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Spatial Variation in the Concentration of Phenolic Compounds and Nutritional Elements in the Needles of Spruce in Northern Taiga Forests

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Abstract—Patterns of lateral intrabiogeocenotic (between separate elementary biogeoranges) and interbiogeocenotic variability in the content of secondary metabolites and nutritional elements in the different-age needles of spruce (*Picea abies* ssp. *obovata* (Ledeb.) Domin) have been studied along the geochemical transect in spruce forests in northern taiga (Kola Peninsula). The perennial needles of spruce undergrowth (30–40 years) are characterized by a higher concentration of carbon, lignin, high-molecular-weight phenolic compounds, bounded tannins, and wide ranges of lignin/cellulose and lignin/N ratios compared to trees older than 100 years. The needles of spruce trees older than 100 years have significantly more bounded tannins and low-molecular-weight phenols in transitional and accumulative sites than in automorphic locations. The concentration of lignin and lignin/N ratio was significantly higher in the 5–7-year-old needles of spruce trees growing in automorphic conditions, while spruce forests in transitional and accumulative sites have the maximum values of these indicators for the current-year needles. Changes in the chemical composition of spruce needles along the geochemical transect are determined by (1) different concentrations of nutritional elements and secondary metabolites in soils; (2) increased soil moisture from automorphic to accumulative sites; (3) the features of the microbiological activity of soils; and (4) environmental factors (light, temperature, etc.).

Keywords: phenolic compounds, lignin, nutritional elements, forests of northern taiga, age of stand, intraspecific variability, chemical composition of needles, *Picea abies* ssp. *obovata*

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Phenolic compounds are considered as one of the main elements of the interaction of plants with the environment (Zaprometov, 1993; Cheynier et al., 2013). Boreal forests are formed outside the zone of ecological optimum, i.e., in the zone of low temperatures, short vegetation period, nutrient deficiency, high soil acidity, and technogenic pollution. According to the hypothesis of growth/differentiation balance (GDB) (Herms and Mattson, 1992) and hypothesis of carbon/nutrient balance (CNB) (Bryant et al., 1983), plants contribute a significant proportion of assimilable carbon to the production of secondary metabolites under such conditions; phenolic compounds are the most widespread among these metabolites (Cheynier et al., 2013). These hypotheses indicate that the processes of vegetative plant growth prevail over the production of secondary metabolites under favorable growth conditions. The concentration of secondary metabolites increases only when plant growth is limited by lack of mineral nutrients (according to the CNB hypothesis) or when it is limited by another factor (according to the GDB hypothesis) (Matyssek et al., 2012). However, the authors of a number of reviews have doubted (Hamilton et al., 2001; Koricheva, 2002; Stamp, 2003) that these and some other hypotheses reflect the exact understanding of how and why secondary plant metabolites and their content change. Thus, studies have shown that carbon and nitrogen metabolisms are bound by a complex regulatory mechanism (Fritz et al., 2006). An alternative oxidative pressure hypothesis was proposed in (Close and McArthur, 2002). It shows that the distribution and abundance of many phenolic compounds can be explained as a response of plants to photo-oxidative damage.

The content of phenolic compounds in plants depends on many factors: the stage of ontogenesis (Barton and Koricheva, 2010; Marakaev et al., 2013), type of tissue (Artemkina and Roshchin, 2004), phenotypic plasticity of plants in response to environmental effects, including seasons (Vasil'ev et al., 2001; Artemkina and Roshchin, 2006), method of extraction from plants (Vasil'ev et al., 1999a), habitat (Aitkenhead-

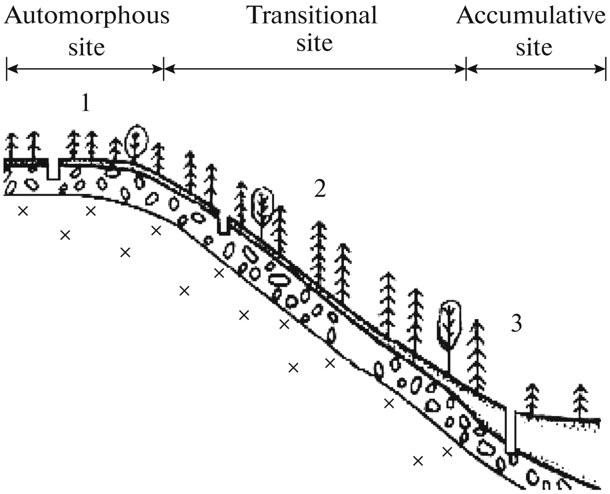

Fig. 1. Schematic profile of the geochemical transect (Umbozero) according to (Manakov and Nikonov, 1981, p. 13). (1) Dwarf-shrub–green-moss spruce forests; (2) green-moss–dogwood–dwarf-shrub spruce forests; (3) sphagnum–ledum spruce forests.

Peterson et al., 2006), plant species (Vasil'ev et al., 1999b), nutritional status of soils (Luzikov et al., 2005), and technogenic pollution (Artemkina, 2010). Many studies have found significant changes in the composition and content of secondary metabolites of needles/leaves of plants, depending on their age (e.g., (Artemkina, 2010; Rummukainen et al., 2013)).

