Influence of north climatic conditions on the peat lipids composition

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Abstract. The paper studies the composition of lipid organic compounds of peat from the northern regions of the Russian Federation. Peat was sampled in the northern taiga, forest-tundra and tundra zones, characterized by various hydrothermal conditions and vegetation cover. n-Alkanes, fatty acids and their ethers, aldehydes, ketones, alcohols, tocopherols, squalene, bi-, tri- and pentacyclic terpenoids, as well as steroids were identified in peat lipids by gas chromatography-mass spectrometry. The dependences of the total content of lipids and the majority of the investigated compounds classes on the ambient temperature and vegetation, as well as the correlation between the composition of n-alkanes and humidity were revealed.

1. Introduction

Hydrothermal conditions are very important in the process of peat formation [1]. The accumulation of green phytomass depends directly on the amount of heat and the duration of the vegetation period [2]. Therefore, an increase in the temperature of the environment will facilitate the deposition and transformation of a larger mass of peat-forming plants into the peat. Sharp cooling leads to a change in the vegetation cover and, as a consequence, to a change in the species composition of plant communities and the products of plant transformation in the process of peat formation. As a result, the composition of peat lipids should respond to changes in temperature conditions. Drying of mire in the result of decreasing atmospheric precipitation causes an increase in the growth and activity of aerobic bacteria, leading to lowering in the content of lipid components in the peat [3].

Understanding the mechanisms that unite vegetation and climate is one of the most important fundamental problems in paleoecological and paleoclimatic studies. It is very important for predicting the future state of the biosphere and assessing the impact of anthropogenic factors on it that may lead to climate change [4]. The peat from the northern taiga, forest-tundra and tundra zones, characterized by different hydrothermal conditions and vegetation cover, was studied to determine the influence of the climatic factor on the composition of peat lipids in the northern regions of the Russian Federation.

2. Samples and analysis

The figure 1 shows the location of the sampling areas.

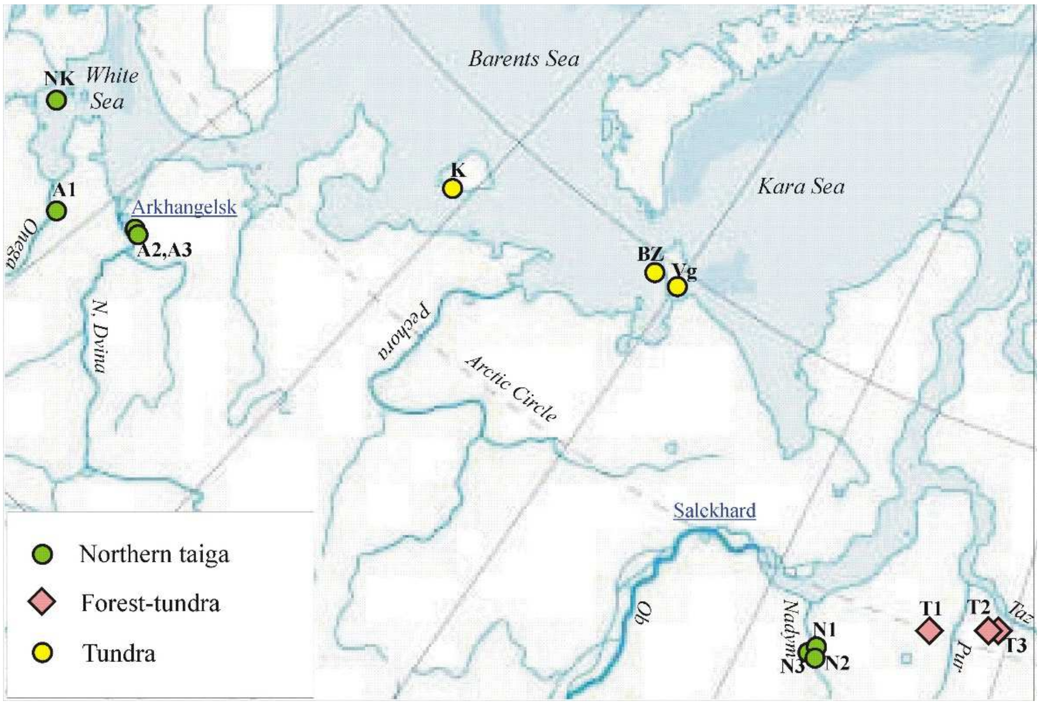

Figure 1. Map of Russian Arctic and location of study sites (see table 1 for identification of site index).

