DEGRADATION, REHABILITATION, AND CONSERVATION OF SOILS

Estimation of Carbon Stocks in Soils of Forest Ecosystems as a Basis for Monitoring the Climatically Active Substances

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Abstract—The eluvozems and soddy eluvozems on two-layered deposits dominating in the soil cover of the Zvenigorod Biostation of Moscow State University, contain, on average, 65–83 t/ha of organic carbon in the organic layer and the upper meter of mineral strata. Carbon stock is minimal (59–68 t/ha) in the coarser-textured soddy eluvozem of the spruce forest and reaches 76–92 t/ha in soils of birch–spruce and pine–spruce forests. Organic layers store 3.3–5.8 t C/ha or 4–9% of the total soil organic carbon stock; the upper mineral layer (0–20 cm) stores 64–69%. Different levels and profile distribution of organic carbon in soils are determined by lithological and textural features of the soil profiles and by the nature of vegetation. The contribution of water-extractable organic carbon to the total organic carbon content in the upper mineral horizons does not exceed 1.3–1.8%; the contribution of microbial carbon is 1.7–2.4%. In acidic loamy soils, the enrichment in calcium and potassium, the cation exchange capacity, the content of exchangeable bases, and the degree of base saturation can serve as indicators of the content and stocks of organic carbon at the ecosystem level. The relationship with the content of clay fractions and oxalate-extractable Al and Fe is manifested to a lesser extent due to the similar origin and properties of soils. The variability of organic carbon stocks in soils is largely determined by its content, the influence of which decreases with depth. Accounting for spatial heterogeneity, field measurements of the soil bulk density and proportion of fine earth, and correct analytical determinations are essential components of the assessment of carbon stocks in soils of forest ecosystems as a part of the national monitoring system for carbon pools and greenhouse gas fluxes.

Keywords: ecological functions, carbon sequestration, organic carbon, labile compounds, microbial biomass, variability, organic layer, Dystric Cambisol

INTRODUCTION

Soil is the largest reservoir of organic carbon (C_{org}) in terrestrial ecosystems, twice as large as the atmospheric carbon pool and three times greater than the carbon pool of biota. It is closely related to the preservation of climate and biosphere as a whole [54, 70]. A significant part of global carbon pool is accumulated in forest ecosystems, the total area of which reaches 4.06 billion ha, or 31% of the land area [38]. The stock of carbon in the world forests is estimated at 861 ± 66 Gt C, including 383 ± 30 Gt C (44%) in soil (to a depth of 1 m), 363 ± 28 Gt C (42%) in living biomass (aboveground and underground), 73 ± 6 Gt C (8%) in dead wood, and 43 ± 3 Gt C (5%) in organic layer [65]. Though a larger part of carbon in forest ecosystems is stored in soils [54, 65], they are typically given less attention than vegetation in carbon budget calculations [41].

In Russia, possessing one-fifth of the world forests, estimates of total stock of organic carbon in forest soils require further elaboration. The stock of C_{org} in forest soils of Russia is estimated at 240.6 Gt C according to averaged data from databases and forest growth conditions zonation [22]. According to other assessments, it reaches 144.5 Gt C with 94.2% of this amount in the one-meter soil layer, and 5.8% in the aboveground organic layer, the pool of C_{org} with the high rate of turnover [63]. About 81% of the total stock of C_{org} in soils of Russian forests is in the Asian part constituting 79.5% of the total area of Russian forests. A larger part of soil C_{org} is accumulated in boreal forests (83 and 93% in European and Asian parts of the country, respectively) [63]. The information about carbon stocks in soils of the zone of mixed coniferous–broadleaved forests of the European part of Russia is few [2, 11] and is often restricted to the upper 20–30 cm layer [19],

though the carbon content is the necessary characteristic in most soil studies.

The capacity for carbon accumulation and preservation is the key function of soil, which determines climate regulation and affects other soil functions [43, 82]. It depends on many soil, biological, climatic, geomorphological, and anthropogenic factors [45, 47, 54, 73, 81, 82] controlling carbon turnover in forests. According to estimates of the stocks of soil C_{org} at European scale (4914 plots of forest monitoring network of the first level (16 × 16 km) in 22 countries of the European Community; ICP Forests UNECE), the most informative predictors and stratifiers of carbon stocks include humus forms and tree species for soil organic layer, reference soil groups for mineral soils, and initial material for peat soils [33]. The role of soils as a sink or source of atmospheric carbon largely depends on climatic factors, as they determine plant growth (contributing to the carbon input into soil), activity of soil microorganisms (promoting the release of carbon from soil to atmosphere), and some other chemical processes in soils [36]. Climate warming can result in the loss of C_{org} from forest soils, which is accompanied by a decrease in soil fertility and a positive feedback effect to climate change [46] with maximum losses expected in high latitudes [1, 45]. However, the response of soil organic matter (SOM) to climate changes remains largely unclear [36, 70], depends on time scale [73], and preservation of carbon in soils is determined not only by bioclimatic conditions but also by soil properties [36, 48].

Modern ideas reflect the paradigm shift from the concept of stable chemical structure of SOM as the basis for its preservation in soils to the idea of microbial nonavailability and interaction between mineral phase and labile compounds as the main mechanisms of organic carbon stabilization in soils [16, 53]. Soil properties determining the degree of stabilization of organic components include the content of fine (silt and clay) fractions, pedogenic oxides of iron and aluminum, polyvalent cations, and soil pH [50, 67, 82]. Interaction with the mineral phase, and particularly with amorphous oxides of Fe and Al, and the occlusion within soil aggregates are the main mechanisms of stabilization in acid and almost neutral soils [52, 69]. The possibility of stabilization and preservation of sequestrated from atmosphere carbon in soil is restricted by saturation capacity depending on soil physical and chemical properties, and first of all on concentrations of silt and clay fractions, which form SOM associated with minerals [5, 52, 74, 81, 82]. Current stocks of this SOM pool in the one-meter layer of non-permafrost mineral soil reach 899 Pg [40]. Though they account for 66 and 70% of carbon in the surface and deep soil layers, respectively, this is only 42 and 21% of the potential mineralogical capacity [40]. Deep soil layers and agricultural soils are most undersaturated with mineral-associated carbon, and this fact indicates the efficiency of carbon sequestration by these soils during several years or decades.

Cations of some metals, including Fe^{3+}, Al^{3+}, Ca^{2+}, and Mg^{2+}, can be essential to SOM stabilization, specifically due to formation of cation bridges in the process of organic matter sorption on mineral surfaces and the formation of complexes with organic molecules [49, 67, 75, 82]. The effective cation-exchange capacity (CEC_{ef}) integrates information about available soil surfaces, on which metal cations are fixed. It can serve as an integral index of potential preservation and change of SOM, which should help to improve forecasts of soil carbon pool response to environmental change [75]. The primary role of potential CEC and base saturation in predicting mechanisms of carbon sequestration was demonstrated in the long-term experiments with plant detritus [48].

As the mechanisms of physical and chemical stabilization play a critical role in the control of carbon accumulation in mineral soils [52], carbon losses caused by climate warming can probably be smaller than it was previously believed [42]. According to the results of analyses of more than 9000 soil profiles, the decrease in soil carbon stock with temperature is more than three times more intense in coarse-textured soil with limited capacity for SOM stabilization than in fine-textured soils with greater stabilization capacity [42].

