-park in Bolshaya Academichekaya Street, urbanozem	1	≥ 23 440	37	18 150	10 680
	2	13 340	18		
	3	10 470	12		
	4	8 910	24		
	5	4 320	5		
	6	3 390	4		

In most cases the soil HA of every studied objects are characterized by their molecular weight compositions, which manifest themselves to varying degrees of dispersion, MM values of individual fractions and their relative contents.

According to the obtained data the HA of zonal sod-podzolic soil in the Experimental Forest which was formed under a mixed timber stand consist of four fractions that differ in MM and their relative content. Fraction 3 with a molecular mass of 5 500 amu and its relative content of 38 % prevails in the HA composition. The next most significant contribution to the total HA mass is the extracted free volume fraction 1 with MM ≥ 23 440 amu with its relative content of 30 %. In quantitative terms fraction 2 is close to it, having a molecular mass of 13 330 amu, which accounts for 24 %. Fraction 4 with MM of 2 460 amu was found in a very insignificant amount of 8 % in the composition of sod-podzolic soil HA.

The bulk of HA molecules is believed (Orlov, 1990) to have average molecular sizes ranging from 20 000 to 80 000 amu. Based on these data, HA of sod-podzolic soil in the urban forest coenosis, experiencing a relatively small anthropogenic load, are characterized by a relatively low degree of dispersion. They are mainly represented by low-molecular fractions (< 20 000 amu), which amounted to 70 % of HA mass, and the weight-average MM of HA amounted to 17 530 amu, whereas weight-average MM of low-molecular fractions was 9 960 amu.

HA of urbanozems in various urban coenoses are characterized by a different molecular-mass composition than sod-podzolic soils usual for the Experimental Forest territory. The differences relate to both the degree of HA dispersion and the values of molecular masses and the relative content of individual fractions.

The interbuilding territory HA consists of only three fractions. Fraction 2 prevails among them with a molecular mass of 11 350 amu and a relative content of 55 %. The lowest content – 5 % caracterizes fraction 3 with MM of 2 090 amu. Fraction 1 with MM ≥ 23 440 amu is contained in amount of 40 %.

In general, the interbuilding territory HA differ significantly from sod-podzolic soil HA. They are less dispersed and the fraction dominating in their composition is absent among the HA fractions of sod-podzolic soil. In addition, they contain 10 % less low-molecular fractions and have a higher approximate weight-average MM of 18 500 amu, weight-average MM of their low-molecular fractions (11 200 amu) is also higher.

The HA of the urbanozem in Dubki Park and the lawn of Timiryazevskaya Street consist of five fractions. In addition to the same dispersion degree their molecular mass composition has a number of similar features. First of all, it should be noted a high content (47–50 %) of extracted free volume fraction 1 with MM $\geq$ 23 440 amu. Along with this they include low-molecular fraction 5 with a relatively close molecular size (2 880–3 390 amu), which is contained in a very small amount (1–4 %). Finally, they have a rather close approximate weight-average MM (19 560–19 980 amu) and the same total content of low-molecular fractions (50–53 %).

The HA of the urbanozems in Dubki Park and the lawn of Timiryazevskaya Street differ in MM absolute values of fractions 2, 3 and 4. Among them there are no fractions of the same size, the nature of the individual fraction contribution to the total HA mass is also different.

Along with the low-molecular fraction 5 the HA of the urbanozem of Dubki Park includes three more low-molecular fractions with MM of 16 980, 13 340 and 9 660 amu, and their relative content is almost the same and amounted to 14 %, 17 % and 18 % respectively. Weight-average MM of all low-molecular fractions is 13 650 amu.

The content of low-molecular fractions in the HA composition of the urbanozem in the lawn of Timiryazevskaya Street is more contrasting. Among them fraction 3 with MM of 12 300 amu and relative content of 29 % clearly dominates. Fraction 4 with MM of 4 320 amu is presented in a very small amount (2 %); fraction 2 with MM of 14 450 amu amounted to 18 %, average MM is 12 890 amu.

Compared with HA of sod-podzolic soil, the HA of the urbanozems in Dubki Park and the lawn of Timiryazevskaya Street are more dispersed compounds, which is associated with the existance of low-molecular fractions that are absent in the HA of sod-podzolic soil, however, the contribution of all low-molecular fractions in total mass of urbanozems HA is less. In this regard, in comparison with sod-podzolic soil HA they have a higher approximate weight-average MM and weight-average MM of low-molecular fractions.

The HA of the urbanozems in Koptevsky Boulevard and the mini-park in Bolshaya Akademicheskaya Street are the most disperse ones, consisting of 6 fractions and having a fairly similar molecular weight composition, which is manifested in the similar MM values and the content of its main fractions. The highest content, amounting to 31–31 %, is a characteristic of extracted free volume fraction 1 with MM ≥ 23 440 amu. The next most important fraction is 4 with MM of 8 220–8 910 amu and the relative content of 24–25 %. This also applies to fraction 3, which in both cases has an MM of 10 470 a.m. and the relative content of 10–12 %. In total, these three fractions account for 66–71 % of the total HA mass; therefore, they mainly determine the characteristics of their molecular weight composition and weighted-average MM values, which are also quite close to each other. The HA of the urbanozem in Koptevsky Boulevard have approximate weighted-average MM of 17 680 amu and of low-molecule fractions – of 10 990 amu, the HA of the urbanozem in the mini-park in Bolshaya Akademicheskaya Street – 18 150 amu and 10 680 amu respectively.