Phenolic plant compounds, including tannins, play an important role in regulating the rate of litter decomposition, which in turn can influence carbon and nutrient cycles in terrestrial ecosystems (Hättenschwiler and Vitousek, 2000; Preston et al., 2009; Makkonen et al., 2012). The rate of litter decomposition is also influenced by the concentrations of carbon, lignin, nitrogen, and other nutritional elements (especially P, Mn, Mg, K, and Ca), as well as by the C/N and lignin/N ratios (Zhang et al., 2008; Berg, 2014; Lukina et al., 2017). In addition, tannins serve as the main means of plant protection against herbivorous animals (Barbehenn and Constabel, 2011).

Siberian spruce (*Picea abies* ssp. *obovata* (Ledeb.) Domin) is one of the most common forest-forming species in forests at their northern habitat boundary (Lukina and Nikonov, 1996). Changes in the chemical composition of needles of this widespread tree species in the boreal zone can significantly influence biogeochemical cycles in taiga forests.

The purpose of this research is to study the spatial intra- and interbiogeocenotic variability in the content of phenolic compounds, including tannins and lignin, as well as mineral elements in the needles of Siberian spruce, which forms the spatial mosaic of the cover in spruce forests of northern taiga.

MATERIALS AND METHODS

The objects of research are in the central part of the Kola Peninsula (67°29′ N, 34°32′ E). The tree layer is dominated by spruce (*Picea abies* × *obovata*) (Manakov and Nikonov, 1981). The grass–dwarf-shrub layer is represented by dwarf shrubs of the genus *Vaccinium*: cranberries (*V. vitis-idaea*), blueberries (*V. myrtillus*), and blueberries (*V. uliginosum*). In addition to Vacciniaceae, crowberry (*Empetrum hermaphroditum*) also occurs here. The moss layer is dominated by green mosses: *Pleurozium schreberi*, *Hylocomium splendens*, and *Sphagnum* spp.

We studied the composition of current-year, 1-year-old, 5–7-year-old, and (if available) 8–11-year-old needles. The stationary plots with spruce associations form three profiles of the geochemical transect, the structural parts of which (elementary landscapes) are characterized by different types of vegetation (Umbozero plot). The stationary plots were established in (1) dwarf-shrub-green-moss spruce forests; (2) green-moss-dogwood-dwarf-shrub spruce forests; and (3) sphagnum-ledum spruce forests (Fig. 1). Needle samples were taken in three replications from trees of different ages at the end of the vegetation period. We estimated the interbiogeocenotic variability in the content of secondary metabolites and nutritional elements in the needles of spruce trees growing in different sites along the geochemical transect. In stationary plots, dominant elementary biogeocenotic ranges (EBGRs), which were formed by spruce trees of different ages (40–50, 120–150, and above 250 years) were identified in different landscape sites (Orlova, 2013). The stationary plots are described in more detail in Orlova et al. (2016). *Picea abies* × *obovata* in different states forms three main types of EBGR: spruce dead cover, spruce dwarf-shrub-green-moss, and spruce undergrowth ranges. Intrabiogeocenotic variability was studied at this level.

The content of chemical elements in the plant samples was determined after decomposing them with concentrated nitric acid (wet ashing). The concentration of K was determined by atomic emission spectrometry; Ca, Mg, and Mn, by atomic absorption spectrometry (Analyst 800 spectrometer); and P, by the colorimetric method.

The total concentration of carbon and nitrogen was determined by Tyurin and Kjeldahl's methods, respectively. The content of soluble condensed tannins (proanthocyanidins) in the samples was quantitatively determined by the photocolorimetric method (555 nm) after reaction of the extracted product with n-butanol solution: HCl (95 : 5) (Ossipova et al., 2001). The concentrations of low-molecular-weight and high-molecular-weight phenolic compounds were determined by the photocolorimetric method (730 nm) using the Folin-Ciocalteu reagent, which is described in detail in (Kanerva et al., 2008). The amount of tannins and phenolic compounds was calculated according to the calibration curves for condensed tannins from leaves of *Betula pubescens* ssp. *czerepanovii* and for tannic acid, respectively. The concentration of lignin, cellulose, and ADF (acid-detergent fiber), which are insoluble in the CTAB solution, was determined by treating the sample with 72% sulfuric acid after preliminary boiling in a cetrimonium bromide (CTAB) solution (10 g of CTAB in 1 L of 0.5 M H_2SO_4) (Rowland and Roberts, 1994).

The results were statistically processed using the Statistica 9.0 software package. The significance of differences in the chemical composition of spruce needles was determined using the nonparametric Kruskal-Wallis test (Kruskal-Walis ANOVA).

RESULTS AND DISCUSSION

Dwarf-Shrub-Green-Moss Spruce Forests (Automorphic Site)

Significant changes have been revealed in the chemical composition of different-age spruce needles that were collected from trees in different EBGRs (Table 1). The concentration of carbon proved to be significantly higher ($p < 0.05$) for current-year needles than for the needles of all other ages in trees older than 150 years in the spruce dead-cover EBGR. In spruce–dwarf-shrub green-moss EBGRs, the needles older than 8 years in spruce trees older than 100 years also accumulated significantly ($p < 0.05$) less carbon than current-year, 1-year, and 5–7-year-old needles. Therefore, trees older than 100 and 150 years accumulate more carbon in the needles of the current and first years. The spruce undergrowth (30–40 years old) had another trend: the concentration of carbon in the 5–7-year-old needles was comparable to that in the current-year needles and significantly ($p < 0.05$) higher than that in 1-year-old needles. At a certain stage, lignification processes end in current-year needles if there are no strong external effects. Since the content of phenolic compounds (along with common carbon) increases in the 5–7-year-old needles of the undergrowth due to allelopathy (see below), it can be concluded that the content of carbon varies depending on changes in concentrations of separate copools in this case. Carbon is positively correlated with the elements of cell walls (bound tannins, 0.446, cellulose, 0.351, lignin, 0.530, ADF, 0.463 ($p < 0.05$ for all elements)). The greater part of carbon pools is included in the cell walls and is not transported from one needle to another. Some substances that are soluble in the CTAB solution (starch, carbohydrates, and extractives, including soluble phenolic compounds and tannins) can be redistributed.

