ISSN 1064-2293, Eurasian Soil Science, 2015, Vol. 48, No. 10, pp. 1110–1119. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © A.A. Larionova, B.N. Zolotareva, Yu.G. Kolyagin, A.K. Kvitkina, V.V. Kaganov, V.N. Kudeyarov, 2015, published in Pochvovedenie, 2015, No. 10, pp. 1232–1241.

SOIL CHEMISTRY

Composition of Structural Fragments and the Mineralization Rate of Organic Matter in Zonal Soils

A. A. Larionova[a], **B. N. Zolotareva**[a], **Yu. G. Kolyagin**[b], **A. K. Kvitkina**[a],
V. V. Kaganov[c], **and V. N. Kudeyarov**[a]

[a] *Institute of Physicochemical and Biological Problems of Soil Science, Russian Academy of Sciences,*
ul. Institutskaya 2, Pushchino, Moscow oblast, 142290 Russia
e-mail: larionova_al@rambler.ru
[b] *Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia*
[c] *Center of Forest Ecology and Productivity, ul. Profsoyuznaya 84/32 str. 14, Moscow, 117997 Russia*

Received August 20, 2014

Abstract—Comparative analysis of the climatic characteristics and the recalcitrance against decomposition of organic matter in the zonal soil series of European Russia, from peat surface-gley tundra soil to brown semidesert soil, has assessed the relationships between the period of biological activity, the content of chemically stable functional groups, and the mineralization of humus. The stability of organic matter has been determined from the ratio of functional groups using the solid-state ^{13}C NMR spectroscopy of soil samples and the direct measurements of organic matter mineralization from CO_2 emission. A statistically significant correlation has been found between the period of biological activity and the humification indices: the C_{HA}/C_{FA} ratio, the aromaticity, and the alkyl/*O*-alkyl ratio in organic matter. The closest correlation has been observed between the period of biological activity and the alkyl/*O*-alkyl ratio; therefore, this parameter can be an important indicator of the soil humus status. A poor correlation between the mineralization rate and the content of chemically stable functional groups in soil organic matter has been revealed for the studied soil series. At the same time, the lowest rate of carbon mineralization has been observed in southern chernozem characterized by the maximum content of aromatic groups (21% C_{org}) and surface-gley peat tundra soil, where an extremely high content of unsubstituted CH_2 and CH_3 alkyl groups (41% C_{org}) has been noted.

Keywords: global climate changes, greenhouse gases, humification, mineralization, humus

DOI: 10.1134/S1064229315100063

INTRODUCTION

The increase of CO_2 concentration in the atmosphere causes a greenhouse effect, which favors global climate changes. This prompted the world community to develop measures for mitigating the greenhouse effect, which should be based on the pattern of carbon assimilation by the plant cover, as well as carbon humification and mineralization in the soil. On the one hand, the development and implementation of measures increasing the productivity of forest, meadow, and agroecosystems will compensate the increase of CO_2 concentration in the atmosphere and bind the carbon dioxide assimilated by plants into stable compounds of soil humus [9]. On the other hand, not only the increases, but even the stabilization of carbon storage in the soil at the current level, will mitigate the implications of the global warming, because the decomposition of soil organic matter (OM) is more sensitive to temperature changes than the assimilation of carbon during the photosynthesis of plants [9, 25].

The classical theories of humification proposed by Kononova, Aleksandrova, and Orlov in the past century imply the formation of condensed polyaromatic compounds—humic acids (HAs), fulvic acids (FAs), and humin—significantly more resistant to decomposition than the original plant residues [1, 8, 15]. However, the results of incubation experiments on the decomposition of polyaromatic hydrocarbons, lignin, and HA isolated from the soil do not confirm the widespread idea of the high chemical stability of humic substances: the microbial community is capable of decomposing any natural substrate [31].

The conclusion about the minor importance of the molecular structure of OM in its stabilization in the soil was based on the wide use of ^{13}C NMR spectroscopy in soil and ecological studies. The synthesis of the accumulated data on the proportions of functional groups of OM revealed no reliable correlations between OM structure, climate, soil type, and humus storage [30]. Moreover, a correlation between the content of structural fragments and the degree of OM humification, i.e., significant structural differences among the main groups of humic substances (HAs, FAs, and humin), cannot be always revealed [28, 30].

In the zonal series of soils of European Russia, from tundra to semidesert, the degree of humification, which is estimated from the C_{HA}/C_{FA} ratio, is determined by the period of biological activity (PBA); i.e., the C_{HA}/C_{FA} ratio is related to the climate and the soil type [4, 13, 17]. Along with the degree of humification, Orlov et al. proposed inclusion the PBA and the degree of benzoidicity of HAs to expand the system of parameters of the soil humus status [17]. The degree of benzoidicity was calculated from the data of elemental analysis and the content of oxygen-containing functional groups [16]. At present, ^{13}C NMR data are used for the determination of an analogous parameter: the degree of aromaticity, which is the ratio between the content of aromatic fragments and the sum of aromatic and aliphatic functional groups excluding the carboxyl groups [20, 22, 30]. For assessing the relationship between the structure of humus and the soil type, HA's in a less representative series from soddy-podzolic to light chestnut soils were studied by ^{13}C NMR spectroscopy [20, 22, 33], and a significantly higher aromaticity was revealed in the steppe soils compared to the soils of the forest zone.

For the more complete characterization of humus, the aromaticity should be assessed not only for HAs, but also for the entire OM pool in a wide variety of soils types from tundra to semidesert, and its relationship with the PBA should be determined. The aromaticity, in the opinion of the authors of this index, should characterize not only the degree of humification, but also the decomposition resistance of OM. The estimation of the relationship between the stability and aromaticity requires direct determinations of OM mineralization from CO_2 emission.