However, not only mineral-associated but also particulate organic matter, which is more susceptible to disturbance, but requires less nitrogen and potentially can be accumulated limitless, is important for SOM accumulation [32]. The distribution of carbon between mineral-associated and particulate organic matter and the C : N ratio affect the SOM stock and mediate the influence of other variables on the stock.

Taking into account the multicomponent character and heterogeneity of SOM, isolation of structural and functional pools of SOM in order to find interactions between SOM composition and functioning becomes a common practice [16, 52]. The subdivision to particulate and mineral-associated organic matter radically differing in formation, stability, and functioning is suggested as the main subdivision of SOM pools [17, 56]. The consensus was reached on isolation of the pool of microbial biomass carbon (C_{mic}) as a sensitive indicator of SOM transformation [14, 82]. It was suggested to isolate the pool of potentially mineralizable SOM along with microbial pool [17]. The concept of SOM eco-functionality with managerial decisions is being developed [43].

The rate of C_{org} sequestration in soils ranges from 100 to 1000 kg C/ha per year [55]. It is higher in soils of cold humid climates than in soils of warm and dry climates, in fine-textured soils than in coarse-textured soils, and in deep soils than in shallow soils. The sequestration of atmospheric CO_2 in soils is called a win—win strategy of adaptation to climate change, mitigation of consequences of this change together

with the improvement of the environment [55]. This objective is pursued by the Four per Mille Initiative directed at the increase of carbon stock in soils by 4‰ (0.4%) per year to compensate for the annual increment of CO_2 concentration in the atmosphere [77]. However, the possibility to fulfil this initiative caused active discussion about the capability of ecosystems at a global scale to absorb significant quantities of carbon [37]. The deficiency of nitrogen and phosphorus, which can restrict plant productivity and, hence, the accumulation of carbon in soils, serves as an obstacle [35, 78]. Additional problems include the deficiency of biomass for introduction to soil and potential saturation of the stock of soil carbon [62, 66]. Social and economic limits can also prevent the large-scale implementation of the methods of carbon sequestration in agriculture [29]. No smaller problems are typical for carbon sequestration in the biomass and soils of forest ecosystems during forest-climate projects, including afforestation, forest restoration, and improvement of forest management [10, 57].

Hence, climate-regulating functions of forest ecosystems, their capacity for carbon sequestration and storage mostly depend on the composition and properties of their most important component, soils. However, the information on soil pools of carbon and their spatial variability and temporal dynamics in forest ecosystems is insufficient and unbalanced [46]. In this regard, relatively intact forest ecosystems of nature reserve Zvenigorod Biostation and Sima Quarry, which serves as an educational and scientific base of Lomonosov Moscow State University, are of great interest. The Soil Science Faculty of the university conducts intense soil-ecological monitoring according to the recommendations of the International Cooperative Program on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) [7]. The aim of our work was to assess the content and stock of organic carbon, including labile and microbial pools, their spatial variability and relationships with soil properties as possible indicators of carbon accumulation in soils of forest ecosystems of the reserve.

OBJECTS AND METHODS

Objects of study. The study was carried out in the territory of regional nature reserve Zvenigorod Biostation and Sima Quarry (ZBS), 12 km from Zvenigorod (Moscow oblast), on the right bank of the Moskva River. Local watershed plateau and valley slopes are covered by coniferous, mixed, and deciduous forests. Undisturbed zonal different-aged spruce–broadleaved forests disappeared from this territory in the recent centuries because of the heavy anthropogenic load [3]. Modern forests are mostly secondary spruce forests with some participation of nemoral components.

Soils of the main types of forest ecosystems on the watershed plateau are developed from the two-layered parent material—mantle loam underlain by glacioflu-

vial sand. Several soils were described: (1) superdeep-eluviated strongly unsaturated sandy loamy contact-bleached eluvozem on two-layered deposits (Dystric Cambisol (Endogeo-abruptic, Ochric, Nechic) under complex pine–spruce forest, (2) deeply eluviated strongly unsaturated sandy loamy ferruginous thin soddy eluvozem on two-layered deposits (Dystric Cambisol (Endogeo-abruptic, Anoloamic, Ochric, Nechic) under birch–spruce forest, and (3) strongly unsaturated loamy sandy pseudofibrous thin soddy eluvozem on two-layered deposits (Dystric Cambisol (Endogeo-abruptic, Endo-arenic, Ochric) under complex spruce forest (Table 1). Representation of the soil cover by given elementary soil areas corresponding to the particular types of phytocenoses was confirmed by the results of preliminary studies, including soil mapping. The depth of the upper boundary of underlying sand layer within the studied sites varied from 38 to 45 cm.

Field methods. The study was carried out on three plots of intensive monitoring that began in 2007 [7] according to recommendations of the ICP Forests [59]. Soil samples at monitoring plots were taken using stratified random method. For this purpose, every plot 30 × 40 m was subdivided to 12 squares 10 × 10 m, in which two randomly selected sampling points were placed; overall, samples were taken from 24 points per plot [7]. The thickness and stock of organic layer (with the help of frame 25 × 25 cm) were measured at every point, and organic layer samples were taken. Bulk density of the upper mineral layer was determined at the same points, and density of lower layers was determined in fivefold in soil pits studied in buffer zones of the plots (within 10 m from the plot boundary). The samples of the mineral part of the soil were taken with an auger from the depths of 0−5, 5−10, 10−20, 20−40, and 40−80 cm; these unified depths corresponded at a first approximation to the genetic horizons of studied soils (Table 1). Individual samples (24 samples for every horizon per plot) were combined in series of six into four composite samples for chemical analyses. Overall, 432 individual soil samples were taken in three types of forest ecosystems, of which 72 composite samples were prepared for analyses. The samples were sieved before the analyses through a 2-mm sieve; fine earth <2 mm was analyzed.

Analytical methods. The total contents of carbon and nitrogen in soil samples were determined by the method of high-temperature combustion on a CNHS-analyzer Vario ELIII (Elementar, Germany). The total carbon content was equated with the organic carbon content because of the absence of carbonates in the soils. Organic carbon stocks were calculated separately for organic layer and lower mineral layers to a depth of 1 m taking into account bulk density values and the fraction of fine earth (<2 mm).