On the whole, *the total concentration of nitrogen* proved to be significantly lower in 5–11-year-old needles in all EBGRs and varied from 0.80 to 1.11%. It is known that nitrogen is an element that can be retranslocated within a tree and accumulate in younger tissues. Similar trends were observed for Siberian spruce many times in our previous studies and studies of other researchers (Kazimirov and Morozova, 1973; Manakov and Nikonov, 1981; Lukina and Nikonov, 1996) and have also been recorded for coast Douglas-fir (*Pseudotsuga menziesii* Mirb. Franco) needles (Horner et al., 1987).

The C/N *ratio* significantly varied (from 51 to 65) in different-age needles of spruce in different EBGRs, while no significant differences were found between the ages due to the similar pattern of the distribution of carbon and nitrogen with respect to the needle ages.

Significant differences in the concentration of carbon and nitrogen and in the C/N ratio were also not found in the needles of the respective spruce ages in different EBGRs.

The concentration of *cellulose* decreased in 5–7- and 8–11-year-old needles compared to the current-year and 1-year needles in all EBGRs and did not differ between EBGRs (Table 1). A similar trend in the change in the concentration of cellulose with respect to the age of needles is observed for the *concentration of ADF* and *lignin* in the needles of spruce older than 100 years both in spruce dead-cover and in dwarf-shrub-green-moss EBGRs. The most significant decrease in lignin in needles with age is characteristic of spruce that form spruce dwarf-shrub–green-moss EBGRs. Carbon deficiency leads to the synthesis of least energy-consuming compounds in spruce needles; most likely, these are soluble phenolic compounds for 5–7- and 8–11-year-old needles; their concentrations increase with time. Positive correlations are revealed between the content of carbon, on the one hand, and content of ADF ($r = 0.463$), cellulose ($r = 0.351$), and lignin ($r = 0.530$) (the correlation coefficients are significant at $p < 0.05$), on the other. The decrease in the content of cellulose and lignin with needle age was previously recorded for *Picea abies* growing in North Bohemia (Czech Republic) (Aitkenhead-Peterson et al., 2006) and decrease in the concentration of cellulose only, for coast Douglas-fir in the United States (Horner et al., 1987) and ADF only, for *Picea abies* in England (Hatcher, 1990).

Similar to the concentration of total carbon, the content of lignin proved to be significantly ($p < 0.05$) lower in the 1-year needles of spruce undergrowth (30–40 years) than in its current-year and 5–7-year-old needles. The concentrations of ADF and lignin in 5–7-year-old needles were significantly higher in spruce undergrowth than in trees older than 100 years. The lignin/cellulose and lignin/N ratios in 5–7-year-old needles were also higher for the spruce undergrowth. The synthesis of "expensive" metabolites (positive correlations between carbon and lignin concentrations, $r = 0.530$) is activated in the 5–7-year-old needles of the spruce undergrowth, where the maximum concentration of carbon was recorded. In addition, allelopathy may occur between the spruce under-

Table 1. Chemical composition of *Picea abies* × *obovata* needles in green-moss–dwarf-shrub spruce forest