The aims of the work were to reveal correlation between the PBA, the rate of mineralization, and the OM aromaticity for assessing the relationship between the climate, the soil type, and the structure of soil OM and to determine the importance of chemical stability as a mechanism of OM stabilization in different soil types of European Russia.

OBJECTS AND METHODS

The studied zonal soils expand from north to south in European Russia. The climatic parameters, the composition of plant communities, and the properties of soils significantly vary in the zonal series (Tables 1, 2). Soil samples of predominantly loamy composition were taken from the 0–10-cm layer under natural zonal plants, passed through a 2-mm sieve, air dried, and transported to the laboratory.

The decomposition constants of OM were determined from the cumulative loss of CO_2 during incubation. The soil samples were incubated at constant temperature and water content in four replicates for a year. For this purpose, 10 g of soil was put in a vial of 100 mL and wetted to 70% of field water-holding capacity. The sealed vials were incubated at a constant temperature of 22°C. The water content of the samples was maintained constant by the periodical addition of small water volumes up to the initial sample weight. Gas samples were taken on the 1st, 3rd, 5th, 7th, 10th, and 14th days and then weekly. The soil respiration rate was determined from the accumulation of CO_2 in the intervals between gas samplings. The vials were periodically ventilated, when the concentration of CO_2 in the gas samples exceeded 2%.

The cumulative curve of CO_2 emission was approximated for the period of experiment using the equation

$$Y_t = 1 - A_1 e^{-k_1 t} - (1 - A_1) e^{-k_2 t}, \qquad (1)$$

where Y_t is the cumulative loss of $C{-}CO_2$ for time t expressed as the portion of the initial C_{org} content in the soil; A_1 is the proportion of the labile pool; and k_1 and k_2 are the decomposition constants of the labile and recalcitrant pools, respectively.

The microbial biomass (C_{mic}) in the soil was determined by the substrate-induced respiration method [25]. Soil samples of 2 g were wetted to 60% of field water-holding capacity and preincubated at 22°C for 7 days. After the end of preincubation, a glucose solution was added to the soil at a rate of 10 mg/g soil. The substrate-induced respiration was determined from the accumulation of CO_2 3 h after the addition of glucose. The value of C_{mic} was calculated from the substrate-induced respiration data (V_{SIR}) using the equation

$$C_{mic} = 40.04 V_{SIR} + 3.75. \qquad (2)$$

The group composition of humus was determined by the Ponomareva–Plotnikva method [14].

The structural fragments of OM were studied by solid-state ^{13}C NMR spectroscopy. To remove iron compounds, which degrade the quality of ^{13}C NMR spectra, the soil samples were treated with 10% HF [28]. An HF solution (50 mL) was added to 5 g of soil; the mixture was left to stand for 12 h and centrifuged at 3000 rpm. The precipitate was fivefold washed with distilled water and dried at 50°C. The absence of acid in the precipitate was controlled from the supernatant pH.

The ^{13}C NMR spectra of soil samples were recorded on a Bruker Avance-II NMR 400 spectrometer with a frequency of 100.4 MHz and a 4-mm two-channel MAS detector. ^{13}C NMR spectra were recorded using pulsed procedures with controlled polarization transfer. The positions of peaks in the spectrum (chemical shift) were referred to the position of the CH_2 groups in the structure of adamantan.

For identification, the spectra were subdivided into regions corresponding to different structural fragments [20, 22, 28]: 0–45 ppm, unsubstituted alkyls (aliphatic fragments composed of CH_2 and CH_3 groups); 45–110 ppm, *O*-alkyl groups of carbohydrates and proteins; 110–140 ppm, unsubstituted or alkyl-substituted aromatic structures (H(C)-aryls); 140–160 ppm, *O*-substituted (phenolic) aromatic fragments (*O*-aryls); 160–190 ppm, carbonyls of the COOH groups; 190–220 ppm, carbonyls of aldehydes and ketones.

Table 1. Ecosystem's characteristics of the zonal series

Natural-geographical zone	Location	Geographical coordinates	Vegetation	Soil name	Soil abbreviation
Subshrub tundra, Komi Republic, Vorkuta district	Plots of the Institute of Biology, Komi Science Center, RAS Ural Branch	67°32′ N, 64°08′ E	Moss dwarf birch-willow forest	Loamy surface-slightly gley peat soil	PSG
Middle taiga, Komi Republic, Syktyvkar suburb	Plots of the Institute of Biology, Komi Science Center, RAS Ural Branch; station of 17 km	61°33′ N, 50°37′ E	Green moss bilberry-spruce forest	Loamy sandy iron-illuvial podzol on morainic medium loam	P
		61°34′ N, 50°38′ E	Herbaceous birch forest	Loamy slightly soddy-slightly podzolic soil	PS
Southern taiga, Novgorod oblast, Valdai district	Secondary forest on the former agricultural land of the Iviron monastery	58°00′ N, 33°24′ E	Oxalis spruce forest with mountain ash and spruce understory	Loamy sandy soddy-medium podzolic soil on medium morainic loam	SP
Deciduous forest zone, Moscow oblast, Serpukhov district	Experimental Field Station of the Institute of Physicochemical and Biological Problems of Soil Science	54°50′ N, 37°34′ E	Secondary deciduous forest	Medium loamy gray forest soil	GF
Southern forest-steppe, Voronezh oblast, Talovaya district	Kamennaya Step' Reserve, plot 2, mown fallow (120 years)	58°00′ N, 33°24′ E	Grass-herbaceous steppe	Medium loamy ordinary chernozem	OC
Steppe, Volgograd oblast, Rudnya district	Kozlovskaya forest belt, central part, virgin steppe	50°58′ N, 44°21′ E	Herb-feather grass steppe	Medium loamy southern chernozem	SC
Dry steppe, Volgograd oblast, Oktyabr'skii district	Peregruznoe village, virgin area	48°01′ N, 44°2′ E	Sheep fescue-wormwood-herb steppe, projective cover 80%	Medium loamy nonsolonetzic chestnut soil	C
Semidesert, Astrakhan oblast, Akhtuba district	Bogdinsko-Baskunchakskii State Natural Reserve, Zelenyi Sad plot	48°03′ N, 46°54′ E	Wormwood semidesert, projective cover 30%	Loamy sandy brown semidesert soil	BSD