To characterize labile fractions of carbon and nitrogen, concentrations of organic carbon and total

Table 1. Soil properties in forest ecosystems of the ZBS (mean ± half-width of 95% confidence interval, $n = 4$ (composite samples composed of 6 individual samples))

Soil	Horizon	Depth cm	Sampling depth cm	Bulk density[*]	Fine earth (<2 mm) fraction	Clay <0.002 mm	CEC$_{ef}$	pH$_{H_2O}$
				kg/m^3	%	%	cmol$_c$/kg	
Complex herb−wood sorrel pine−spruce forest (5S4P1B)								
Contact-bleached eluvozem	O	0−2	O	190 ± 60	–	–	37 ± 11	5.2 ± 0.2
	AYel	2−4	0−5	1150 ± 50	99 ± 0.9	5.3 ± 1.8	7.5 ± 2.2	4.8 ± 0.4
	ELf	4−12	5−10	"	98 ± 1.5	3.9 ± 0.8	4.0 ± 0.7	4.7 ± 0.3
	EL	12−48	10−20	1400 ± 20	98 ± 1.5	4.9 ± 1.4	2.5 ± 0.2	4.8 ± 0.3
			20−40	"	97 ± 2.9	4.7 ± 1.1	1.9 ± 0.2	4.7 ± 0.2
	Del	48−60	40−80	1410 ± 30	97 ± 2.0	3.3 ± 1.0	1.7 ± 0.4	5.0 ± 0.2
	Df	60−99	–	1430 ± 30	98 ± 0.3	–	–	–
Herb stone bramble−wood sorrel birch−spruce forest (5S4B1As)								
Ferruginous soddy eluvozem	O	0−2	O	170 ± 50	–	–	59 ± 5.5	5.7 ± 0.2
	AY	2−6	0−5	1090 ± 40	99 ± 1.0	6.8 ± 1.4	8.7 ± 2.2	5.1 ± 0.1
		6−10	5−10	1170 ± 60	99 ± 0.4	5.1 ± 3.4	3.9 ± 0.5	4.8 ± 0.2
	AYel	10−16	10−20	1150 ± 60	99 ± 0.7	7.0 ± 1.6	2.8 ± 0.5	4.8 ± 0.2
	ELf	16−36	20−40	1280 ± 80	99 ± 0.2	5.1 ± 0.9	2.1 ± 0.2	4.9 ± 0.1
	Del	36−51						
	Df1	51−77	40−80	1390 ± 90	98 ± 2.3	4.1 ± 0.8	2.1 ± 0.3	5.1 ± 0.2
	Df2	77−106	–	1470 ± 30	96 ± 4.1	–	–	–
Complex herb−wood sorrel spruce forest (8S2As+Li)								
Pseudofibrous soddy-eluvozem	O	0−3	O	120 ± 40	–	–	59 ± 27	5.5 ± 0.4
	AY	3−7	0−5	860 ± 150	99 ± 0.5	3.9 ± 1.4	7.9 ± 2.8	4.7 ± 0.5
	AYel	7−22	5−10	1070 ± 40	95 ± 9.8	4.8 ± 0.4	3.3 ± 0.1	4.6 ± 0.3
			10−20	"	96 ± 2.9	5.1 ± 1.5	2.7 ± 0.5	4.8 ± 0.2
	ELf	22−54	20−40	1370 ± 50	87 ± 13	2.7 ± 1.0	2.0 ± 0.9	5.0 ± 0.3
	Df	54−84	40−80	1130 ± 70	92 ± 2.6	3.1 ± 1.0	1.7 ± 0.4	5.1 ± 0.2
	Dff	84−107	–	1200 ± 40	100 ± 0.1	–	–	–

*For bulk density, $n = 5$.

concentration of nitrogen were determined in water extracts (soil : solution 1 : 4) from fresh samples of upper mineral horizons of soils without roots. The extracts were filtered through membrane filters with 45 μm pore size. The microbial biomass carbon and nitrogen were determined with fumigation-extraction method [80] in the same soil samples. Concentrations of carbon and nitrogen in solutions were measured on a Shimadzu TOC-V$_{CPN}$ analyzer. All results were calculated per absolutely dry mass.

To analyze the results, we also used data on particle-size composition, contents of the elements extracted with "aqua regia", contents of oxalate-extractable aluminum (Al$_o$), iron (Fe$_o$), and manganese (Mn$_o$), exchangeable cations, and acidity in the same composite soil samples presented in previous work [7].

Treatment of the results. In order to test the suitability of the most commonly used pedotransfer func-

tions for evaluation of bulk density, we compared the values calculated with the help of these functions with experimentally determined values. Two pedotransfer functions predicting bulk density (BD, g/cm^3) on the basis of data on the SOM content estimated from the loss on ignition (LOI, %) [28, 44], the humus content (HUM, %), and the mid-depth of the given layer (MID, cm) [21]:

$$BD = \frac{1}{(0.548 + 0.0588 \times LOI)},$$

$$BD = a_1 - \frac{a_2}{(MID + a_3)} + \frac{a_4}{(HUM + a_5)},$$

where a_1−a_5 are the parameters determined by the soil type (for the soils close to those studied by us, their values are 0.252, 9.110, 9.939, 110.999, and 78.805, respectively) [21]).

The results were treated by the methods of descriptive statistics and assuming the normality of distribution of the properties in soil samples, including composite samples. Significance of difference between mean values was estimated according to two-sample *t*-test for independent samples, corresponding to the absence of overlapping of confidence intervals. The relationships of the contents and stocks of organic carbon with other soil properties were analyzed using correlation analysis and principal component (PC) method [9, 76]. The interrelationships between soil properties were illustrated by correlation ordination diagrams as mutual disposition of their characteristics in the space of two first PCs of soil properties.
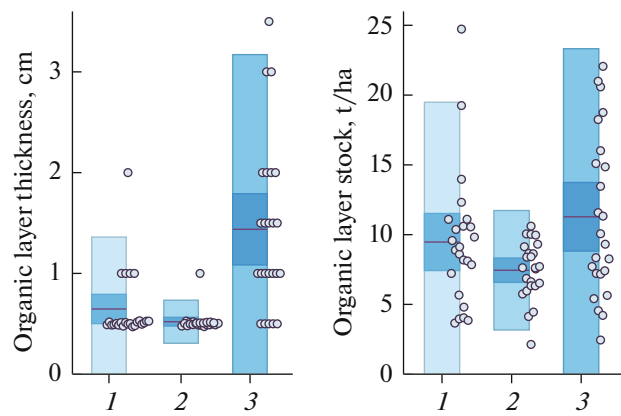

Fig. 1. Spatial distribution of organic layer thickness and stock in forest ecosystems of the Zvenigorod Biostation: (*1*) pine–spruce forest, (*2*) birch–spruce forest, and (*3*) spruce forest. Horizontal bar designates mean values; rectangle, 95% confidence intervals of the mean (dark blue) and measured values (light blue). Light circles along the ordinate axis represent measured values, the scattering of which along the ordinate axis is proportional to local density of their distribution.
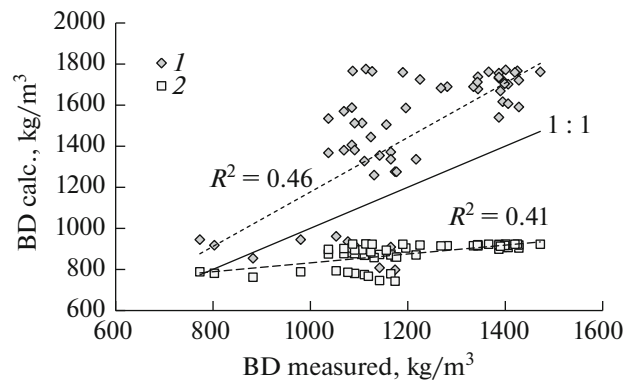
RESULTS AND DISCUSSION

Organic layer thickness and stock in spruce forests of ZBS with high participation of broadleaved species were low. Organic layer thickness increased from the birch–spruce forest to pine–spruce and spruce forests, but did not exceed 1.5 cm (Fig. 1). Organic layer stock increased in the same direction with average values from 7.4 t/ha in birch–spruce forest (minimum) to 9.5 t/ha in pine–spruce forest, and 11 t/ha in spruce forest. The difference between average organic layer stocks in spruce and birch–spruce forests was statistically significant. Organic layer stock in forest ecosystems is determined by the quantity of plant litter and the rate of its decomposition, which in turn depends on the litter quality, biological activity of the soil, and abiotic factors (temperature, moisture, aeration, soil pH, etc.). Relatively low input of plant litter with domination of birch residues in its composition (75% [8]), high biological activity, and favorable hydrothermal conditions determined intense decomposition and low accumulation of organic layer in birch–spruce forest. Our results are in agreement with previously obtained estimates of organic layer stocks (11−20 t/ha) in other types of spruce forests in ZBS [6].