Table 1. Identification of the site index*** (* Fuscum peat, ** Sphagnum peat of bog hollows, *** All peat samples were taken from the depth of 0-0.2 m).

Index	Region / District	T, °C	Average precipitation, mm
A1	Arkhangelsk	1.5	575
A2*	Arkhangelsk	0.8	558
A3	Arkhangelsk	0.8	558
N1**	Nadymskiy	-6.6	449
N2	Nadymskiy	-6.6	449
N3	Nadymskiy	-6.6	449
T1	Tasovskiy	-7.0	482
T2*	Tasovskiy	-8.2	458
T3**	Tasovskiy	-8.2	458
		Islands:	
NK	Nemecky Kuzov	0.8	445
K	Kolguev	-2.7	344
BZ	Bolshoy Zincovy	-6.3	359
Vg	Vaygach	-6.3	359

The studied highbog peat samples from the northern taiga were selected within the Arkhangelsk region and on one of the islands of the White Sea, where the current average annual temperatures range from 1.5°C to 0.8°C (table 1). The average annual precipitation is 575-558 mm in the continental part and 445 mm on the island Nemecky Kuzov. In the investigated section of the northern taiga subzone of Western Siberia the temperature is much lower, the amount of precipitation is close to one on the island Nemecky Kuzov. Among these samples there is one of bog hollows peat and the peat from arid areas. The investigated area of the forest-tundra zone (Western Siberia) is characterized by the lowest annual temperatures (among the studied areas) (table 2), the amount of precipitation is 458-482 mm. The samples also include peat located within swamps, as well as on elevated areas. They

IOP Conf. Series: Earth and Environmental Science **138** (2018) 012016 doi:10.1088/1755-1315/138/1/012016

are characterized by different amounts of precipitation and by different air humidity. The peat from tundra subzone was selected on three islands of the Barents Sea. The average long-term temperature at the Island Kolguev (northern tundra) is -2.7° C, the amount of precipitation is low. The amount of precipitation is higher in the arctic tundra on island Bolshoj Cinkovy and in the south of island Vaigach, where the average long-term temperature is about -6.3°C [2]. A detailed description of selection and preparation conditions and peat analysis is given in [5]. The data on the composition of n-alkanes were used to calculate the moisture index: Paq = $(C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})$ [6]. It provides an approximate measure of the sedimentary input from submerged/floating aquatic macrophytes relative to that from emergent and terrestrial species.

3. Results and discussion

Acyclic alkanes, fatty acids and their ethers, ketones, alcohols, aldehydes and squalene, as well as bicyclic tocopherols and sesquiterpenes (BCT), tricyclic diterpenes (TDT), tetracyclic steroids and pentacyclic triterpenoids (PCT) were identified in the peat lipids (figure 2).