Table 2. Climatic characteristics and properties of soils (A1 horizon) in the zonal series

Soil	Mean annual value		Number of days		pH_{KCl}	C_{org}, %	C_{HA}/C_{FA}	C_{mic}, μg C/g
	t, °C	precipitation, mm	*t* > 10°C	PBA*				
PGS	–6.3	550	43	43	4.4	2.64 ± 0.21	0.58	144 ± 38
P	0.4	514	102	102	4.0	0.44 ± 0.02	0.32	88 ± 5
PS	0.4	514	102	102	4.8	2.65 ± 0.13	0.37	440 ± 100
SP	3.2	653	120	120	5.6	3.21 ± 0.13	0.70	480 ± 32
GF	3.9	582	137	137	5.9	3.15 ± 0.17	0.99	620 ± 9
OC	5.2	459	149	149	6.8	7.60 ± 0.12	3.15	1250 ± 13
SC	5.5	390	159	154	6.9	4.61 ± 0.15	2.33	786 ± 20
C	7.2	378	166	116	7.1	2.31 ± 0.08	0.97	400 ± 8
BSD	7.8	243	175	50	7.4	0.53 ± 0.03	0.38	92 ± 6

* (PBA) period of biological activity.

The content of C_{org} in the soil was determined on a Vario EL III CHN analyzer.

The concentration of CO_2 was determined on a Kristallux-4000 chromatograph with a thermal conductivity detector. The gas mixture was separated in 3-m columns packed with Porapak-Q at 50°C.

The results of analyses were calculated per oven-dry soil basis.

The relationship between the PBA and the degree of humification (C_{HA}/C_{FA}) was estimated using the equation proposed by Morozov [13]

$$\gamma = \gamma_* + a(\beta - \beta_*)^n\theta(\beta - \beta_*), \quad (3)$$

where $\gamma = C_{HA}/C_{FA}$; β = PBA; γ_* and β_* are the critical (minimum) values of C_{HA}/C_{FA} and PBA (0.3 and 43, respectively). The value of θ is equal to 1, if $\beta > \beta_*$, and θ is 0, if $\beta < \beta_*$. The duration of PBA for the studied soils was calculated from the data of the nearest meteorological stations [18]. The numbers of droughty days in the dry-steppe and semidesert zones were borrowed from the agroclimatic reference book [12]. After the calculation of parameters *a* and *n* for the studied soils, the following expression was obtained:

$$C_{HA}/C_{FA} = 0.3 + 5 \times 10^{-8}(\text{PBA}–43)^{3.6}\theta(\text{PBA}–43). \quad (4)$$

Parameters of Eqs. (1) and (3) were calculated using the Markquardt algorithm [21].

RESULTS AND DISCUSSION

For all zonal soils, the obtained ^{13}C NMR spectra include a set of maximums typical for soil OM: alkyls, *O*-alkyls, aryls, and carbonyls. The most contrast spectra of OM from surface-gley peat soil and typical chernozems are given in Fig. 1. The content of alkyl groups is maximum in the tundra soil and minimum in the ordinary chernozem. Extreme contents of aromatic groups were also observed in these soil types: the minimum content of aryls (9%) was in OM of gley tundra soil, and their maximum content (21%) was found in OM of ordinary chernozem.

The calculated contents of functional groups in OM of zonal soils (Fig. 2) indicate that similar contents of *O*-alkyls (the main components of plant residues) were typical for the spectra of all soils. The

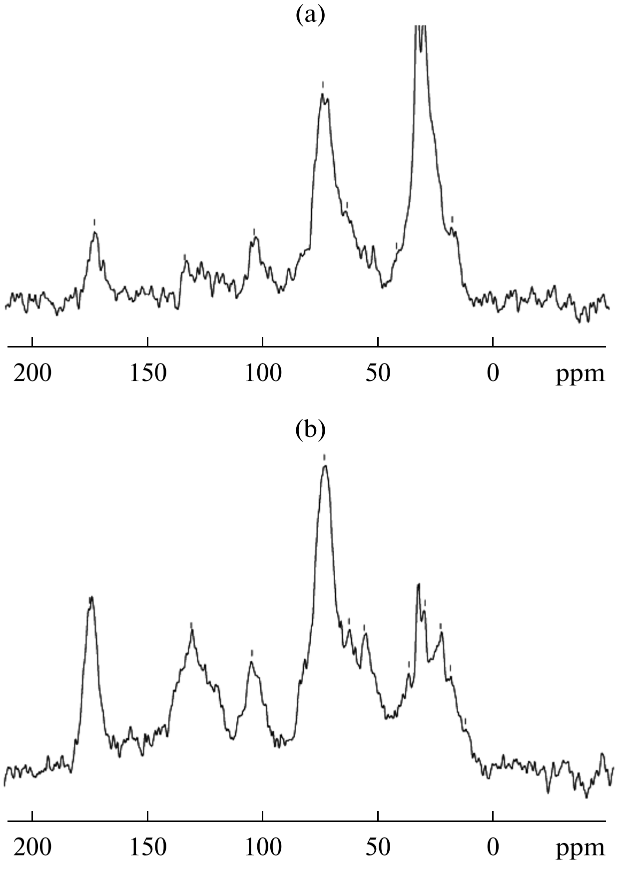

Fig. 1. ^{13}C NMR spectra of organic matter from (a) surface-gley peat soil and (b) typical chernozem.