Organic layer stocks in studied forests of coniferous-broadleaved zone are several times lower than the mean value for forest ecosystems of Europe (4.12 kg/m^2) and correspond to lower values of their interquartile range (0.1−21.1 kg/m^2 [33]).

Bulk density (BD) of the organic layer increased, on average, from 117 kg/m^3 in spruce forest to 170 kg/m^3 in birch–spruce forest and 189 kg/m^3 in pine–spruce forest due to more close packing of fragmented and decomposed residues of needle litter of conifers in comparison with leaf litter of deciduous species. These values are close to organic layer density in European forest ecosystems averaging 117 kg/m^3 with interquartile range from 17.8 to 360 kg/m^3 [33].

Bulk density of the mineral part of soils varied in the range from 860 to 1170 kg/m^3 in the layer of 0−10 cm and increased with depth to 1130−1410 kg/m^3 in the layer of 40−80 cm. The maximum values character-

Fig. 2. The relationship between measured and calculated bulk density values; calculations according to two pedo-transfer functions: (*1*) [44] and (*2*) [21].

ized contact-bleached eluvozem under pine–spruce forest; minimum bulk density was found for the loamy sandy pseudofibrous soddy-eluvozem under spruce forest. Variation coefficient of bulk density varied from 17 to 20% in the organic layer and from 1 to 11% in mineral soil horizons.

The results of comparison of BD calculations based on two pedotransfer functions demonstrated their close efficiencies in predicting BD ($R^2 = 0.41−0.46$, Fig. 2). However, the values calculated by both functions differed significantly from experimental data: five-parameter nonlinear function obtained on the basis of data on tundra and forest soils of Russia (748 horizons) [21] underestimated BD, and hyperbolic function [44] recommended for forest soils of

Europe [28, 34] overestimated it. This fact once again emphasizes the necessity of direct determination of soil bulk density in the field to prevent underestimation or overestimation of the stock of organic carbon in soils. The application of pedotransfer functions borrowed from available literature is problematic, if they are not tested and improved at regional scale [28, 34].

Fine earth (<2 mm) was the dominant fraction in all studied soils with a maximum in contact-bleached eluvozem and ferruginous soddy eluvozem (96–99%). Pseudofibrous soddy eluvozem was characterized by a wider range of the fine earth content (87–100%) with maximum variations in the middle part of the profile. Carbon stock in soils is usually estimated per fine earth without taking into account its real content in soils, and this leads to overestimated results [12, 71]. The determination of the fine earth content allowed us to correct estimates of the stocks of organic carbon in studied soils.

However, disregard of skeleton (>2 mm) that may also contain carbon and their consideration just as a "diluter" of fine earth may lead to underestimation of carbon stocks [41]. The contribution of skeleton to total stocks of carbon and nitrogen depends on the nature and content of rock fragments determined by parent material [31]. For example, the stony part of forest soils in Europe averages 20% by volume, and this suggests the importance of special determination of the carbon content in skeleton for correct estimates of the soil carbon stock, especially in regions with the high content of rock fragments [33].

Contents and stocks of organic carbon in soils. The C_{org} content in organic layers varied within a relatively narrow range: on average, from 40.7 to 43.8%. The N content in organic layers varied from 1.3 to 1.6%; and the C : N ratio, from 32 to 40. The maximum C_{org} content and C : N ratio were typical of organic layer under the pine–spruce forest with a difficultly decomposable needle components. The contents of C_{org} (0.18–6.2%) and N (0.01–0.35%) in mineral horizons were much lower, and the C : N ratio narrowed to 14–21 (Table 2). Generally, the distribution of organic carbon and nitrogen in the soil profiles was characterized by a pronounced maximum in organic layer, a sharp decrease in the upper mineral horizon, and a gradual decrease down through the mineral soil profile. These characteristics of the C_{org} distribution are generally typical of taiga soils of Russia [15].

Carbon stocks in soil organic layer of forest ecosystems of the ZBS amounted to 3.3–5.8 t/ha (variation coefficient 16–24%); nitrogen stocks comprised 0.12–0.21 t/ha (variation coefficient 11–36%). These values are 1.9–3.3 times lower than the average carbon stocks in soil organic layers of spruce forests of southern taiga in European Russia (10.9 ± 1.6 t/ha [23]) and 1.6–2.8 times lower than carbon stocks in soil organic layers of mixed forests in European Russia (9.1 t/ha [25]), but they are within the lower part of the range of presented estimates (0.9–58.1 t/ha [23]). Carbon stocks in soil organic layer of the ZBS also correspond to the lower part of the wide range of estimates for forest soils of Europe (1.3–70.8 t C/ha [28]).

Mineral part of soils in forest ecosystems of the ZBS accumulates significant amounts of carbon. Especially great amounts of carbon (41–58 t/ha) are stored within the upper 20 cm, where most plant roots were concentrated (Fig. 3). Carbon stocks in the one-meter layer of the mineral part of soils reach 59–79 t/ha. Thus, the total carbon stock in the organic layer and 1-m-deep mineral soil layer reaches 65–83 t/ha. Nitrogen stocks in the organic layer and 1-m-deep mineral soil layer constitute 3.9–5.2 and 4.1–5.3 t/ha respectively. Averaged variation coefficients do not exceed 6–9%. Maximum carbon stocks (82–83 t/ha) are found in the eluvozem and soddy eluvozem under pine–spruce and birch–spruce forests. Soddy eluvozem of a coarser texture under spruce forest is characterized by a lower carbon stock (65 t/ha). These values agree well with estimates of carbon stocks in soils of different categories under the main forest-forming species in the zone of coniferous-broadleaved forests of the European part of Russia [20]. In a recent study of coniferous–broadleaved forests, total carbon stocks in the organic layer and one-meter mineral soil layer for soils on loamy parent materials were found to increase from 61 t/ha at the early stage of succession to 66 and 68 t/ha at the intermediate and late stages, respectively [11]. Total carbon stocks in the organic layer and 1-m-deep mineral layer of sandy soils varies from 46 t/ha under sedge–herb pine forest to 60 and 65 t/ha in dwarf-shrub–green-moss pine forest and polydominant broadleaved forest, respectively [11].