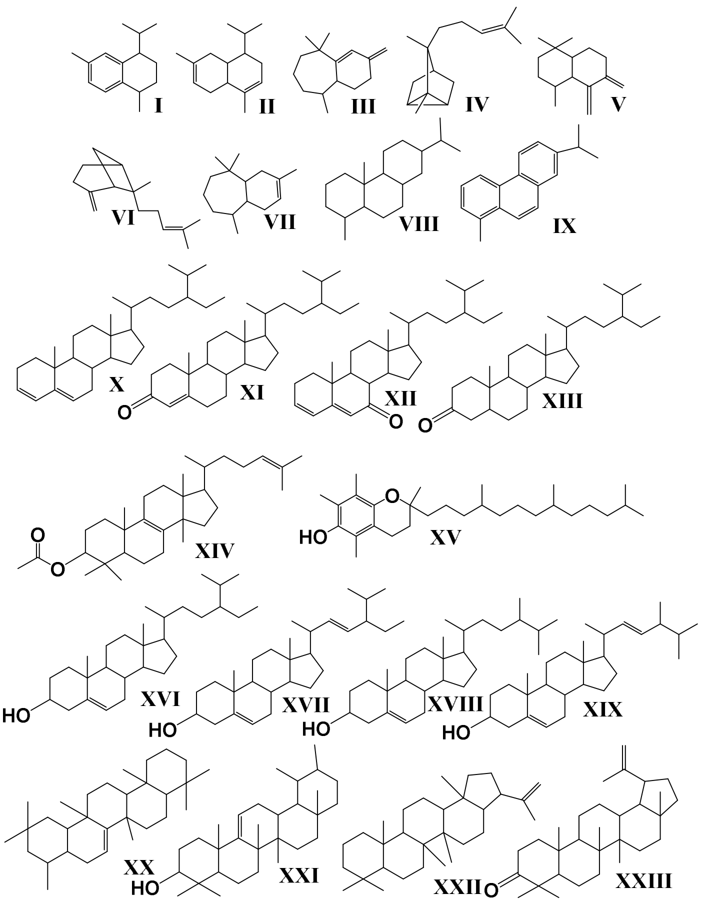

Figure 2. Major structural varieties of cyclic compounds in the peat lipids composition:
I-calacorene, II-δ-cadinene, III-himachala-3(12),4-dien, IV-santalene, V-1,1,4α-trimethyl-5,6-dimethylene-decahydronaphtalene, VI-bergamotene, VII-himachalen, VIII-18-norabietane, IX-retene, X-stigmast-3,5-dien, XI- stigmast-4-en-3-one, XII-stigmast-3,5-dien-7-one, XIII-stigmastane-3-one, XIV-lanosterol acetate, XV-α-tocopherole, XVI- sitosterol, XVII-stigmasterol, XVIII-campesterol, XIX-crinosterol, XX-D-friedoolean-14-ene, XXI-ursen-3-ol, XXII-diploptene, XXIII-lup-20(29)-en-3-one.

Table 2. Group composition of the peat lipids from north taiga subzone.

Pattern index	A1	A2	AP	N2	N1*	N2	N3
North latitude	63°82'	64°20'	64°19'	64°57'		65°18'	
Eastern longitude	38°49'	40°37'	40°41'	35°10'		72°53'	
Lipid groups				Content, mcg/g of dry peat			
n-Alkanes	32.6	17.4	62.5	90.0	47.1	130.6	45.1
Fatty acids	15.6	4.9	5.4	8.8	9.3	10.3	9.5
Fatty acids esters	2.4	0.4	0.6	1.4	1.3	2.0	1.5
Ketones	16.7	2.8	5.1	10.8	1.6	18.7	11.4
i-Alcohols	1.8	1.1	1.1	0.7	7.7	1.5	1.0
n-Aldehydes	12.3	2.7	6.1	47.1	2.1	20.5	2.7
Squalene	4.6	1.5	0.9	4.0	1.3	0.7	1.4
Tocopherols	0.5	3.7	4.0	1.1	0.7	2.6	10.2
Bicyclic terpenoids	6.2	0.3	0.6	1.9	0.05	0.7	0.1
Tricyclic terpenoids	1.9	0.1	2.2	1.3	0.02	1.4	0.4
Pentacyclic terpenoids	12.8	76.3	50.4	21.6	0.9	18.8	17.5
Steroids	4.6	6.5	7.1	5.9	8.0	16.1	15.0

There is no dependence between the total lipid content in the peat, the temperature and the humidity of the environment. At the same time the average content of the peat lipids clearly reduces from the northern taiga to the tundra natural climatic zone (figure 3). It indicates a predominant influence of characteristic plant communities of natural zones on the content of peat lipids.

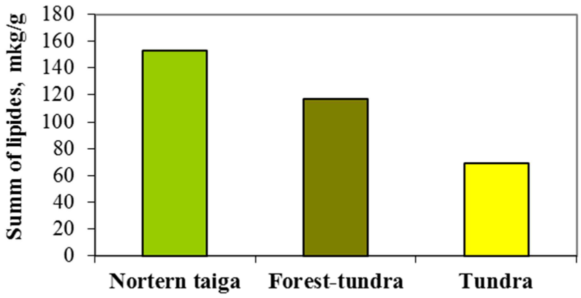

Figure 3. Average lipid content in the peat from various zones.

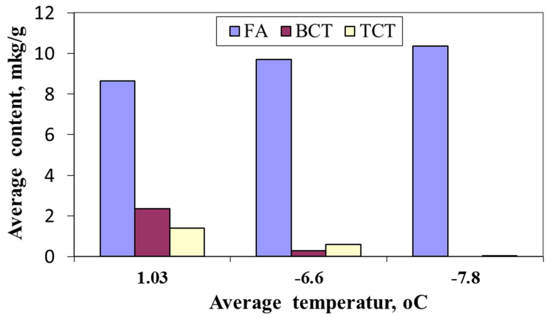

Figure 4. Average content of fatty acids (FA), BCT and TCT versus temperature of site.