Component	Automorphic site										
	spruce dead-cover EBGR				spruce dwarf-shrub–green-moss EBGR				spruce undergrowth EBGR		
	current year	1-st year	5th–7th year	8th–11th year	current year	1st year	5th–7th year	8th–11th year	current year	1st year	5th–7th year
C, %	57.1(3.2)	52.3(0.4)	50.0(1.9)	51.4(1.9)	56.4(1.3)	54.0(0.8)	53.5(1.6)	51.2(2.0)	55.7(0.5)	52.9(1.7)	56.7(0.6)
N, %	0.92(0.12)	0.92(0.03)	0.80(0.03)	0.87(0.09)	1.11(0.04)	1.02(0.00)	0.82(0.01)	0.83(0.10)	0.98(0.05)	1.00(0.08)	0.89(0.02)
C/N	65(10)	57(2)	63(1)	60(6)	51(0)	53(1)	65(2)	63(10)	57(3)	54(4)	63(1)
ADF, %	38.9(0.6)	35.6(1.2)	33.6(0.9)	32.4(0.4)	38.4(1.3)	36.1(2.6)	33.2(1.9)	31.9(1.8)	42.1(1.6)	34.5(1.0)	38.2(0.3)
Lignin, %	17.7(0.5)	15.5(0.7)	15.1(0.2)	15.3(0.6)	18.1(0.4)	17.0(1.4)	15.4(0.7)	13.9(0.8)	17.7(0.2)	14.3(0.2)	17.9(2.2)
Cellulose, %	20.9(0.5)	19.6(0.6)	17.6(0.7)	15.7(0.4)	20.0(1.1)	18.6(1.3)	17.1(1.1)	16.8(1.0)	21.2(0.3)	17.0(1.3)	17.1(0.9)
Lignin/cellulose	0.85(0.03)	0.79(0.01)	0.86(0.02)	0.98(0.06)	0.91(0.04)	0.91(0.03)	0.90(0.02)	0.83(0.00)	0.89(0.02)	0.80(0.02)	1.14(0.06)
Lignin/N	20(2)	17(1)	19(1)	18(1)	16(1)	17(2)	19(2)	17(3)	20(1)	15(1)	23(2)
LPC, mg g^{-1}	28.0(0.9)	30.8(1.0)	33.2(1.0)	37.9(0.8)	26.9(1.3)	32.6(0.4)	34.8(1.1)	35.6(2.5)	22.2(1.7)	29.9(1.0)	30.3(0.3)
HPC, mg g^{-1}	36.9(4.7)	37.3(1.7)	46.0(4.4)	57.4(1.5)	32.4(3.5)	35.2(2.2)	36.7(3.6)	57.2(1.5)	37.8(2.4)	53.7(0.6)	65.0(0.4)
SPC, mg g^{-1}	64.9(4.0)	68.1(1.3)	79.2(3.7)	95.3(0.7)	59.3(4.8)	67.8(2.6)	71.5(3.1)	92.8(1.0)	59.9(1.6)	83.6(1.4)	95.3(0.2)
ST, mg g^{-1}	66.9(5.6)	68.8(7.0)	49.9(8.6)	45.8(5.0)	60.0(1.9)	60.9(4.1)	45.9(3.8)	41.4(0.0)	72.2(1.3)	79.5(8.2)	47.4(11.2)
BT, mg g^{-1}	6.7(0.3)	6.6(0.2)	4.3(0.2)	4.1(0.0)	6.0(0.4)	5.4(0.0)	4.6(0.2)	4.2(0.2)	8.4(0.4)	7.0(0.8)	6.8(0.8)
K, mg g^{-1}	8.4(0.5)	6.4(0.6)	3.7(0.2)	2.9(0.2)	9.3(0.7)	6.6(0.5)	3.8(0.3)	3.2(0.3)	8.3(0.5)	6.5(0.3)	4.0(0.1)
Ca, mg g^{-1}	3.9(0.4)	6.4(0.5)	13.7(1.4)	15.7(1.2)	3.7(0.4)	7.1(0.5)	12.3(0.7)	14.0(1.5)	3.5(0.4)	5.4(0.4)	9.8(0.7)
Mg, mg g^{-1}	1.04(0.07)	0.95(0.09)	0.70(0.15)	0.64(0.13)	1.16(0.05)	1.07(0.05)	0.75(0.10)	0.65(0.14)	0.94(0.01)	0.79(0.02)	0.43(0.04)
Mn, mg g^{-1}	0.8(0.1)	1.2(0.2)	2.4(0.5)	2.8(0.5)	0.8(0.1)	1.3(0.2)	2.0(0.3)	2.1(0.4)	1.0(0.1)	1.4(0.1)	2.5(0.1)
P, mg g^{-1}	1.7(0.1)	1.5(0.1)	1.2(0.2)	1.0(0.2)	1.8(0.1)	1.6(0.1)	1.2(0.1)	1.0(0.1)	1.9(0.0)	1.6(0.0)	1.2(0.0)

In Tables 1–3: ADF, substances that are insoluble in CTAB; LPC, low-molecular-weight phenolic compounds, HMC, high-molecular-weight phenolic compounds, SPC, sum of phenolic compounds, ST, soluble tannins, BT, bound tannins. The mean values and standard error (n = 3–5) are given.

growth and dwarf shrubs (Blanco, 2007), which may result in an increase in the content of lignin (phenolic compounds) in response to the growing conditions.

The total concentration of *phenolic compounds* (high-molecular-weight + low-molecular-weight phenols) increased with age of spruce needles, regardless of the type of EBGR, while the concentration of high-molecular-weight and low-molecular-weight phenols increased. The proportion of high-molecular-weight phenolic compounds increases in 5–7- and 8–11-year-old needles: the concentration varies from 54 in the current-year needles to 62 in the falling needles of spruce trees older than 100 years and from 63 in the current-year needles to 68 in the falling needles of spruce undergrowth (30–40 years old). The increase in the concentrations of phenolic compounds with age of needles was previously determined for conifers (Horner et al., 1987; Artemkina et al., 2016). The content of phenolic compounds was significantly higher in the 1-year-old and 5–7-year-old needles of spruce undergrowth than in the needles of the same age in spruce trees older than 100 years ($p < 0.01$ and $p < 0.01$, respectively). This may result from the allelopathic effect due to the competition for mineral nutrition between the spruce undergrowth and dwarf shrubs of the *Ericaceae* and *Empetraceae* families (Blanco, 2007). No similar effects were revealed between trees older 100 years and dwarf shrubs.

Unlike phenolic compounds, the concentrations of *soluble tannins* decrease in the 5–7- and 8–11-year-old needles of spruce trees in all studied EBGRs. At the same time, their concentration in the current-year and 1-year-old needles was significantly higher in spruce undergrowth (30–40 years old) than in spruce trees older than 100 years: the concentrations of soluble proanthocyanidins were significantly higher in the current-year and 1-year-old needles of the spruce undergrowth than in the same needles in dead-cover spruce trees ($p < 0.05$ and $p < 0.04$, respectively) and shrub–green-moss ($p < 0.01$ and $p < 0.05$, respectively) EBGRs. This increase in the concentration may also result from the allelopathic effect due to the competition for mineral nutrition between the spruce undergrowth and shrubs or reflect the trend towards the protection against herbivorous animals (Barbehenn and Constabel, 2011). Another influential factor can be the light regime in this case (Kashulin et al., 2009; Kivimäenpää et al., 2014). The spruce undergrowth grows in open forest areas under higher illumination conditions and the concentration of phenolic compounds decreases with an increase in the forest density (Plaksina et al., 2009).