Vertical differentiation of the stocks of organic carbon in soil profiles is clearly pronounced. Organic layer accumulates only 4.0–8.9% of the total stock of organic carbon in organic and mineral horizons to a depth 100 cm. The upper mineral horizons (0–20 cm) contribute 64–69% to the total organic carbon stock, or 69–73% of organic carbon stock in the 1-m-deep mineral soil layer. The contribution of middle-profile sandy horizons (40–80 cm) to the total carbon stock in the 1-m-deep mineral layer of forest soils of the ZBS is low (11–16%), and the contribution of the lower sandy layer (80–100 cm) is negligibly small (1–2%). Appreciably smaller value characterizes the contribution of the upper 20 cm to carbon stock in the one-meter layer of forest soils in Europe: on average, it is only 50% for 4914 monitoring plots of the ICP Forests [33]. An even lower contribution of the upper 20-cm-thick layer to the total organic carbon stock in the 1-m-deep layer is seen from data on 2700 soil profiles from three global databases: 33, 42, and 50% for soils under shrubs, meadows, and forests [47]. If soil sampling is performed to a greater depth, the contribution of deep (>20 cm) layers to the total carbon stock reaches 27–77% [41].

Table 2. Contents and stocks of carbon and nitrogen in soils of forest ecosystems of the ZBS: M, mean value; $CI_{1/2}$, half-width of 95% confidence interval; $n = 4$ (mixed samples composed of six individual samples)

Layer	Parameter	C	N	C : N	C	N
		%			t/ha	
Contact-bleached eluvozem						
O	M	43.8	1.29	40	4.59	0.14
	$CI_{1/2}$	2.4	0.32		1.79	0.08
0−5	M	6.2	0.35	21	35.3	1.98
	$CI_{1/2}$	1.3	0.07		7.85	0.43
5−10	M	2.0	0.11	20	11.2	0.64
	$CI_{1/2}$	0.38	0.02		2.28	0.15
10−20	M	0.81	0.05	19	11.1	0.69
	$CI_{1/2}$	0.21	0.01		2.84	0.17
20−40	M	0.34	0.03	16	9.13	0.68
	$CI_{1/2}$	0.06	0.01		1.82	0.18
40−80	M	0.19	0.02	15	10.3	0.82
	$CI_{1/2}$	0.04	0.003		1.96	0.17
80−100	M	0.05	−		1.40	−
	$CI_{1/2}$	0.03	−		0.81	−
Ferruginous soddy eluvozem						
O	M	40.7	1.5	33	3.28	0.12
	$CI_{1/2}$	4.6	0.17		0.81	0.02
0−5	M	5.3	0.32	20	28.7	1.70
	$CI_{1/2}$	0.71	0.05		5.00	0.32
5−10	M	2.2	0.14	18	12.6	0.82
	$CI_{1/2}$	0.38	0.02		1.81	0.08
10−20	M	1.1	0.08	17	12.7	0.86
	$CI_{1/2}$	0.40	0.03		4.06	0.28
20−40	M	0.42	0.03	15	10.6	0.83
	$CI_{1/2}$	0.11	0.01		3.36	0.35
40−80	M	0.23	0.02	15	12.7	0.96
	$CI_{1/2}$	0.07	0.002		3.61	0.13
80−100	M	0.05	−		1.41	−
	$CI_{1/2}$	0.03	−		0.82	−
Pseudofibrous soddy eluvozem						
O	M	43.1	1.60	32	5.79	0.21
	$CI_{1/2}$	6.6	0.29		1.78	0.05
0−5	M	5.4	0.32	19	22.9	1.37
	$CI_{1/2}$	0.83	0.05		5.30	0.29
5−10	M	1.7	0.11	19	8.75	0.54
	$CI_{1/2}$	0.13	0.01		0.51	0.07
10−20	M	0.96	0.06	18	9.85	0.64
	$CI_{1/2}$	0.22	0.01		2.34	0.12
20−40	M	0.42	0.03	16	10.0	0.72
	$CI_{1/2}$	0.10	0.01		2.64	0.19
40−80	M	0.18	0.01	14	7.47	0.62
	$CI_{1/2}$	0.03	0.004		1.76	0.21
80−100	M	0.02	−		0.49	−
	$CI_{1/2}$	0.01	−		0.30	−

Contact-bleached eluvozem   Ferruginous soddy eluvozem   Pseudofibrous soddy eluvozem
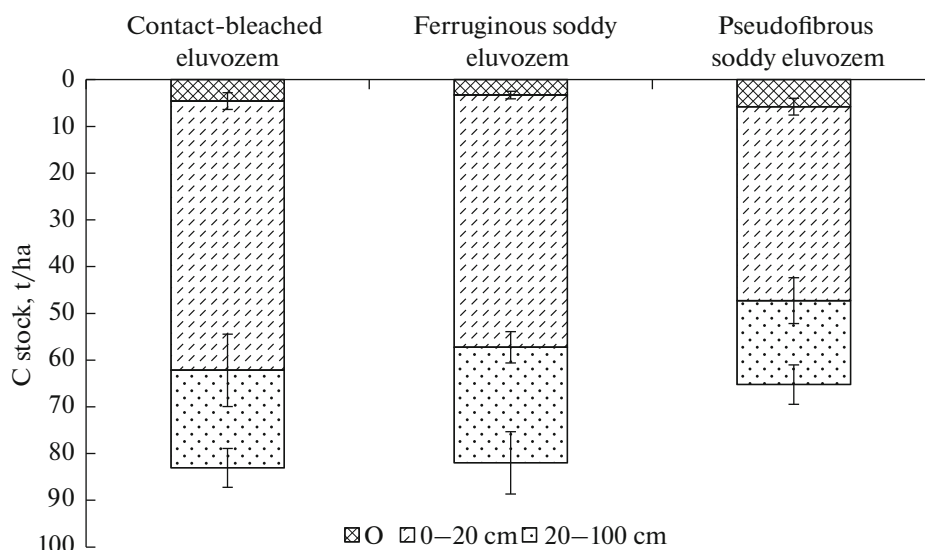

Fig. 3. The stocks of organic carbon in organic (O) and mineral layers (0—20 and 20—100 cm) of soils in forest ecosystems. Mean values and their 95% confidence intervals are presented.

Vertical differentiation of organic carbon stocks in soils is apparently determined by bioclimatic and lithological features, including soil texture. Qualitative composition of plant litter and increased biological activity in combination with favorable climatic conditions determines quick decomposition and small thickness of organic layer, and, hence, its low contribution to the total carbon stock. Typical for forest soils carbon accumulation in the upper mineral layers is enhanced by the surface root system of spruce, and a sharp decrease in carbon stock with depth is enhanced by the textural heterogeneity of the soil profiles formed on two-layered deposits with the upper loamy layer underlain by sand and loamy sand.

Water-extractable organic compounds of carbon reflect the composition of dissolved organic matter (DOM)—one of the most mobile and actively circulating fractions among the pools of soil organic matter. This is a continuum of organic substances of different nature <0.45 μm in size: from low-molecular-weight labile disaccharides, amino acids, and soluble phenols [60, 61, 79] to relatively stable aromatic compounds, deriving from lignin [50]. The sources of DOM in forest ecosystems are represented by fresh litter and organic layer [51], root exudates [30], necromass of soil microorganisms and animals, and atmospheric organic substances of biogenic (pollen, plant residues, bacteria, and viruses) and anthropogenic (soot and dust) origins [72] passing through crowns and then redistributed in soil with preferential water flows [61].