The average content of fatty acids in continental peat samples with a constant individual composition slightly increases with decreasing the ambient temperatures (figure 4). In the peat sampled on tundra islands, the content of these compounds is much lower than in the other samples. The maximum content of fatty acids, as well as squalene and ketones, is fixed in the peat from the northern taiga in the area of the maximal temperature and amount of precipitation among the studied samples. The increased content of alcohols is fixed in the bog hollows peat. The content of aldehydes sharply increases in the peat from islands Nemeckij Kuzov and especially Kolguev, where aldehydes dominate among other classes of lipids. Such a high content of aldehydes can be a consequence of the participation of excrements of numerous nesting migratory birds in the formation of peat lipids [7]. It is confirmed by the predominance of 5β-isomers among cholestanones in the peat from the island Kolguev.

The content of acyclic ketones in the peat decreases from the north taiga to the forest-tundra and is minimal in the bog hollow peat.

The BCTs content in the northern taiga peat sharply decreases from the zone of positive ambient temperatures to the zone of negative ones (figure 4). A similar change is observed for TCTs. The content of the other classes of lipid organic compounds in the peat does not depend on the ambient temperatures.

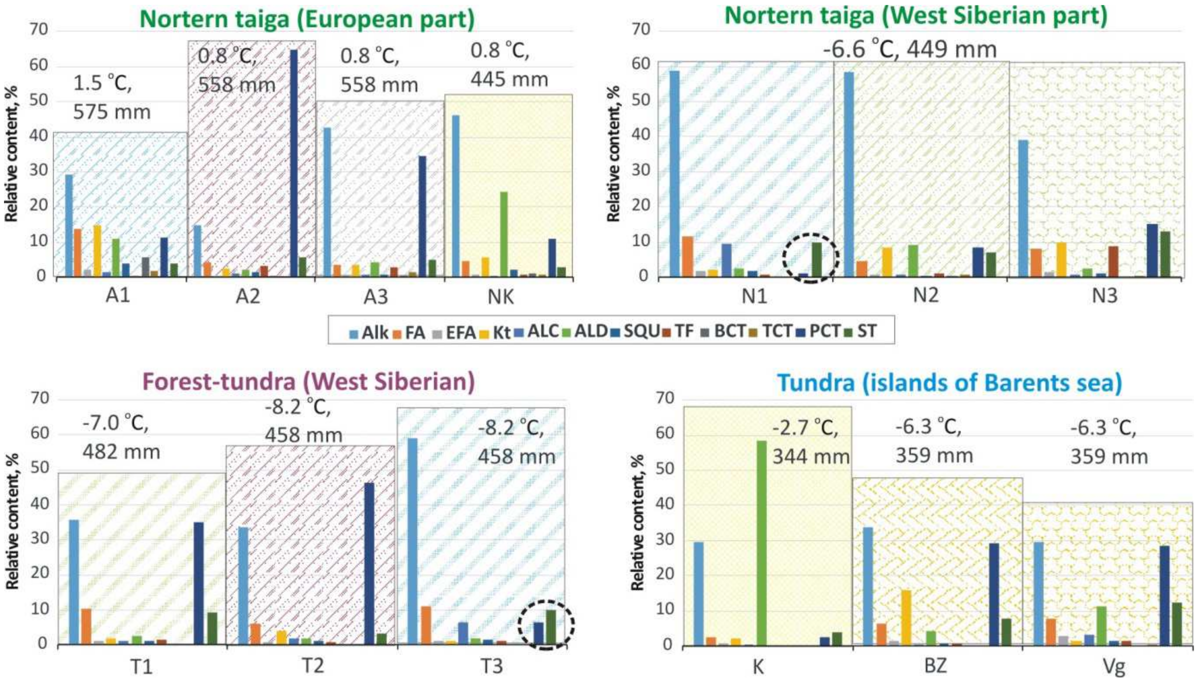

Figure 5. Relative content of separate groups of compounds in the peat lipids from the northern taiga, forest-tundra and tundra: Alk – n-alkanes, FA – fatty acids, EFA – esters of fatty acids, Kt – ketones, ALC – alcohols, ALD – aldehydes, SQU – squalene, TF – tocopherols, BCT – bicyclic sesquiterpenes, TCT – tricyclic diterpenes, PCT – pentacyclic triterpenoids, ST – steroids.