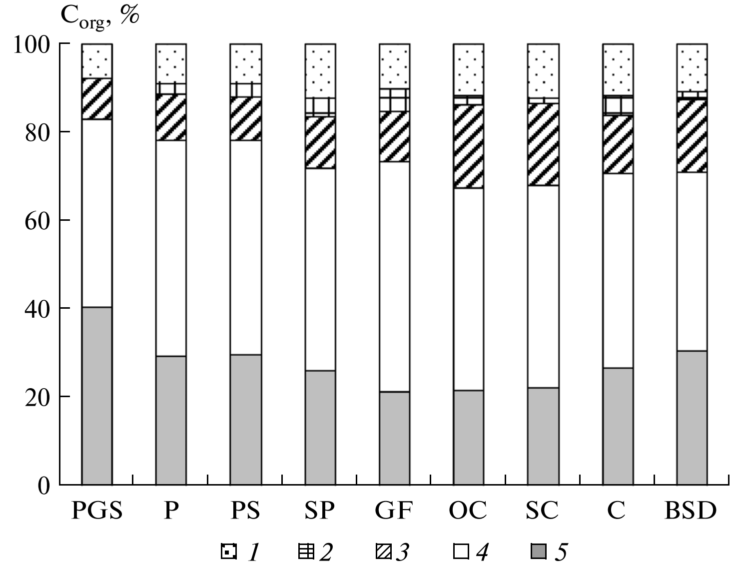

Fig. 2. Distribution of C_{org} among functional groups ((*1*) carbonyls, (*2*) *O*-aryls, (*3*) aryls, (*4*) *O*-alkyls, (*5*) alkyls) in the zonal series of soils.

decrease in the proportion of these structural fragments is the major transformation process of plant residues during humification in the all soils. In plant residues, the content of *O*-alkyls is 60–85% [29, 32]; the proportion of these fragments in OM is significantly lower: 44.8 ± 8.5% on the average [30]. In the studied zonal soils, the content of *O*-alkyls was 42–48%. Even in the soils developed under unfavorable hydrothermal conditions (gley tundra and brown semidesert soils), the content of *O*-alkyls similar to that in chernozemic soils was observed. Thus, deep transformation of the original plant material occurs in all zonal soils, even under slow biological turnover at low temperature (surface-gley peat soil) and water content (brown semidesert soil), which indicates adaptation of the waste-degrading microbial community to unfavorable environmental conditions.

In Fig. 2, all zonal soils are arranged on the abscissa according to their location from north to south, and the dependence of alkyl content on the geographical latitude of soils has an aspect of a U-shaped curve. The content of alkyls first decreased when going from the tundra soils (40.5%) to the chernozems (21.5%), and then increased again from the chernozems to the brown semidesert soils.

According to the content of aromatic components, the studied soils were subdivided into two groups: (1) the soils of the tundra and taiga zones that developed under bushy and woody plants and (2) the soils of the steppe series. The first group included the soils in which the content of aromatic groups gradually increased from 9 to 16%. In the soils of the second groups, the content of aryls was 18–21%. The determination error of functional groups was 1–2%; therefore, it may be stated that the soils of the steppe series little differed in the content of aromatic fragments.

Carboxyl groups were uniformly distributed among the types of the studied soils. The soils of the northern areas (gley tundra and podzolic soils) were characterized by a decreased content of COOH groups (8–9%); in the other soil types, the content of carboxyl groups was 11–12%.

The processing of dry-steppe soils (chestnut and brown semidesert ones) was accompanied by significant losses in C_{org}, to 25 and 40% of the original OM content, respectively. At the removal of iron from the other zonal soils, the losses of C_{org} were 2–7%. In spite of these values, the quantitative analysis of spectra in brown semidesert soils was successfully performed only after the HF treatment. In preliminary experiments with gray forest soils and ordinary chernozem, the comparison of spectra before and after the HF treatment revealed no significant differences between the ratios of functional groups. An analogous result was obtained earlier for soils of the Lower Carbonic, although the HF treatment resulted in significant losses of OM [23]. Therefore, at the current stage of studies, the ^{13}C NMR spectra of zonal soils can be compared, in spite of different OM losses at the removal of iron from the samples.

The soils of the zonal series have loamy texture, but in some cases (podzol and brown semidesert soil), the upper horizons consist of loamy sands. The comparison of the contents of functional groups in the OM of iron-illuvial podzol and loamy soddy-slightly podzolic soil in the zone of podzolic soils shows similar structures of OM in the both soil types (Fig. 2). The main differences were observed for the content of C_{org}: 0.44 and 2.65%, respectively; i.e., the content of OM in the

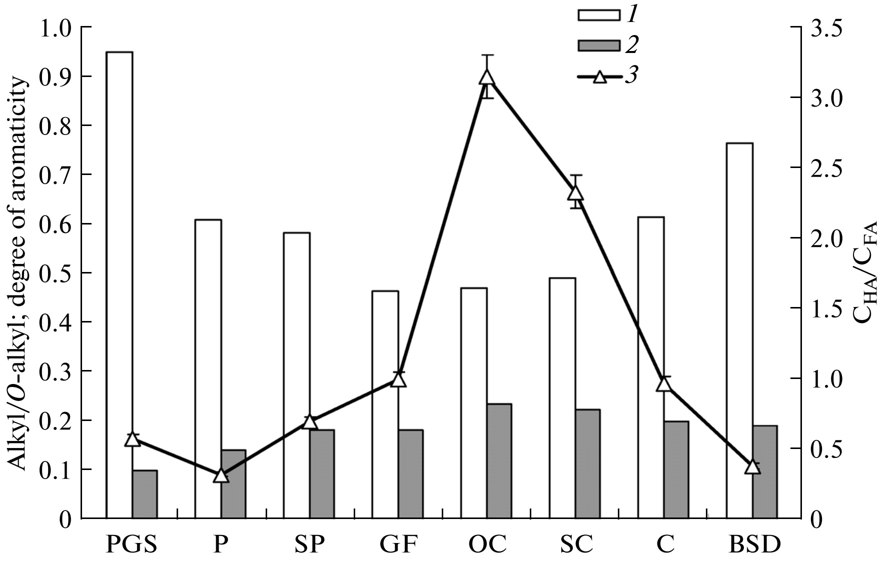

Fig. 3. Indices characterizing the OM humification depth in the zonal series of soils: (*1*) alkyl/*O*-alkyl ratio; (*2*) degree of aromaticity; (*3*) C_{HA}/C_{FA} ratio.