Concentrations of water-extractable organic carbon in the upper mineral horizons increases in summer up to 830 ± 130 mg/kg in eluvozem under pine—spruce forest and 980 ± 66 mg/kg in soddy eluvozem under birch—spruce forest (Fig. 4a). The maximum concentration of water-extractable nitrogen is also observed in the upper mineral horizon of the soil under birch—spruce forest (120 ± 20 mg/kg); in the other soils, it averages 81—84 mg/kg. The C : N ratio is narrow (9—13). The contribution of water-extractable organic carbon and nitrogen to the total contents of C_{org} and N in soils does not exceed 1.3—1.8% and 2.4—3.9%, respectively. This agrees with usually low content of DOM in the SOM. However, these labile compounds are the priority substrate for soil microbiota and play the key role in the control of microbial activity and the rate of organic matter mineralization [79]. It was found that DOM contributes essentially to the accumulation of stable fraction of organic matter in soils [43, 50, 68]. Hence, soil functions of sustaining primary production (via the release of nutrients during organic matter decomposition) and climate control (carbon sequestration) require support via the input of labile organic substances [43].

Carbon and nitrogen of microbial biomass. Soil microorganisms play a critical role in the carbon cycle in ecosystems, controlling mineralization as well as formation of organic matter. The content of microbial biomass carbon (C_{mic}) belongs to the main microbiological indicators of carbon storage [82] and organic matter transformation as the most important ecological function of soils [14]. Global stock of C_{mic} and microbial biomass nitrogen (N_{mic}) in the layer of 0—30 cm reaches 16.7 and 2.6 billion tons; in the one-meter soil layer, 23.2 and 3.7 billion tons, respectively [83]. Microbial necromass can constitute more than a half of SOM [58], especially in deep soil horizons [64], and microbial residues and exudates can give up to 50% [27] and even 80% of carbon in stable fractions [82]. Consumption and transformation of carbon compounds by microorganisms are necessary for long-time preservation of SOM [37, 43, 68].
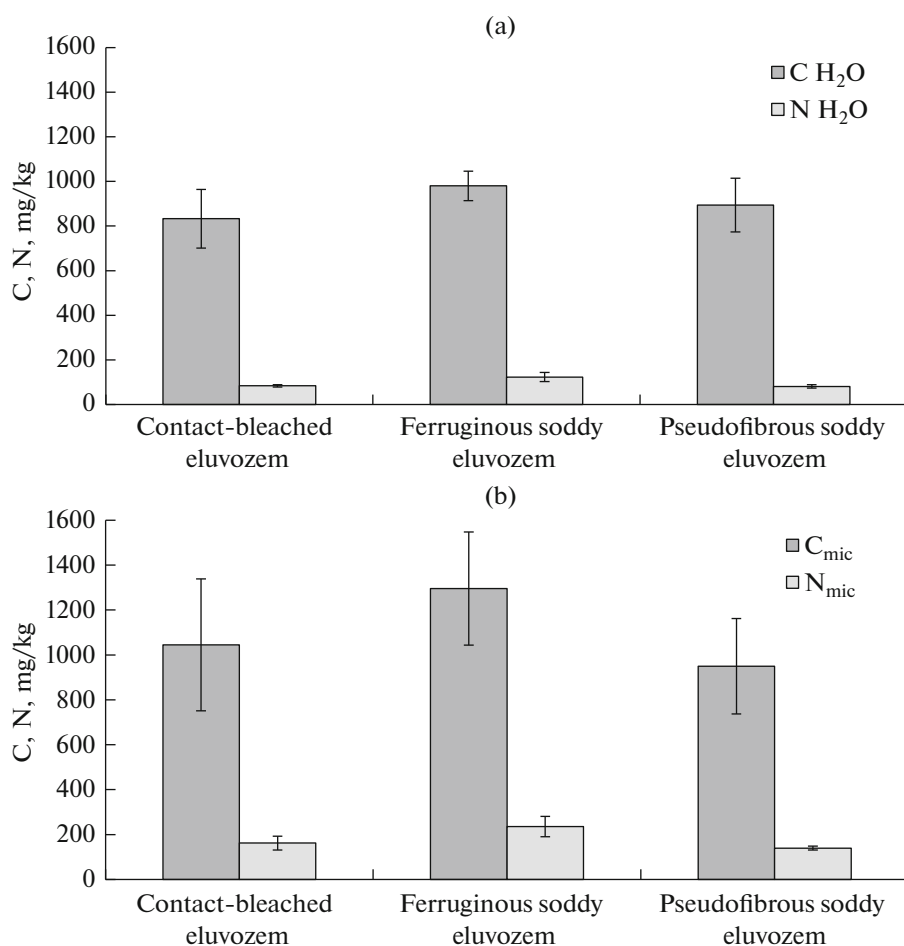
Fig. 4. Concentrations of (a) water-soluble and (b) microbial biomass carbon and nitrogen in soils of forest ecosystems. Mean values and their 95% confidence intervals are presented.

Concentrations of C_{mic} and N_{mic} in the upper soil horizons in summer period varied within the ranges of 950−1300 mg/kg and 140−240 mg/kg, respectively, with from minimum values in the soddy eluvozem under spruce forest and maximum values in the soddy eluvozem under birch−spruce forest (Fig. 4b). The obtained values are within the range 50−2000 mg C_{mic}/kg [26]. Close concentrations of C_{mic} in the upper mineral soil horizon were obtained earlier for the spruce−broadleaved forest (1568 ± 156 mg/kg) and green-moss spruce forest (1370 ± 42 mg/kg) near the city of Zvenigorod [18]. The ratio between C_{mic} and N_{mic} in the studied soils is low and varies within a narrow range (6−8); some differences can be attributed to the influence of plant litter of different qualities and differences in the composition of microbial community. It is known that fungi are characterized by an increased C : N ratio in comparison with bacteria [39]. The C : N ratio in microbial biomass (6−8) is significantly smaller than that in the SOM (19−21). On a global scale, the C_{mic} : N_{mic} ratio remains relatively stable, from 8 : 1 to 12 : 1, in comparison with a large gradient in resources used by soil microorganisms; it is considered to be relatively homeostatic, and the average C_{mic} : N_{mic} ratio in the layer of 0−30 cm is taken equal to 10 [39].

The C_{mic}/C_{org} ratio serves as an indicator of carbon availability for soil microorganisms and of changes in the SOM; it varies within 0.27−4.8% [26]. In the studies soils, it remains within a narrow range of 1.7−2.4% attesting to the quasiequilibrium state of the SOM. A decrease in this ratio can reflect increased acidity and limited availability of nitrogen according to [82]. The contribution of N_{mic} to the total nitrogen content in soils of the ZBS varies within 4.3−7.4%, whereas available literature gives the range from 0.5 to 15.3% [26]. Similar to concentrations of microbial carbon and nitrogen, the C_{mic} : C_{org} and N_{mic} : N ratios are higher in the gray-humus (AY) horizon of soil under the birch−spruce forest, which attests to a better quality of this substrate for microorganisms in comparison with the AY horizons under the pine−spruce and spruce forests.