In the most part of the studied samples n-alkanes predominate in the peat lipids. PCTs predominate in the fuscum peat samples (A-2, T-2) regardless of the environment temperature and humidity. The bog hollows peat is characterized by the predominance of steroids over PCTs and the increased proportion of acyclic alcohols among the peat lipids, which present in trace amounts in other samples (figure 5).

Table 3. Group composition of the peat lipids from forest-tundra and tundra zones.

Pattern index	T1	T2	T3*	K	BZ	Vg
North latitude	66°19'	67°20"'		69°01′	69°52'	69°43'
Eastern longitude	76°54'	78°45"		49°22′	59°27'	60°03'
Lipid groups	Content, mcg/g of dry peat					
n-Alkanes	30.1	46.2	74.2	36.4	17.6	9.6
Fatty acids	8.8	8.3	14.0	3.0	3.4	2.5
Fatty acids esters	1.0	1.2	1.7	0.9	0.7	0.9
Ketones	1.5	5.6	1.5	2.7	8.2	0.4
i-Alcohols	1.1	2.8	8.0	0.4	0.2	1.0
n-Aldehydes	2.2	2.6	2.6	72.2	2.3	3.7
Squalene	0.9	1.5	1.8	0.1	0.4	0.5
Tocopherols	1.2	1.0	1.3	0.1	0.3	0.5
Bicyclic terpenoids	0	0	0	0	0	0.03
Tricyclic terpenoids	0.005	0.01	0.1	0.03	0.01	0.1

Pentacyclic terpenoids	29.5	63.3	8.3	3.1	15.2	9.3
Steroids	7.9	4.4	12.6	4.7	4.0	4.0

The high content of the C_{23} homologue among n-alkanes was noted in the peat of the bog hollows and in the areas with the elevated amount of atmospheric precipitation (figure 6). This compound corresponds to moisture-loving plants [8]. In the other studied samples from the zones with a reduced amount of atmospheric precipitation, the content of C_{23} n-alkane is not so high. Some odd n-alkanes (C_{25}-C_{31}) predominate in these samples. It corresponds, for example, to cotton grass predominated by C_{31} n-alkane, to some species of sedges and horsetail, characterized by the dominance of C_{29}, to green moss and woody plants with a predominance of C_{27} [8-11].

The value of Paq moisture index [6] decreases with a decrease in humidity from 0.39 to 0.15 for the peat of northern taiga lying at positive temperatures. In the mainland peat from the northern taiga and forest tundra, lying at a negative temperature, Paq decreases from 0.65-0.71 to 0.48-0.32; the maximum value (0.79) is recorded in the bog hollows peat. In the peat sampled on the island, the decrease in humidity leads to a decrease in the value of Paq from 0.50-0.61 to 0.13.