A similar but less pronounced regularity is observed for cell-wall-bound condensed tannins.

Mineral elements (especially P, Mn, Mg, K, and Ca) can influence the rate of litter transformation (Berg, 2014). One of the main factors of variation in the composition of spruce needles is their age. Low-mobile elements, such as Ca and Mn, tend to accumulate in needles with age, which is also indicated by our data. The concentration of elements that can be retranslocated within plants (K and P), as well as the concentration of the medium-mobile element, Mg, decrease in 5–7- and 8–11-year-old needles. These patterns have been previously demonstrated by us and other researchers (Manakov and Nikonov, 1981; Helmisaari, 1992; Lukina and Nikonov, 1996) many times. The concentration of Ca in the 1- and 5–7-year-old needles was significantly lower in the spruce undergrowth than in spruce trees older than 100 years, which can be explained by the lower content of this element in the litter (Orlova et al., 2016). The concentrations of K, Mn, and P in the needles did not significantly differ between the trees of different ages in different EBGRs. The content of Mg is significantly lower ($p < 0.05$) in the needles of the spruce undergrowth than in the needles of spruce trees older than 100 years, which may also be determined by the content of the element in the litter (Orlova et al., 2016) and, possibly, by the higher concentration of chlorophyll, which includes Mg, in the needles of older trees (Croft et al., 2014).

Green-Moss Dogwood–Dwarf-Shrub Spruce Forests (Transitional Site)

The transitional site includes only spruce dead-cover and spruce dwarf-shrub–green-moss EBGRs (Table 2). The concentration of carbon and nitrogen and C/N and lignin/cellulose ratios, as well as the concentration of cellulose and soluble and bound tannins, in needles were similar in spruce trees forming both types of EBGR. Higher concentrations of lignin and, accordingly, a wider range of the lignin/N ratio were determined for the 5–7-year-old needles of spruce trees at the age of 110–135 years in dwarf-shrub–green-moss EBGRs compared to the same needles of 190–220-year-old spruce trees in spruce dead-cover EBGRs. The needles of 190–220-year-old spruce are richer in phenolic compounds due to an increase in the concentration of high-molecular compounds in their composition, which is consistent with the hypothesis of growth/differentiation balance (Herms and Mattson, 1992). Spruce trees at the age of 190–220 years grow very slowly and the content of high-molecular-weight phenolic compounds increases in their needles. It is known that the strategies for synthesizing phenolic compounds also change depending on the succession stage and age of plants (Boege and Marquis, 2005; Wam et al., 2017).

Among mineral elements, one can note the higher content of Ca and Mn in 5–7-year-old needles and Mg in current-year needles in dead-cover spruce in EBGRs compared to the needles in spruce–dwarf-shrub–green-moss EBGRs, which is determined by differences in the content of these elements in the litters (Orlova et al., 2016).

Table 2. Chemical composition of *Picea abies* × *obovata* needles in the green-moss—dogwood—dwarf-shrub spruce forest and sphagnum—ledum spruce forest

Component	Transitional site						Accumulative site		
	spruce dead-cover EBGR			spruce dwarf-shrub—green-moss EBGR			spruce dwarf-shrub—green-moss EBGR		
	current year	1st year	5th—7th year	current year	1st year	5th—7th year	current year	1st year	5th—7th year
C, %	51.4(1.3)	50.7(1.6)	47.3(0.5)	51.0(0.7)	50.0(2.9)	48.8(1.0)	50.6(0.7)	49.1(2.9)	51.2(1.6)
N, %	1.03(0.07)	1.05(0.05)	0.90(0.04)	1.08(0.04)	1.01(0.05)	0.90(0.06)	0.95(0.05)	0.95(0.04)	0.85(0.04)
C/N	51(4)	48(2)	53(2)	47(1)	50(5)	55(4)	54(3)	52(4)	61(4)
ADF, %	39.7(0.6)	37.0(1.3)	29.8(0.5)	39.7(2.5)	35.2(0.9)	33.2(0.3)	40.0(1.7)	37.0(2.4)	32.7(1.0)
Lignin, %	18.8(0.4)	16.4(0.4)	12.8(0.2)	19.5(1.6)	15.6(0.4)	14.7(0.3)	20.4(0.7)	15.8(1.2)	13.4(0.2)
Cellulose, %	20.6(0.2)	20.1(1.0)	16.0(0.2)	19.8(1.6)	19.0(0.7)	17.4(0.2)	19.5(2.1)	21.0(1.2)	18.8(0.9)
Lignin/cellulose	0.91(0.02)	0.82(0.03)	0.80(0.01)	0.99(0.11)	0.82(0.03)	0.84(0.02)	1.07(0.14)	0.75(0.02)	0.72(0.02)
Lignin/N	19(3)	16(1)	15(1)	19(1)	16(1)	17(1)	20(1)	16(1)	16(1)
LPC, mg g^{-1}	31.9(2.7)	34.5(3.7)	38.4(2.7)	32.0(2.7)	33.9(2.6)	36.7(2.3)	35.2(0.9)	38.4(1.0)	46.1(1.3)
LPC, mg g^{-1}	33.3(2.9)	35.1(4.2)	40.5(2.3)	26.2(1.2)	30.5(5.7)	34.3(3.0)	32.5(2.0)	36.2(3.2)	35.7(2.0)
SPC, mg g^{-1}	65.2(3.5)	69.5(4.7)	78.9(1.4)	58.1(2.5)	64.4(3.0)	71.0(1.3)	67.7(2.9)	74.6(3.7)	81.8(1.9)
ST, mg g^{-1}	40.1(2.2)	38.2(1.6)	31.0(1.6)	42.6(2.4)	38.1(1.9)	29.8(1.3)	45.5(5.2)	39.0(1.9)	33.0(2.9)
BT, mg g^{-1}	8.1(1.3)	6.6(0.5)	6.0(0.7)	8.2(1.0)	6.6(0.8)	6.3(1.5)	6.8(1.2)	5.9(0.3)	4.7(0.5)
K, mg g^{-1}	10.6(0.9)	6.3(0.4)	3.4(0.2)	9.8(0.7)	6.3(0.2)	4.2(0.3)	9.4(0.9)	5.4(0.4)	3.7(0.2)
Ca, mg g^{-1}	6.4(0.8)	9.3(1.1)	19.1(2.0)	5.6(0.5)	8.0(1.1)	14.6(2.7)	5.7(0.8)	7.9(1.0)	13.8(1.8)
Mg, mg g^{-1}	0.96(0.07)	0.93(0.09)	0.73(0.13)	0.88(0.06)	0.89(0.03)	0.74(0.07)	1.04(0.05)	1.06(0.08)	0.80(0.11)
Mn, mg g^{-1}	0.7(0.2)	1.0(0.3)	1.8(0.5)	0.7(0.1)	0.9(0.2)	1.4(0.3)	0.6(0.1)	0.8(0.2)	1.2(0.4)
P, mg g^{-1}	1.8(0.1)	1.5(0.1)	1.0(0.1)	1.8(0.1)	1.6(0.1)	1.3(0.1)	1.2(0.1)	1.1(0.1)	1.1(0.1)