Data analysis. Significant weak direct correlation between the contents of C_{org} and fine fractions of silt and clay ($r = 0.34$ and 0.31, $P \geq 0.95$, $n = 60$) was found

in the mineral part of the soils with the help of *correlation analysis*. The mineral part of the soils is also characterized by significant direct relationships between the contents of C_{org} and N and the contents of acid-soluble Ca ($r = 0.66$), K ($r = 0.69$), and Na ($r = 0.51$) and oxalate-soluble Fe_o ($r = 0.42$). Inverse relationships exist between the contents of C_{org} and oxalate-soluble Al_o ($r = -0.37$) and exchangeable acidity ($r = -0.48$). Soil organic matter plays a significant role in the distribution of biophilic elements, such as Mn, and this is confirmed by the high average values of correlation coefficients between C_{org} and acid- ($r = 0.69$), oxalate-soluble ($r = 0.87$), and exchangeable ($r = 0.98$) forms of Mn. The contents of exchangeable Ca ($r = 0.93$), Mg ($r = 0.88$), and K ($r = 0.70$), effective ($r = 0.95$) and potential ($r = 0.98$) CEC, and degree of base saturation ($r = 0.76-0.87$) are closely and very closely connected with the C_{org} content. The contents of exchangeable forms of potentially toxic metals Ni ($r = 0.89$), Cd ($r = 0.90$), Co ($r = 0.56$), and V ($r = 0.88$) also correlate with it. Direct correlations between C_{org} and CEC_{ef} in the upper and in the lower soil layers were found earlier, when surveying more than 1000 forest ecosystems of Switzerland formed under a wide range of bioclimatic and soil conditions [75].

The stock of C_{org} in mineral layers of soils of forest ecosystems closely correlated with the C_{org} content ($r = 0.92-0.97$) and with all the above-listed properties (with lower r values). Similar regularities were found for 12 plots of the CarboEurope monitoring network in Europe, where variations of C_{org} stock in undisturbed soils with low stone content are mainly determined by the C_{org} contents, whereas in stony soils they depend on the bulk density and the fraction of fine earth [71].

Correlations between C_{org} and silt and clay fractions ($r = 0.69, 0.68; P \geq 0.95$); oxalate-soluble Al_o, Fe_o, and Mn_o ($r = 0.58, 0.87, 0.94$); and exchangeable acidity ($r = 0.72$) increase with depth in the layers of 10–80 cm, whereas correlations between C_{org} and acid-soluble Ca and K and exchangeable bases decrease with depth. Close and very close correlation between C_{org} and acid- ($r = 0.94$), oxalate-soluble ($r = 0.94$), and exchangeable ($r = 0.92$) forms of Mn; the exchangeable ($r = 0.79$) and potential ($r = 0.93$) CEC are preserved in the soil profiles. The influence of C_{org} content on its stock somewhat weakens with depth ($r = 0.46$), and the influence of fine fractions and pedogenic oxides tends to increase (though $r = 0.33-0.40$ is small).

The suitability of different factors (clay minerals, specific surface area, oxides of metals, cations of Ca and Mg, microorganisms, soil fauna, aggregation, particle-size distribution, genetic soil type, natural vegetation, land use and management, geomorphology, parent rock, and climate) to indicate actual and potential accumulation of carbon in soils of the temperate zone was analyzed for different spatial scales in a recent review [82]. Fine mineral fraction was identified as the key component to determine stabilization of C_{org} in most soils. On the contrary, the results of analysis of data on more than 5500 soils profiles along environmental gradients of continental scale suggested a relatively small contribution of clay fraction to the accumulation of C_{org} in soils and the dominant role of exchangeable Ca or oxides and hydroxides of Fe and Al, depending on climate and acidity [67]. Narrow range of changes in the properties of soils close in their origin and conditions of formation within the ZBS territory make it difficult to find corresponding relationships.

The results of analysis of variations of soils properties with *principal component method* clearly reflect vertical differentiation of soil horizons in the process of soil formation. The main variation in the weights (for two first principal components) of soil sampling points in different ecosystems is presented in Fig. 5a. Common (Euclidean) distance between the points/layers characterizes their closeness according to the totality of all analyzed soil properties. Two first PCs describe, respectively, 46.6 and 20.0% of the total variance in soil properties, and this exceeds the contribution of any other PC by more than five times (third PC, 12.4% and further in descending order). First PC, is largely determined by the CEC_{ef} and the contents of exchangeable Ca, N and C ($\geq 8\%$ each), significant contributions also belongs to exchangeable Mg, stocks of C and N, total acidity, and base saturation (6–7% each); to Mn (5.3%), Ca (5.2%), and acid-soluble and exchangeable K (4.8% each). Second PC is mostly determined by the contents of sand and silt ($\geq 14\%$ each); oxalate-soluble Fe (11.9%) and Al (9.8%); exchangeable acidity and Al in its composition (8.6% each); the contents of clay (6%), Fe, Mg, and Al (5.4, 5.2, and 4.9%, respectively); and the soil pH (4.8%).

Two groups of the layers are clearly isolated on ordination diagram of the plane of two first PCs along the first PC and correspond (from left to right) to carbon-enriched uppermost mineral layer AY/AYel and to other mineral horizons. In the latter group, consecutive distribution of layers according to their depth along the first PC is disturbed by isolation of the deepest layer (40–80 cm) along the second PC, which reflects the change in the composition of parent material (underlying sand layer). The difference between soil types/subtypes is not pronounced, except for a tendency for some separation of pseudofibrous soddy eluvozem with coarser texture along the second PC.