The differences between the HA of these soils are due to the MM values and the relative content of fractions 2, 5, and 6. The HA of the urbanozems in Koptevsky Boulevard has the MM value of fraction 2 of 14 450 amu, with the relative content of 19 %, and the HA of the urbanozem in the mini-park in Bolshaya Akademicheskaya Street has less MM of fraction 2 of 13 340 amu, although its content is the same. The lowest molecular fractions 5 and 6 also differ from each other. In the HA of the urbanozem in Koptevsky Boulevard these fractions have MM of 3 130 and 1 780 amu with a relative content of 10 % and 5 %, whereas in the HA of the urbanozem in the mini-park in Bolshaya Akademicheskaya street its value is 4 320 and 3 390 amu with 5 % and 4 %, respectively.

On the whole, the HA of the urbanozems in Koptevsky Boulevard and in the mini-park in Bolshaya Akademicheskaya Street, as well as the HA of sod-podzolic soil, consist mainly of low-molecular fractions but they are more dispersed compounds with higher average MM. They are formed by fractions which are absent in the HA of sod-podzolic soil, with the exception for the HA of the urbanozem in the mini-park in Bolshaya Akademicheskaya Street, which, like the HA of sod-podzolic soil, contain a fraction with MM of 13 340 amu, approximately at the same quantity.

Thus, the HA of urbanozems are characterized by a different molecular mass composition compared with the HA of zonal sod-podzolic soil of the protected area that was slightly changed as a result of human activity influence. The differences relate to both the degree of HA dispersion and the MM values of the individual fractions, as well as the approximate weight-average MM of HA and weight-average MM of low-molecular fractions. They can be explained by various reasons but obviously the anthropogenic factor plays a key role.

In contrast to the soils of forest conservation and protected areas, the urban soils, which form the main background of the soil cover in cities, are much more prone to anthropogenic impact which affects their regimes and properties, including the molecular weight HA composition. This may be due to the fact that in urban soils the humification process takes place under qualitatively different conditions in comparison with zonal sod-podzolic soil of natural coenosis. This can be explained by both different chemical and physicochemical properties of urban soils, and by the change in the nature of vegetation. The replacement of mixed timber stands, which is a natural condition of soil formation, with grassland vegetation or mainly deciduous trees with abundant grassy cover affects the scale and chemical composition of plant litter annually entering the soil. Changes in the conditions for humification process, as well as introduction into constructing soil profile of organogenic materials which already contain formed humic substances, will affect HA qualitative characteristics and, in particular, their molecular masses. At the same time, it is of great importance the fact that the HA of these organogenic materials is resistant to environmental conditions usual for urbanozems. It is possible that some part of low-molecular fractions of urbanozems HA has not formed as a result of humification process in urban soils, has not remained from the original soil and has not entered soil profile during its formation. They can be a product of larger HA molecules destruction which were part of the organogenic substances used while urbanozems were creating and turned out unstable under other conditions compared to those in which they were originally formed. One way or another, the discrepancy between the molecular weight composition of urbanozem HA and the molecular mass of the HA formed under zonal soil formation type can lead to instability of organic profile of artificially created urban soils and its accelerated degradation, as a result of which the soil cover cannot properly perform its environmental functions.

CONCLUSIONS

1. Humic acids of urban soils have a complex molecular weight composition and consist of various fractions that differ in their molecular weights and relative content.

2. The humic acids of zonal sod-podzolic soil consist of four fractions with molecular weight from 2 460 to ≥ 23 440 amu with the prevalation of low-molecular fractions, which account for 70 % of the total mass of humic acids.

The humic acids of urbanozems consist of five to six fractions with molecular masses from 1 780 to ≥ 23 440 amu, less frequently of three fractions with molecular weight from 2 090 to ≥ 23 440 amu, the contribution of low-molecular fractions in the total mass of humic acids varies from 50 % to 69 %.

3. At urban conditions the anthropogenic impact on composition and properties of soil organic part prevails over the natural factors of soil formation, which causes a change in dispersion degree and an increase in the approximate weight-average molecular mass of urbanozem humic acids, compared to the humic acids of zonal sod-podzolic soil by 150– 2 450 amu, and the average molecular mass of their low-molecular fractions – by 720–3 690 amu.

REFERENCES

1. Aleksandrova L.A., *Organicheskoe veshchestvo pochvy i protsessy ego transformatsii* (Soil organic matter and its transformation processes), Leningrad: Nauka, 1980, 288 p.

2. Karpukhin A.I., Ilakhun A., Torshin S.P., *Koordinatsionnye soedineniya organicheskikh veshchestv pochv s ionami metallov i vliyanie kompleksonatov na ikh dostupnost'* (Coordination compounds of soil organic substances with

metal ions and the effect of complexonates on their availability), Moscow: VNIIA, 2010, 272 p.