See Table 1.

Comparison of the Chemical Composition of Spruce Needles in Different Sites along the Geochemical Transect

The chemical composition of needles of spruce forming different types of spruce forests was compared taking into account the type of EBGR.

The spruce dead-cover EBGR occurred only in the automorphic and transitional sites. The main changes in the chemical composition are observed in 5—7- and 8—11-year-old needles (Tables 1 and 2). The concentration of lignin, cellulose, ADF, high-molecular-weight phenolic compounds, Mn, and P decrease in these needles; the lignin/cellulose and lignin/N ratios decrease in spruce needles in transitional conditions compared to automorphic ones. This can be explained by a more active growth of spruce in transitional conditions. An increase in the content of low-molecular-weight compounds in needles in this case leads to a change in the sum of phenolic compounds only at the qualitative level. The concentrations of soluble tannins decrease, since the forest density increases and the illumination decreases, while the concentration of bound tannins and Ca in spruce needles increases in transitional conditions. In addition, the content of carbon decreases and that of N increases in the needles of all ages under transitional conditions, which leads to a decrease in the C/N ratio. This may be due to the absorption of N during the more active spruce growth owing to the additional lateral flow of nutrients (Manakov and Nikonov, 1981). All identified changes are significant ($p < 0.05$). A significant increase in the concentration of K and decrease in the content of Mg are also observed in the current-year needles under transitional conditions compared to automorphic conditions, which can be explained by the known phenomena of antagonism between K and Mg and between Mg and NH_4 (Kabata-Pendias and Pendias, 1989).

The spruce dwarf-shrub—green-moss EBGR covers all sites along the geochemical transect. Lignin concentrations decrease in 5—7-year-old needles and, on the contrary, increase in the current-year needles of spruce in the accumulative landscape compared to the transitional and automorphic sites. Accordingly, the lignin/cellulose and lignin/N ratios expand in the current-year needles and narrow in the 5–7-year-old needles along the geochemical transect. Lignin and cellulose are static and cannot be redistributed from one age class of needles to another. Lignin and the levels of cellulose in 5–7-year-old needles depend on growth conditions during needle production. It has been established that the lignin concentration in different-age needles varies differently under diverse growing conditions (Aitkenhead-Peterson et al., 2006).

Cellulose accumulates in 5–7-year-old needles in the accumulative site. It can be assumed that the synthesis of the most energy-consuming element (lignin) is reduced more significantly than that of the less energy-consuming element (cellulose) in spruce needles and litter in this site under limited carbon conditions. The sum of phenolic compounds reaches the highest values in the accumulative landscape due to an increase in the proportion of low-molecular-weight phenols. We recorded the maximum concentrations of phenolic compounds in the organogenic horizon of the litter in the same site (Artemkina et al., 2018); this may have a certain effect on the availability of nitrogen for plants and microbiological activity, which are inversely related to the content of phenolic compounds in spruce needles. In addition, the concentrations of phenolic compounds increase in spruce needles with increase in surface overwetting (Luzikov et al., 2005). The content of soluble tannins in needles significantly decreases in transitional and accumulative conditions compared to automorphic ones; their level is minimal in needles of all ages in transitional sites. In transitional conditions, the forest density is higher and, accordingly, the illumination is lower; this is why the concentrations of soluble tannins decrease in these sites (Plaksina et al., 2009). The concentrations of bound tannins reach the maximum level in transitional conditions in the needles of all ages. Presumably, optimal conditions for the formation of this pool of phenolic compounds were formed in this site: light, temperature, soil moisture, and mineral nutrition (Blanco, 2007). The concentration of carbon in needles is significantly lower for spruce in transitional and accumulative conditions than for spruce in automorphic conditions; this is possibly due to a more intensive growth of spruce trees. The C/N ratios vary from 50 to 60 in transitional and accumulative conditions.