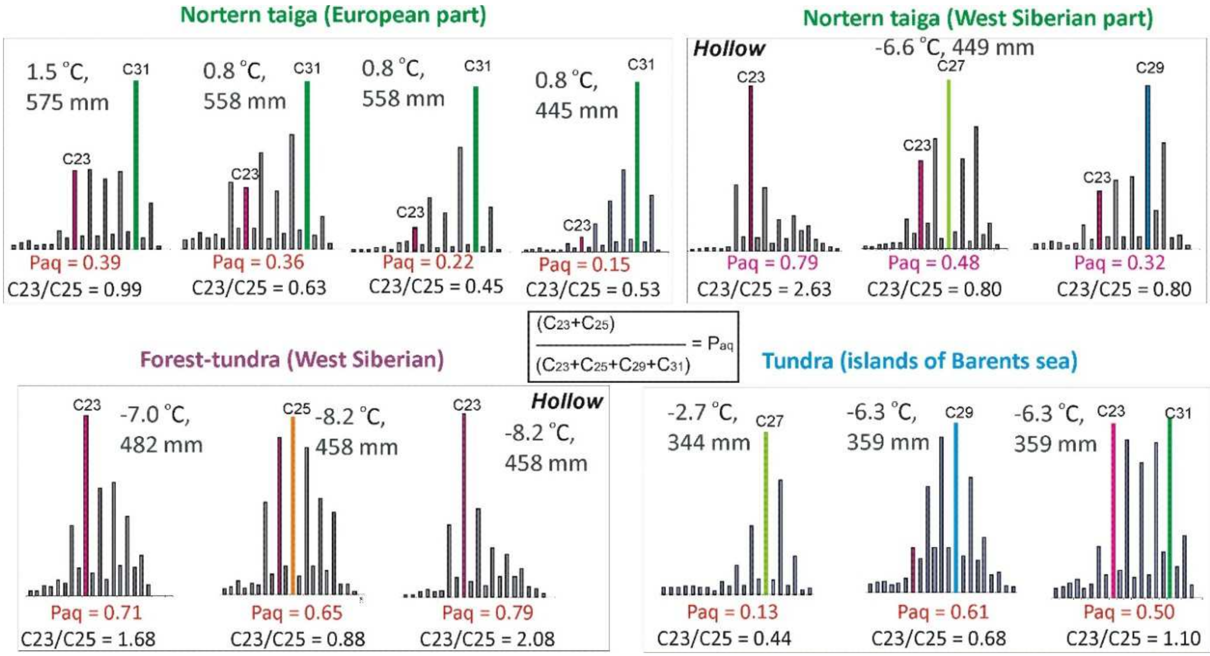

Figure 6. Molecular-mass distribution of n-alkanes in peat samples from the northern taiga, forest-tundra and tundra.

The ratio of moisture-loving sphagnum mosses (C_{23} predominates) to sphagnum mosses of arid areas (C_{25} predominates) [12] can be estimated by the ratio C_{23}/C_{25} n-alkanes. The changes of the Paq values and the proportion of moisture-loving sphagnum mosses residues in the peat ($C_{23}/(C_{25}+C_{23})$) has a similar tendency with increasing amount of atmospheric precipitation for the most part of the peat samples (figures 7, 8).

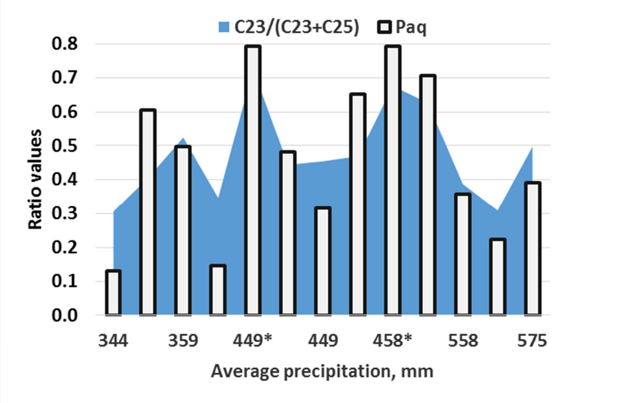

Figure 7. Influence of the amount of atmospheric precipitation on the value of the moisture index and the proportion of moisture-loving sphagnum mosses in the peat composition.

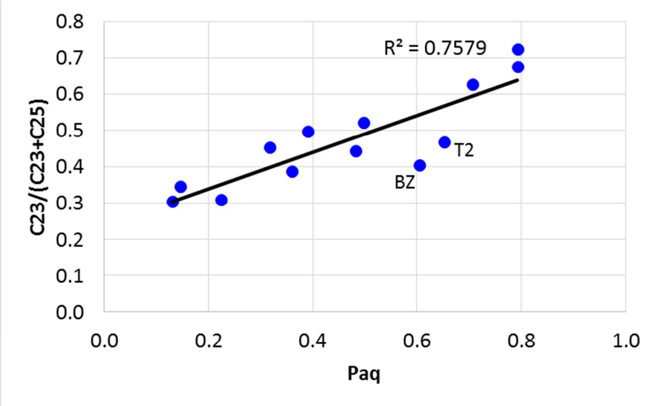

Figure 8. Correlation of moisture index and the proportion of moisture-loving sphagnum mosses in the peat composition.

The peat from the island Bolshoy Zinkovy is characterized by the increased Paq value. It may be explained by the limited distribution of vascular plants and the participation of their residues in the peat formation on this island. The discrepancy between Paq and the C_{23} proportion in the fuscum peat T2 is caused by the absence of moisture-loving sphagnum mosses residues in the peat. It results in a low value of the ratio $C_{23}/(C_{23}+ C_{25})$. If these peat samples are excluded from the data array, the coefficient correlation between the Paq values and the n-alkane C_{23} proportion increases to 0.93.

The figure 7 shows that the amount of atmospheric precipitation is not decisive in the formation of n-alkanes composition in the peat of the subarctic areas. The n-alkanes composition parameters proposed by (Ficken, 2000) for characterising the moisture reflect the intensity of atmospheric precipitation only within the limited areas. They directly depend on water saturation degree of the peat deposit surface and sharply increase in the bog hollows peat.