soil of sandy texture was lower than in the soils of medium-loamy texture by six times. With consideration for the similar distributions of functional groups in OM of podzols with different textures, we think that this factor may be ignored at the first stage of OM analysis in zonal soils. The effect of soil texture on the content of OM functional groups in all soil zones should be assessed in further studies.

In spite of the diversity of plant communities and climatic conditions, it was revealed that OM has similar structure in different soil types of the Russian Plain. In the series from tundra to semidesert, the vegetation productivity varies by about five times [3] and the duration of PBA varies by more than four times. At the same time, the content of functional groups in OM of zonal soils varies by no more than two times. The structural similarity of OM can be related to the high adaptation capacities of microbial communities humifying plant residues in different soil types. The obtained results agree with the literature data. The sets of functional groups in OM of tundra and podzolic soils were similar to those in tundra soils of Alaska [26] and podzols of European Russia [11]. An analogous tendency was revealed at the comparison of the changes in the HA structural fragments in the series from soddy-podzolic to dry-steppe soils [20, 22, 33] with the changes in the OM functional groups in analogous soils of the studied zonal series. An increase in the content of aromatic fragments is observed in the series from soddy-podzolic soils to chernozems, and the differences between the chernozems and the soils of dry steppes (chestnut and light chestnut soils) are related to the content of aliphatic fragments.

In the studied zonal series, the C_{HA}/C_{FA} ratio varied in a wider range (0.3–3.2) than the other humification parameters: the alkyl/*O*-alkyl ratio (0.4–1.0) and the degree of aromaticity (0.10–0.23) (Fig. 3). The changes of the alkyl/*O*-alkyl ratio in the zonal series were analogous to those in the content of *O*-alkyls; i.e., they represented a U-shaped curve with a minimum in the zone of chernozems. The degree of OM aromaticity, like the content of aryls, increased when going from the tundra soils to the chernozems and remained almost unchanged from the chernozems to the brown semidesert soils. The C_{HA}/C_{FA} ratio corresponded to the known tendency: a maximum was observed in the zone of chernozems, as were minimums in the podzols and the brown semidesert soils.

The changes in the main indicators of OM structure agree with those of PBA in the zonal series (Fig. 4). The alkyl/*O*-alkyl ratio is inversely proportional to the PBA, and the degree of aromaticity directly depends on the PBA.

Some authors recommend the alkyl/*O*-alkyl ratio to be used as an index for the quantitative characterization of the degree of humification [29, 32, 34]. The fact is that the relative accumulation of aromatic fragments is not always observed during the transformation of plant material [32, 34].

The value of R^2 for the linear regression between the PBA and the alkyl/*O*-alkyl ratio was high: 0.88 (Fig. 4a). The value of R^2 for the relationship between the PBA and the degree of aromaticity was significantly lower: 0.53 (Fig. 4b). From Eq. (4), a close nonlinear correlation existed between the PBA and the C_{HA}/C_{FA} ratio, which is traditionally considered as the main humification index [6, 17]; the R^2 value was 0.73 (Fig. 3c). Thus, the correlation between the alkyl/*O*-alkyl ratio and the PBA was more significant

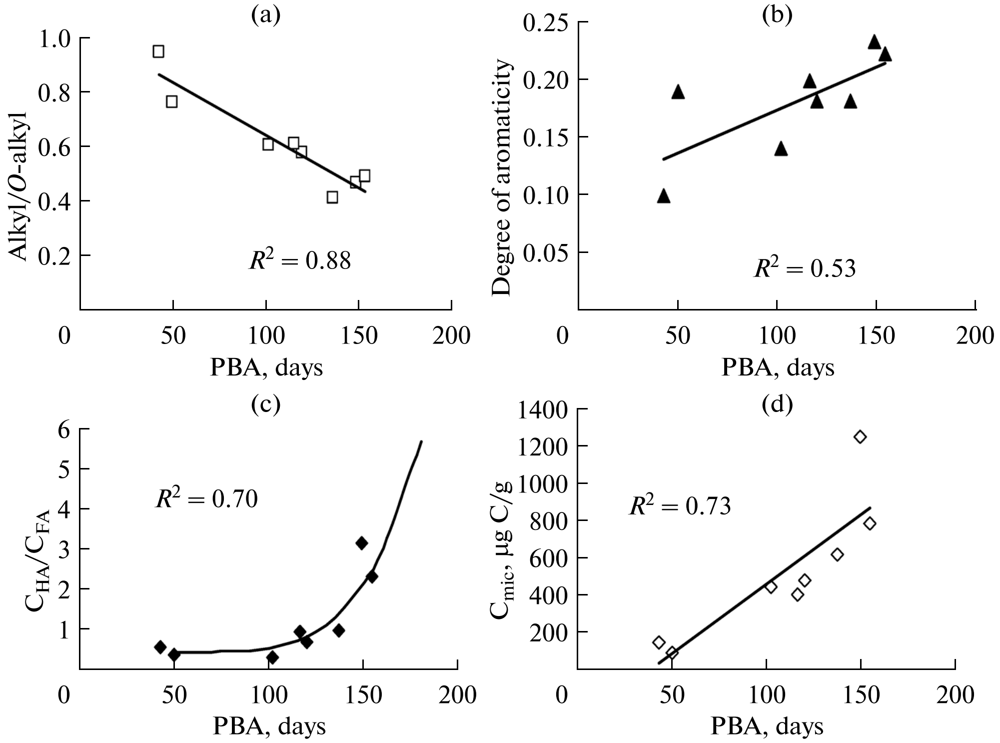

Fig. 4. (a) The alkyl/*O*-alkyl ratio, (b) the aromaticity, (c) the C_{HA}/C_{FA} ratio, and (d) C_{mic} as functions of the PBA in the zonal series of soils.