Ca concentrations increase in the 5–7-year-old needles of spruce under transitional conditions compared to automorphic and accumulative conditions; the same pattern is observed in spruce dead-cover EBGRs. K concentrations do not vary significantly with respect to the site. The content of Mg in current-year needles decreases in transitional conditions compared to the automorphic site, which can be explained by antagonism phenomena: here, there is more nitrogen in the needles; in turn, ammonia nitrogen is a well-known magnesium antagonist. The content of Mn in needles increases upslope for all ages, which may be due to the high content of manganese compounds in the forest litters, which are available for plants, under automorphic conditions (according to our unpublished data). The concentration of P decreases in all needles in accumulative sites. Under overwetting conditions, phosphorus becomes hardly accessible due to its binding by iron and aluminum sesquioxides.

Therefore, the possible explanations for the change in the chemical composition of spruce needles along the geochemical transect of biogeocenoses from automorphic to accumulative sites are (1) different concentrations of nutritional elements and secondary metabolites in soils; (2) the increase in the soil moisture downslope; (3) the features of the microbiological activity of soils; and (4) environmental factors (illumination, temperature, etc.).

The Relationships between Secondary Metabolites and Nutritional in Different-Age Needles of Picea abies × obovata (Comparison between Spruce Older than 100 Years and Spruce Undergrowth)

The results of the correlation analysis of the relationship between secondary metabolites and nutritional elements in the different-age needles of spruce older than 100 years and its undergrowth (30–40 years) are given in Table 3. A wide variety of dependencies of the formation of pools of phenolic compounds on mineral components in different-age needles of spruce trees of different ages is revealed. Despite the variety of relationships, we can distinguish separate characteristics that influence the concentration of phenolic compounds and are inherent only in spruce older than 100 years or only in spruce undergrowth.

For instance, the content of Ca, Mg, and Mn in annual and perennial needles of spruce undergrowth was negatively correlated with the sum of phenolic compounds, while the content of N, with the concentration of soluble tannins. This is consistent with the Carbon/Nutrient Balance (CNB) Theory (Bryant et al., 1983), which postulates that vegetative plant growth prevails when the amount of mineral nutrition elements is sufficient, while the synthesis of secondary metabolites is limited in this case. The formation of lignin in all undergrowth needles positively depends on K, Mn, and P concentrations. These data contradict the “carbon/nutrients” theory. However, it is known that an increase in K concentration stimulates lignification processes in *Picea abies* needles under alkaline conditions. Mn stimulates the activity of some enzymes (peroxidases), which, in turn, also activate lignification processes in needles (Mandre, 2002).

In older spruce trees, K negatively influences the content of the sum of phenolic compounds in current-year and 1-year-old needles, which is also consistent with the CNB theory (Bryant et al., 1983). Ca is positively correlated with soluble tannins and negatively

Table 3. Coefficients of correlation between the concentration of phenolic compounds and mineral nutritional elements in different-age needles of *Picea abies* × *obovata* in different states

Elements	Mature spruce trees						Spruce undergrowth					
	SPC	LPC	HPC	ST	BT	lignin	SPC	LPC	HPC	ST	BT	lignin
Current-year needles												
N	–0.282	–0.568	–0.155	0.513	–0.787	0.156	0.181	0.959	–0.550	**–0.957**	–	0.388
K	**–0.682**	–0.576	–0.588	–0.239	–0.090	0.507	0.965	–0.364	0.878	0.371	–	**0.886**
Ca	0.321	–0.163	0.392	**0.581**	**–0.551**	–0.260	0.495	–0.917	0.958	0.920	–	0.296
Mg	0.086	–0.821	0.312	**0.735**	0.733	–0.200	–0.480	–0.821	0.260	0.817	–	–0.657
Mn	0.259	–0.368	0.379	**0.780**	–0.391	–0.208	0.668	–0.811	0.997	0.815	–	**0.492**
P	–0.387	–0.263	–0.351	**0.541**	–0.297	0.469	0.917	0.299	0.386	–0.292	–	**0.981**
1-year-old needles												
N	–0.809	–0.477	–0.551	0.506	–0.912	–0.198	0.439	0.696	–0.141	**–0.662**	–	0.976
K	**–0.693**	–0.418	–0.468	0.522	–0.847	–0.025	–0.232	0.081	–0.738	–0.035	–	**0.892**
Ca	–0.435	–0.457	–0.197	**0.587**	**–0.528**	–0.498	**–0.635**	–0.364	–0.959	0.406	–	0.604
Mg	**0.541**	–0.211	0.629	**0.660**	0.602	0.121	**–0.826**	–0.610	–1.000	0.645	–	0.356
Mn	–0.224	–0.722	0.138	**0.882**	–0.188	–0.258	**–0.685**	–0.426	–0.976	0.466	–	**0.549**
P	–0.417	–0.857	0.017	**0.711**	–0.179	–0.386	–0.753	–0.512	–0.992	0.550	–	**0.465**
5–7-year-old needles												
N	–0.028	0.200	–0.069	0.075	0.190	–0.073	1.000	–0.367	0.693	**–0.880**	0.752	–0.317
K	–0.452	0.148	–0.413	–0.173	0.225	–0.297	0.339	–1.000	0.914	–0.746	0.876	**0.784**
Ca	0.475	–0.617	0.538	**0.529**	**–0.769**	–0.295	**–0.695**	–0.416	0.039	0.268	–0.047	0.903
Mg	**0.923**	–0.579	0.905	**0.976**	–0.673	–0.459	**–0.581**	–0.545	0.185	0.123	0.101	0.956
Mn	0.384	–0.595	0.456	**0.550**	–0.802	–0.226	**–0.525**	–0.600	0.251	0.056	0.167	**0.974**
P	0.427	–0.600	0.493	**0.598**	–0.668	–0.419	–0.141	–0.870	0.618	–0.348	0.548	**0.983**
8th–11th-year-old needles												
N	–0.426	0.305	–0.635	–0.273	0.416	0.353	–	–	–	–	–	–
K	0.489	0.566	0.354	0.044	0.964	–0.823	–	–	–	–	–	–
Ca	0.140	0.775	–0.149	0.316	0.343	0.112	–	–	–	–	–	–
Mg	**0.526**	0.865	0.276	**0.868**	–0.054	0.064	–	–	–	–	–	–
Mn	0.554	0.871	0.307	**0.667**	0.165	–0.061	–	–	–	–	–	–
P	0.345	0.691	0.131	**0.537**	–0.042	0.213	–	–	–	–	–	–