Calacorene and δ-cadinene predominate among BCTs in the peat at the temperature of +15°C, δ-cadinene and himachal-3(12), 4-diene – at the temperature of +0.8°C, δ-cadinene and santalene – at the temperature of -6.6 ° C. 1,1,4α-trimethyl-5,6-dimethylenedecahydronaphthalene predominates in the bog hollows peat. Further slight decrease in the BCTs concentrations is observed with a decrease of temperature in the forest-tundra. The main compounds among them are bergamotene and himachalene. In the bog hollows peat the main BCTs is 1,1,4α-trimethyl-5,6-dimethylene-decahydronaphthalene. In the tundra peat BCTs are presented only in the south of the island Vaigach. The predominant compounds among them are santalene and bergamotene.

In the peat from the positive temperatures zone TCTs are presented by decarboxylated derivatives of abietic and dehydroabietic acids with predominance of 18-norabietan in the most part of the samples. TCTs are absent in the peat from the island Bolshoy Zinkovy. In the peat from negative temperature zones they are represented by retene in low concentration.

The investigated peat steroids are presented by stigmast-3,5-dien and also by C_{27}-C_{31} structures with a ketonic, alcohol or acetate substituent. The total concentration of steroids C_{29} is maximum in all samples (figure 9). Among them prevails the group of ketones (dominated by stigmast-4-en-3-one, stigmasta- 5,7-dien-3-one or stigmastan-3-one). The concentration of 24-methylenecycloartanone (C_{31}) in the peat is not high. Lanosterol acetate predominates among the steroids in the shrub-sphagnum peat (N3) from north taiga, which differs from the others by the increased content of tocopherols (figure 5). Sitosterol and stigmasterol predominate among the steroids in the forest-tundra zone in the area with high humidity (T1) and in the bog hollows peat (T3) respectively. Saturated stigmastanones prevail in the peat from the island Kolguev with minimal amount of precipitation.

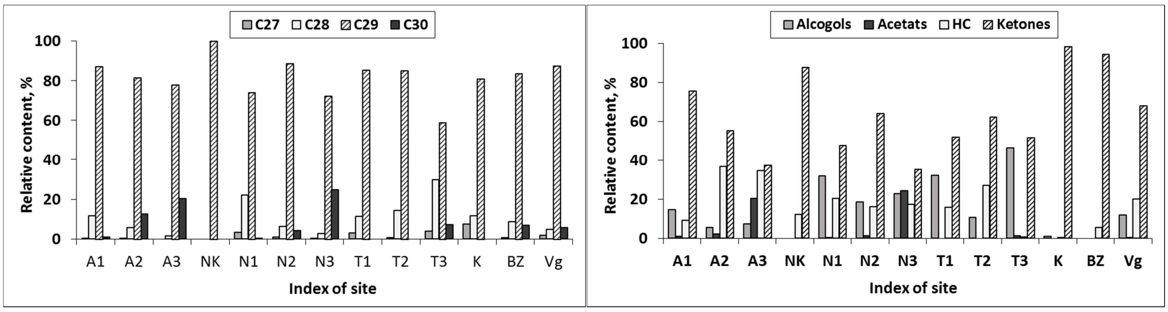

Figure 9. Relative amount of steroid groups in the peat lipids.

The bog hollows peat samples differ from the others in the increased relative content of C_{28} steroids (figure 9), with the predominance of campesterol and crinosterol and steroid alcohols in general. The peat samples from the areas with a low amount of precipitation are characterized by the minimum proportion in the composition of steroids in the compounds with an alcohol group or their absence. A significant amount of lanosterol derivatives was detected only in the peat from the northern taiga. The amount of these compounds does not depend on the temperature and humidity of the environment and is determined by the plant communities of this natural zone. In particular, in the investigated dwarf birch *Betula nana* lanosterol occupies an appreciable position in the composition of steroids.

PCTs are presented by perhydropicene structures that predominate in most part of the studied peat samples and include derivatives of oleanene, ursene, hopanoids and lupene.