than that between the C_{HA}/C_{FA} ratio and the PBA. This was due to the nonmonotonic increase of the C_{HA}/C_{FA} ratio with increasing PBA in the series from the tundra soils to the chernozems. The C_{HA}/C_{FA} ratio in the tundra soil (0.58) was higher than that in the podzol (0.32). This could be related to the high spatial variability of the C_{HA}/C_{FA} ratio in both tundra and podzolic soils. From literature data, the C_{HA}/C_{FA} ratio varies from 0.15 to 0.86 in the upper horizons of podzols [2] and from 0.08 to 3.2 in those of tundra soils [7].

The alkyl/*O*-alkyl ratio—which showed the highest linear correlation with the PBA—can be recommended, along with the C_{HA}/C_{FA} ratio, for the characterization of the soil humus status. The degree of OM aromaticity was found to be a less appropriate parameter in the studied soils, because it insignificantly varied in the series from the chernozems to the soils of dry steppes. The obtained relationships between the humification indices should be specified with consideration for other soil types and the spatial variability of these values within each soil zone.

The decomposition rate constants of the recalcitrant pool of soil OM in the zonal series varied by three times and had a bimodal distribution depending on the geographical latitude (Fig. 5). The minimum values (9×10^{-5} days^{-1}) were observed in the tundra and chernozemic soils. The soils of forests and dry steppes had almost similar values of this parameter; the decomposition constants of their stable pools were (2.2–2.8) × 10^{-4} days^{-1}. Therefore, an insignificant correlation was observed between the decomposition constant of the stable pool and the content of stable functional (alkyl or aromatic) groups. At first sight, the obtained data confirm the current idea about the low significance of chemical stability as a mechanism of OM stabilization [31]; however, in our opinion, the high stability of OM in the chernozems and the tundra soils is closely related to the content of chemically stable functional groups. The maximum content of aromatic groups (20–21%) was observed in OM of the ordinary and southern chernozems; the tundra soils contained 40% unsaturated alkyls. Both functional groups impact the hydrophobic properties of OM; i.e., they increase its resistance to decomposition [28]. The increased content of aromatic fragments in humus is traditionally considered to be the main reason for the stability of chernozem [15]. The stability of OM in the tundra soil with an extremely high content of alkyls indicates that these functional groups, as well as the aromatic groups, favor the low rate of OM decomposition by microorganisms. The increased content of alkyls in OM is usually observed in flooded soils (peat and bog-podzolic ones) [11, 26]. Probably, the excessive moistening of the surface-gley peaty tundra soil results in the formation of OM enriched with stable alkyl groups.

The stability of OM depends not only on the content of slowly decomposable structural fragments, but

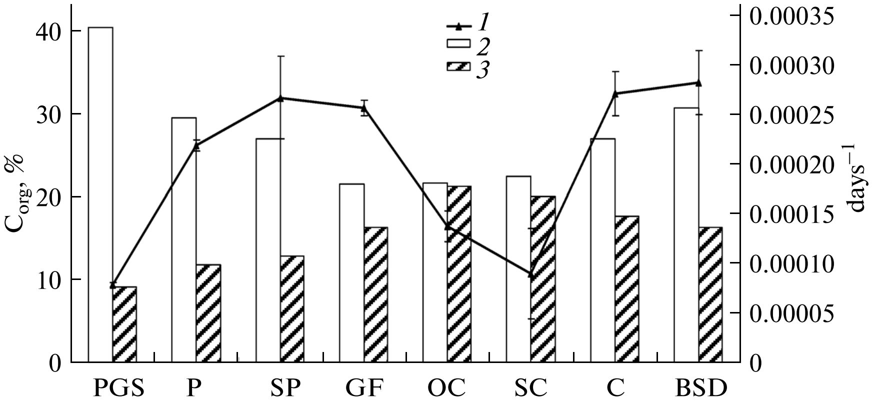

Fig. 5. (*1*) Mineralization rate constants of the recalcitrant OM pool and the contents of chemically stable functional groups ((*2*) alkyls and (*3*) aryls) in the zonal series of soils.

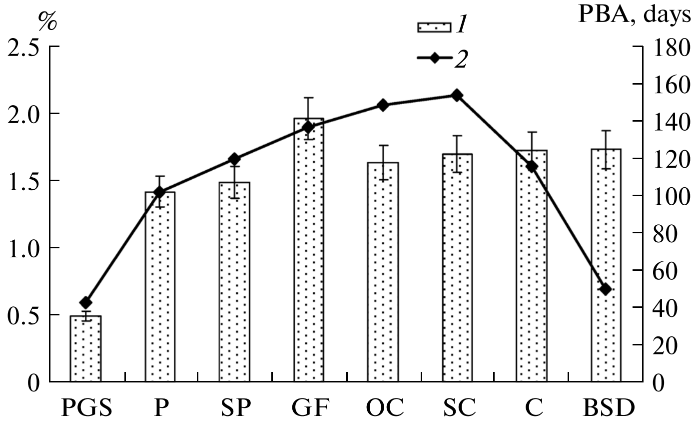

Fig. 6. (*1*) The C_{mic}/C_{org} ratio and (*2*) the PBA values in the zonal series of soils.

also on the amount of microbial biomass (C_{mic}) in the soil. In the zonal series, the value of C_{mic} varied by about an order of magnitude, from 88 to 1250 μg C/g soils, and corresponded to the content of organic carbon; i.e., it increased with increasing content of OM. The content of microbial carbon also closely correlated with the duration of the PBA (Fig. 4d).