Diagram of properties (Fig. 5b), associated with diagram of sampling points (Fig. 5a) represents a projection of the properties of soil horizons—contents and stocks of carbon and nitrogen, acid- and oxalate-soluble elements, acidity, and cation-exchange properties (solid arrows)—on the plane of the first two PCs. Arrow length reflects the degree of representation of the property by the two first PCs; cosine of angle
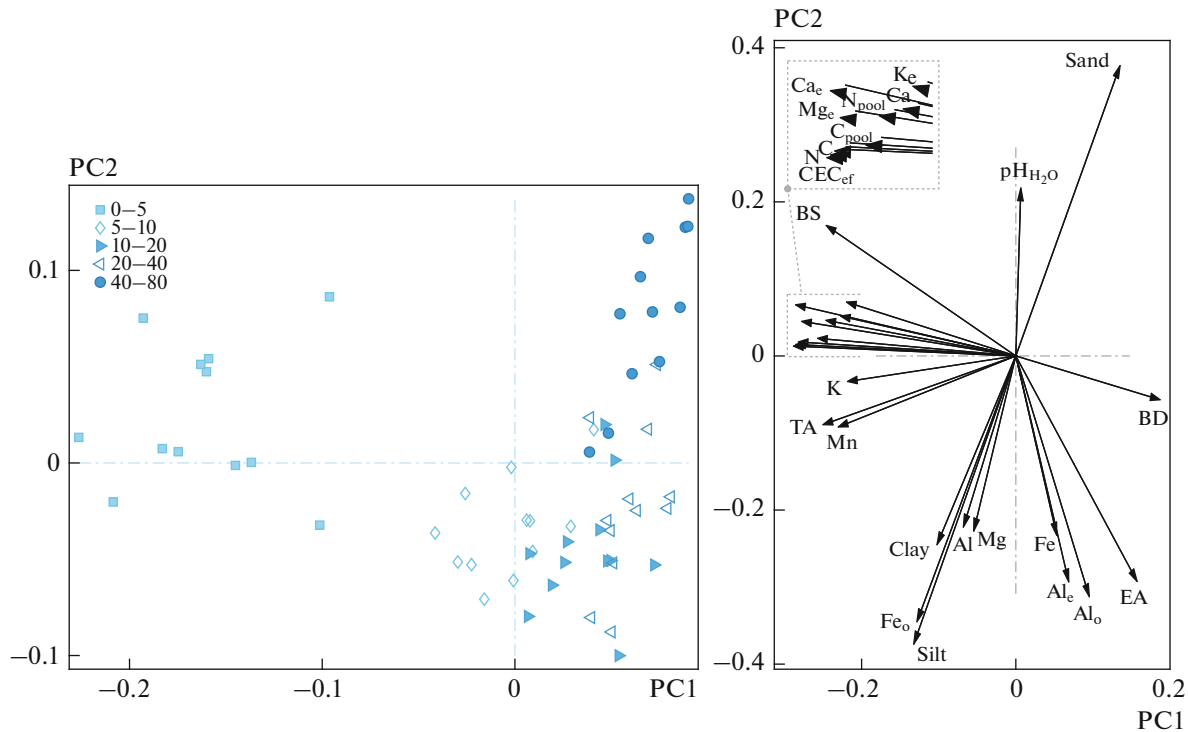
Fig. 5. Complementary diagrams of (a) soil sampling points and (b) generalized soil properties in forest ecosystems. Soil properties are given by arrows. Symbols of the chemical elements designate concentrations of their compounds in the layers of 0–5, 5–10, 10–20, 20–40, and 40–80 cm; indices o and e designate oxalate-soluble and exchangeable forms of the elements. EA is exchangeable acidity; TA is total acidity; CEC_{ef} is effective CEC; BS is base saturation; BD is soil bulk density; and pool is an element pool.

between arrows approximates the coefficient of correlation between the corresponding properties. The diagram of properties agrees well with the results of correlation analysis and reflects the association of increased contents and stocks of carbon and nitrogen with the increased contents of calcium, potassium, and exchangeable bases and with high CEC_{ef}. The stock of C_{org} is mainly connected with the C_{org} content.

Thus, the results of correlation and multiparameter analyses in general attest to certain interrelationships between the contents and stocks of C_{org} in the mineral part of soils and the soil texture; presence of pedogenic oxides; contents of calcium, potassium, and exchangeable bases; and the CEC value. This is in agreement with regularities reported in literature [48, 75, 82]. However, the strength of relationships can be different in dependence on the features of soil formation, contrast of properties, and composition and volume of the sample. Increased contents of fine fractions and pedogenic oxides are not always directly accompanied by the increase in the C_{org} stock in soils.

The sources of *uncertainty* in the assessment of C_{org} stocks include insufficient accounting of spatial variability of soils because of the usually small sample volume. The great spatial heterogeneity of carbon stock in comparison with its moderate temporal changes requires the development of scientifically based and economically feasible schemes of soil sampling for the

purposes of monitoring C_{org} temporal dynamics [46]. This is especially true for forest ecosystems, which are often characterized by a pronounced mosaic structure and high spatial variability of soils [6, 28, 71]. Correct comparison of the stocks of soil carbon in space and their changes in time is hindered by different approaches to soil sampling, sample preparation, and chemical analyses [28, 46]. Most estimates include upper soil horizons and do not properly reflect carbon stocks in deep [19, 41]. The measurements of carbon contents, bulk density and fine earth fraction [46], as well as organic carbon content in the skeleton [31] are equally important for reliable estimates of the C_{org} stocks. The deficit of field determinations of soil bulk density, enforced use of empirical pedotransfer functions to calculate it [28, 34], and virtual absence of determinations of the fine earth fraction [12, 41] and carbon content in rock fragments [31] increase significantly the uncertainty of estimates of carbon stocks. The results of preliminary analysis of data from the CarboEurope network plots demonstrates that regular taking of 100 soil samples might be good compromise between pragmatism and possibility to find the changes in soil C_{org} at the scale of forest sites of 7–8 ha in area over a decade [71]. This sampling method was recommended to monitor soil C_{org} in the zone of tower coverage of several hectares at ecological-climatic stations of the integrated carbon observation system in

Europe. Analysis of composite samples allows optimizing the expenses. When sampling in smaller areas, minimization of soil disturbances becomes of great importance.

Special attention should be given to analytical methods of carbon determination and their interpretation. The problems and limitations of the traditional and widely applied Tyurin's method (dichromate oxidation), with the help of which most of data on C_{org} in soils of Russia and many other countries have been obtained, are well known [4, 24, 28]. The method of dry (high-temperature) combustion in automatic analyzers is recommended for monitoring the contents and stocks of organic carbon on the basis of theoretical and metrological viewpoints [4]. However, even the latter method does involve discrepancy, because the obtained data on the total carbon content are often automatically equated with the organic carbon content without proper account for the inorganic carbon even in the soils with neutral and slightly alkaline reaction [13].

CONCLUSIONS

Eluvozems and soddy eluvozems (Dystric Cambisols) developed from two-layered (loam over sand) deposits in the territory of the Zvenigorod Biostation store about 65−83 t/ha of organic carbon in the organic layer and 1-m-deep mineral layer. Organic layer accumulates 3.3−5.8 t C/ha or 4−9% of the total stock of C_{org}. Upper mineral horizons (0−20 cm) make a much greater contribution (64−69%) to the total stock of C_{org}.

Different levels of carbon accumulation in soils are determined by the lithological features and character of vegetation. Carbon stocks are minimal in loamy sandy soddy eluvozem of spruce forest (59−68 t/ha) and reach 76−92 t/ha in sandy loamy soils of birch−spruce and pine−spruce forests.

The contributions of water-soluble compounds to the total contents of C_{org} and N do not exceed 1.3−1.8 and 2.4−3.9%, respectively. The share of microbial biomass carbon in the total organic carbon reflects carbon availability to soil microorganisms and varies within a narrow range (1.7−2.4%) typical of forest soils and attesting to the equilibrium state of the SOM.

At soil type/ecosystem level, the soil enrichment with calcium and potassium, CEC, contents of exchangeable bases, and base saturation can serve as indicators of the C_{org} content and stock in acid loamy soils. The dependence of C_{org} content on the contents of silt and clay fractions and pedogenic oxides is less pronounced because of close origin and properties of soils.

Reliable information on the state and dynamics of soil properties is necessary for the assessment of carbon sequestration potential of forest ecosystem and climate change mitigation. Regular evaluation of the stocks of organic carbon in soils, the fractions of its labile and microbial pools, and spatial variability should become the basis of monitoring climatically active substances in forest ecosystems, forecasting possible changes of ecosystem functions in response to external influence, and developing the strategy for achieving the goals of sustainable development.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

CONSENT TO PARTICIPATE

Informed consent was obtained from all individual participants included in the study.

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