See the notations in Table 1. –, Undetermined; $p < 0.05$. The correlation coefficients discussed in the article are in bold.

correlated with bound tannins in all needles except 8–11-year-old needles. This element is bound with cell wall elements, in particular, with pectin substances (Medvedev, 2004) (probably, also with tannins), thereby strengthening the cell walls. The positive correlation of Ca with soluble phenolic compounds, which include tannins, was previously recorded for *Pinus nigra* (Giertych et al., 1999). Mg is positively correlated with the value of the sum of phenolic compounds in all needles except current-year needles. Mg, Mn, and P are positively correlated with the content of soluble tannins in needles of all ages. The complexation of different classes of phenolic compounds with metals and nonmetals reduces the probability of leaching of these physiologically important elements, which has already been shown in our previous studies and the research of other authors (Kraus et al., 2003; Artemkina and Gorbacheva, 2006).

Therefore, mineral elements significantly influence the quantitative and even qualitative characteristics of phenolic compounds.

CONCLUSIONS

Our research has revealed the patterns of lateral intrabiogeocenotic (between separate EBGRs) and interbiogeocenotic variability in the content of secondary metabolites and nutritional elements in different-age needles of spruce trees along the geochemical transect in spruce forests in northern taiga.

Age of needles. One of the main factors of variation in the composition of spruce needles is their age. The low-mobile elements (Ca and Mn) accumulate in needles with age. The content of elements that can be retranslocated inside plants (K, P, and Mg) decreases in older needles. Such patterns cover all studied EBGRs. With rare exceptions, the concentration of lignin, soluble and bound tannins, and N and C decreases with the age of needles. On the other hand, the concentrations of both low-molecular-weight and high-molecular-weight phenolic compounds increase and, as a consequence, their total amount grows.

Intrabiogeocenotic differences. The aging needles (8–11 years old) of 110–135-year-old spruce that forms dwarf-shrub–green-moss EBGRs contain less lignin, phenolic compounds, and tannins and has a lower lignin/N ratio than that for the needles of 190–220 year-old spruce trees that form dead-cover EBGRs, as well as spruce undergrowth EBGRs (30–40 years), which is possibly determined by more balanced nutrition. The maximum concentrations of carbon and lignin were found in 5–7-year-old needles of spruce undergrowth. The spruce undergrowth is also characterized by a high concentration of high-molecular-weight phenolic compounds and tannins and wider ranges of the lignin/cellulose and lignin/N ratios in the needles than the respective ratios for trees older than 100 years. These differences are determined by the age of the trees and their growing conditions (allelopathy, light, mineral nutrition, etc.), which should be taken into account in further studies.

Interbiogeocenotic differences. Significant differences are found in the content of secondary metabolites and some nutritional elements in the needles of spruce in different sites. The needles of spruce trees contain significantly more bound tannins and low-molecular-weight phenols in transitional and accumulative biogeocenoses than in automorphic sites. The lignin concentration and lignin/N ratio in older needles are significantly higher under automorphic conditions, while the maximum values in current-year needles are characteristic of transitional and accumulative sites. Lignin is static and cannot be redistributed between different-age needles. The concentration of lignin in different-age needles depends on growth conditions during needle production; therefore, the concentration of lignin in different-age needles varies differently under diverse growing conditions. The concentrations of soluble tannins, Mn, P, and carbon decrease from automorphic to accumulative sites, while Ca, on the contrary, increases in this direction. The C/N ratio narrows in transitional conditions; the content of Mg in current-year needles is minimal under these conditions. The revealed differences are related to the growing conditions (microclimatic conditions) of spruce trees in different sites along the geochemical transect, as well as to the manifestation of antagonism between the elements.

Mineral elements significantly influence the quantitative and even qualitative characteristics of phenolic compounds, which is expressed both in positive and in negative correlations of some nutritional elements with the content of phenolic compounds. Such differences in the chemical composition of *Picea abies* × *obovata* needles can further influence the processes of litter transformation and, consequently, the carbon and nutrient cycles in different spruce EBGRs.

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COMPLIANCE WITH ETHICAL STANDARDS

Conflict of interests. The authors declare that they have no conflicts of interest.

Statement on the welfare of animals. This article does not contain any studies involving animals performed by any of the authors.

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