The correlation between the OM microbial component and the PBA becomes poor if the content of microbial carbon is calculated per unit OM carbon. In contrast to the PBA, the C_{mic}/C_{org} ratio insignificantly varies depending on the soil type (Fig. 6). The proportion of microbial carbon in most soils of the zonal series is 1.5–2% C_{org}, which is typical for the soils developed under natural vegetation [19, 24] and indicates the adaptation of the microbial community to the environmental conditions. Only in the tundra soil OM is depleted in the microbial component: the proportion of C_{mic} is only 0.5% C_{org}. In other words, a relatively smaller microbial biomass is involved in the decomposition of OM in the soils with unfavorable temperature and water regimes than in the soils developed under optimum climatic conditions. Thus, the high recalcitrance of OM in surface-gley peat soil is related not only to the chemical stability of OM, but also to the smaller biomass of soil microorganisms developed under low temperature and excess of moisture.

CONCLUSIONS

In the zonal series of soils in European Russia, the main differences in the structure of OM are related to the contents of alkyl and aromatic fragments. The contents of *O*-alkyl and carbonyl groups have no clear trends and vary in the ranges of 43–50 and 8–13% C_{org}, respectively. The content of aromatic functional groups increases from 9 to 21% C_{org} when going from the tundra soils to the ordinary chernozems, and then decreases to 17% C_{org} when going from the southern chernozems to the brown semidesert soils. The distribution of unsubstituted alkyl groups among the soil types has a U-shaped form: their content decreases from 41 to 22% when going from the surface-gley peat tundra soils to the southern chernozem and increases again to 31% C_{org} in the brown semidesert soils. A statistically significant correlation is found between the PBA and the humification indices (C_{HA}/C_{FA} ratio, alkyl/*O*-alkyl ratio, degree of OM aromaticity). The closest correlation is observed between the PBA and the OM alkyl/*O*-alkyl ratio; therefore, this index is recommended to be included to broaden in the system of parameters of the soil humus status after the synthesis of OM structure in a wider variety of Russian soils.

The decomposition constants of the recalcitrant OM pool calculated from the cumulative CO_2 emission indicate a poor correlation between the aromaticity and the rate of OM mineralization. Among the soils of the zonal series, the lowest mineralization rate constants are observed in the southern chernozem and the surface-gley peat tundra soil. The maximum proportion of stable aromatic groups in OM is found in the chernozem, and an extremely high content of unsubstituted alkyl (CH_2 and CH_3) groups is noted in the tundra soil. The high stability of soil OM in the tundra soil is related to the maximum content of chemically stable alkyl groups and the low content of microbial biomass (0.5% C_{org}). In the other soils, the content of C_{mic} is 1.5–2% C_{org}, which apparently does not limit the decomposition of OM.

More universal generalizations of tendencies in the stability of OM require the study of the spatial heterogeneity of OM within the soil zone, as well as the quantitative assessment of the effect of soil texture and mineralogy on the composition of functional groups and the mineralization of OM.

ACKNOWLEDGMENTS

This work was supported in part by the Russian Foundation for Basic Research (project no. 14-04-01738), the Program of the Presidium of the Russian Academy of Sciences (program 4), the Grant of the President of the Russian Federation (project no. NSh-6123.2014.4), and the Russian Science Foundation (project no. 14-14-00625).