3. Kolesnikov M.P., Molekulyarno-vesovoe raspredelenie guminovykh kislot po dannym gel'-khromatografii na sefadeksakh (Molecular weight distribution of humic acids according to gel chromatography on Sephadexes), *Pochvovedenie*, 1978, No. 4, pp. 32–41.

4. Lishtvan I.I., Kalutskii F.N., Abramets A.M., Yanuta Yu.G., Monich G.S., Aleinikova V.N., Glukhova N.S., Fraktsionirovanie guminovykh kislot kak metod polucheniya standartizirovannykh guminovykh materialov (Fractionation of humic acids as a method of obtaining standardized humic materials), *Vestnik BGU*, 2012, Series 2, No. 2, pp. 7–11.

5. Mamontov V.G., Syunyaev N.K., Afanas'ev R.A. Molekulyarno-massovyi sostav guminovykh kislot obyknovennogo chernozema pri oroshenii (Molecular mass composition of humic acids of ordinary black soil under irrigation), *Plodorodie*, 2009, No. 3 (48), pp. 28–30.

6. Mamontov V.G., Filatova A.I., Komaristaya S.S., Ryabova O.B., Smarygin S.N., Chernichkin R.V. Svoistva gorodskikh pochv (na primere SAO g. Moskvy) (Properties of urban soil (by the example of the Northern Administrative District of Moscow)), *Plodorodie*, 2016, No. 6 (93), pp. 56–58.

7. Okolelova A.A., Baranovskaya V.A. Gumusovye kisloty stepnykh pochv Nizhnego Povolzh'ya i ikh izmenenie pod vliyaniem orosheniya (Humic acids of steppe soils of the Lower Volga region and their change under the influence of irrigation), In: *Organicheskoe veshchestvo pakhotnykh pochv* (Organic matter of arable soil), Moscow: Pochv. in-t im. V.V. Dokuchaeva, 1987, pp. 135–142.

8. Orlov D.S., *Gumusovye kisloty pochv i obshchaya teoriya gumifikatsii* (Soil humic acids and general theory of humification), Moscow: MGU, 1990, 325 p.

9. Orlov D.S., Grishina L.A. *Praktikum po khimii gumusa* (Workshop on the chemistry of humus), Moscow: MGU, 1981, 272 p.

10. Osterman L.A., *Khromatografiya belkov i nukleinovykh kislot* (Chromatography of proteins and nucleic acids), Moscow: Nauka, 1985, 536 p.

11. Popov A.I., *Guminovye veshchestva: svoistva, stroenie, obrazovanie* (Humic substances: properties, structure, education), St.Petersburg, 2004, 248 p.

12. Rishar K., Giio Zh., Aguer Zh.-P., ter Khalle A., Trubetskaya O.E., Trubetskoi O.A., Rol' fraktsionirovaniya pri izuchenii fotokhimicheskikh svoistv gumusovykh veshchestv (The role of fractionation in the study of the photochemical properties of humic substances), *Rossiiskii khimicheskii zhurnal*, 2008, Vol. LII, No. 1, pp. 107–113.

13. Strigutskii V.P., Navosha Yu.Yu., Smychnik T.P., Bambalov N.N., Issledovanie struktury guminovykh kislot metodom nelineinoi EPR-spektroskopii (Study of the structure of humic acids by the method of nonlinear EPR spectroscopy), *Pochvovedenie*, 1992, No. 1, pp. 147–151.
14. Chichagova O.A., Tarasova T.I., Svoistva raznovozrastnykh guminovykh veshchestv (Properties of humic substances of different ages), *Pochvovedenie*, 1992, No. 1, pp. 94–99.
15. Goh K.M., Williams M.R., Changes in molecular weight distribution of soil organic matter during soil development, *Soil Science*, 1979, Vol. 30, pp. 747–755.
16. Goh K.M., Williams M.R., Distribution of carbon, nitrogen, phosphorus, sulphur and acidity in two molecular weight fractions of organic matter in soil chronosequences, *Soil Science*,1982, Vol. 33, No. 1, pp. 73–87.
17. Khan S.V., Friesen D., Gel-filtration of humic acids extracted from the black solonetzic soil and black chernozemic soils of Alberta, *Soil Science*, 1972, Vol. 114, No. 1, pp. 73–74.
18. Piccolo A., Conte P., Molecular size of humic substance, supramolecular associations versus macromolecular polymers, *Advances in Environmental Research*, 2000, No. 3 (4), pp. 508–521.
19. Swift R.S., Posner A.M., Nitrogen, phosphorus and sulphur content of humic acid fractionated with respect to molecular weight phosphorus, sulphur, *Soil Science*, 1972, Vol. 23, No. 1, pp. 50–57.
20. Tan K.H., Giddens J.E., Molecular weights and spectral characteristics humic and fulvic acids, *Geoderma*, 1972, Vol. 8, No. 4, pp. 221–229.