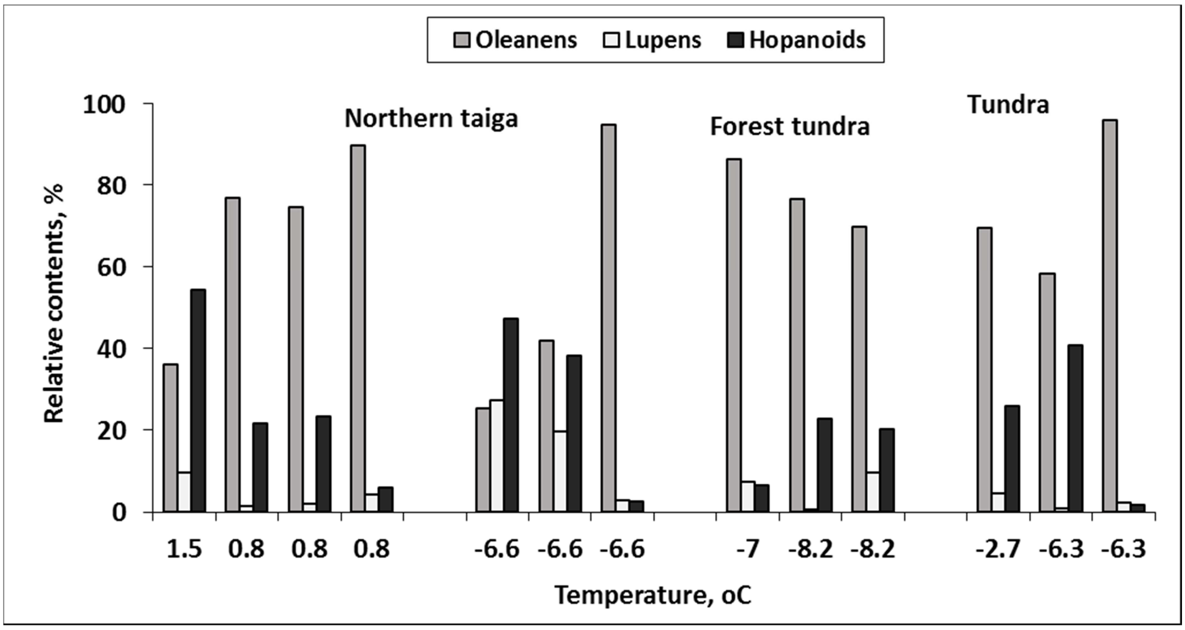

Figure 10. Relative amount of PCTs groups in the peat lipids.

Lupene derivatives are presented in a subordinate amount. Fuscum peat samples are characterized by the minimum content of these compounds regardless of the temperature and humidity of the environment. There is no dependence of the PCT composition on the climatic conditions and the water regime in the deposits. A high content of hopanoids is noticeable. It exceeds the concentration of perhydropicenes in the peat A1 sampled in the region with the maximum temperature and the amount of atmospheric precipitation.

4. Conclusion

Regardless of the ambient temperatures the bog hollows peat differs from the one sampled from the dry areas by the dominance of C_{23} among n-alkanes, 1,1,4α-trimethyl-5,6-dimethylene-decahydronaphthalene among sesquiterpenoids, the increased proportion of campesterol derivatives and compounds with alcohol substituents in the composition of steroids. They are also characterized by the predominance of steroids over pentacyclic triterpenoids, the increased proportion of acyclic alcohols, and by low content of acyclic ketones. Fuscum peat samples differ in the predominance of pentacyclic triterpenoids among the peat lipids.

The peat samples from the areas with reduced precipitation are characterized by the minimum proportion of steroid compounds with an alcohol group or their absence.

The moisture index and the ratio of C_{23} and C_{25} n-alkanes, previously proposed for estimating the moisture level in the process of peat formation, reflect the intensity of atmospheric precipitation only within restricted areas.

The average content of the peat lipids regardless of the environment temperature and humidity decreases from the northern taiga to the tundra natural and climatic zones, indicating a predominant effect of characteristic plant communities of individual zones.

The decrease of the ambient temperatures in the continental peat samples leads to the slightly increase of the content of fatty acids. The concentrations of bicyclic sesquiterpenoids and tricyclic diterpenoids sharply decrease from the zone of positive temperatures to the zone of negative ones. Among sesquiterpenoids the content of calacorene, δ- and γ-cadinene reduces, santalene and bergamotene appear. Diterpenoids in the peat from the zone of positive temperatures are represented by decarboxylated derivatives of abietic and dehydroabietic acids with the predominance of 18-norabietan in the most part of the samples, the samples from the negative temperature zone – only by retene.

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