REFERENCES

1. L. N. Aleksandrova, *Soil Organic Matter and Its Transformation* (Nauka, Leningrad, 1980) [in Russian].
2. B. F. Aparin, I. V. Zaboeva, G. S. Lipkina, N. A. Nogina, E. N. Rudneva, T. V. Rusakova, A. V. Sloboda, and I. S. Urusevskaya, *Podzolic Soils of the Central and East European Parts of the Soviet Union: On the Sand Soil-Forming Rocks* (Nauka, Leningrad, 1981) [in Russian].
3. N. I. Bazilevich and A. A. Titlyanova, *Biotic Circulation on the Five Continents* (Siberian Branch, Russian Academy of Sciences, Novosibirsk, 2008) [in Russian].
4. O. N. Biryukova and D. S. Orlov, “A period of biological activity of soils and its relationship with the group composition of humus,” Biol. Nauki, No. 4, 115–119 (1978).
5. A. Ya. Vanyushina and L. S. Travnikova, “Organic—mineral interactions in soils: a review,” Eurasian Soil Sci. **36** (4), 379-387 (2003).
6. L. A. Grishina, *Humification and Humus Status of Soils* (Moscow State University, Moscow, 1986) [in Russian].
7. B. N. Zolotareva, L. A. Fominykh, L. T. Shirshova, and A. L. Kholodov, “The composition of humus in permafrost-affected soils of the Bol’shezemel’skaya and Kolyma tundra areas,” Eurasian Soil Sci. **42** (1), 36–48 (2009).
8. M. M. Kononova, *Problem of Soil Humus and Modern Challenges of Its Study* (Academy of Sciences of the Soviet Union, Moscow, 1951) [in Russian].
9. V. N. Kudeyarov, G. A. Zavarzin, S. A. Blagodatskii, A. V. Borisov, P. Yu. Voronin, V. A. Demkina, I. V. Yevdokimov, D. G. Zamolodchikov, D. V. Karelin, A. S. Komarov, I. N. Kurganova, A. A. Larionova, V. O. Lopes De Gerenu, A. I. Utkin, and O. G. Chertov, *Carbon Reserves and Fluxes in Terrestrial Ecosystems of Russia* (Nauka, Moscow, 2007) [in Russian].
10. A. A. Larionova, B. N. Zolotareva, I. V. Yevdokimov, S. S. Bykhovets, Y. V. Kuzyakov, and F. Buegger, “Identification of labile and stable pools of organic matter in an agrogray soil,” Eurasian Soil Sci. **44** (6), 628–640 (2011).
11. E. D. Lodygin, V. A. Beznosikov, and S. N. Chukov, *Structural and Functional Parameters of Humic Substances in Bog-Podzolic Soils* (Nauka, St. Petersburg, 2007) [in Russian].
12. *The World Agroclimatic Handbook* (Gidrometeoizdat, Leningrad, 1937) [in Russian].
13. A. I. Morozov, “About relationship of the period of biological activity (PBA) and humification depth,” Pochvovedenie, No. 5, 118–120 (1993).
14. D. S. Orlov and L.A. Grishina, *Practical Manual on Humus Chemistry* (Moscow State University, Moscow, 1981) [in Russian].
15. D. S. Orlov, *Humic Acids of Soils and General Theory of Humification* (Moscow State University, Moscow, 1990) [in Russian].
16. D. S. Orlov, V. A. Baranovskaya, and A. A. Okolelova, “Degree of benzoid content in humic acids and its determination,” Dokl. Akad. Nauk SSSR, No. 6, 1479–1482 (1987).
17. D. S. Orlov, O. N. Biryukova, and M. S. Rozanova, “Revised system of the humus status parameters of soils and their genetic horizons,” Eurasian Soil Sci. **37** (8), 798–805 (2004).
18. “Temperature of air and soil,” in *Reference Book on Climate in the Soviet Union* (Gidrometeoizdat, Leningrad, 1964–1966), Nos. 1, 8, 13, 28, Part 2.
19. E. V. Stolnikova, N. D. Ananyeva, and O. V. Chernova, “The microbial biomass and its activity and structure in the soils of old forests in the European Russia,” Eurasian Soil Sci. **44** (4), 437–452 (2011).
20. S. N. Chukov, *Structural and Functional Parameters of Soil Organic Matter Affected by Anthropogenic Impact* (St. Petersburg State University, St. Petersburg, 2001) [in Russian].
21. D. M. Himmelblau, *Process Analysis by Statistical Methods* (Wiley, New York, 1970).

22. V. A. Kholodov, A. I. Konstantinov, A. V. Kudryavtsev, and I. V. Perminova, "Structure of humic acids in zonal soils from ^{13}C NMR data," Eurasian Soil Sci. **44** (9), 976–983 (2011).
23. T. V. Alekseeva, P. B. Kabanov, A. O. Alekseev, S. V. Gubin, and V. A. Alekseeva, "Middle-Late Mississippian palaeosols and palaeokarsts of southern Moscow basin (Russia): multiproxy study of non-actualistic pedosedimentary systems and record of climate change," Palaeogeogr., Palaeoclimatol., Palaeoecol., 2015, (in press)
24. N. D. Ananyeva, E. A. Susyan, O. V. Chernova, and S. Wirth, "Microbial respiration activities of soils from different climatic regions of European Russia," Eur. J. Soil Biol. **44** (2), 147–157 (2008).
25. J. P. E. Anderson and K. H. Domsch, "A phisiological method for the quantitative measurement of microbial biomass in soils," Soil Biol. Biochem. **10** (3), 215–221 (1978).
26. X. Y. Dai, C. L. Ping, R. Candler, L. Haumaier, and W. Zech, "Characterization of soil organic matter fractions of tundra soils in arctic Alaska by carbon-13 nuclear magnetic resonance spectroscopy," Soil Sci. Soc. Am. J. **65**, 87–93 (2001).
27. M. U. F. Kirschbaum, "The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage," Soil Biol. Biochem. **27**, 753–760 (1995).
28. I. Kögel-Knabner, "^{13}C and ^{15}N NMR spectroscopy as a tool in soil organic matter studies," Geoderma **80**, 243–270 (1997).
29. I. Kögel-Knabner, "The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter," Soil Biol. Biochem. **34**, 139–162 (2002).
30. N. Mahieu, E. V. Randall, and D. S. Powlson, "Statistical analysis of published carbon-13 CPMAS NMR spectra of soil organic matter," Soil Sci. Soc. Am. J. **63**, 307–319 (1999).
31. B. Marschner, S. Brodowski, A. Dreves, G. Gleixner, A. Gude, P. M. Grootes, U. Hamer, A. Heim, G. Jandl, R. Ji, K. Kaiser, K. Kalbitz, C. Kramer, P. Leinweber, J. Rethemeyer, A. Schäffer, et al., "How relevant is recalcitrance for the stabilization of organic matter in soils?" J. Plant Nutr. Soil Sci. **171**, 91–110 (2008).
32. C. M. J. Preston, Nault, and J. A. Trofymow, "Chemical changes during 6 years of decomposition of 11 litters in some Canadian forest sites. Part 2. ^{13}C abundance, solid-state 13C NMR spectroscopy and the meaning of "Lignin," Ecosystems **12**, 1078–1102 (2009).
33. A. Rodionov, W. Amelung, L. Haumaier, I. Urusevskaja, and W. Zech, "Black carbon in the zonal steppe soils of Russia," J. Plant Nutr. Soil Sci. **169**, 363–369 (2006).
34. S. A. Quideau, M. A. Anderson, R. C. Graham, O. A. Chadwick, and S. E. Trumbore, "Soil organic matter processes: characterization by ^{13}C NMR and ^{14}C measurements," For. Ecol. Manage. **138**, 19–27 (2000).

Translated by K. Pankratova