Nonspecific organic compounds in permafrost hummocky peatland

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Abstract. Regularities of vertical distribution of nonspecific organic compounds (NOC) in the tundra peatland and boggy soil of the European Arctic zone have been identified. The content of NOC of the soils under study is mainly predetermined by the botanic composition of plant residues and their decomposition degree. Local maxima of NOC have been found in permafrost layers formed through transformation of high molecular-weight organic compounds following decomposition of woody and grassy vegetation that used to dominate during the Holocene climatic optimum.

1. Introduction

Deep layers of permafrost, which store a huge amount of multilayer information about past processes, may contain relict organic matter for a long time. Carbon pools in peat deposits of the northern hemisphere are estimated to be 1024.00 Pg for the 0–300 cm depth [1]. An approach to reconstructing the past climate and environmental conditions in northern latitudes by means of various indicators of chemical and biological origin is becoming more and more widespread [2]. A comprehensive assessment of the accumulation and subsequent transformation of nonspecific organic compounds can help assess the stability of tundra ecosystems and identify the impact of global climate change on their structural and functional parameters [3, 4].

Various peat-forming plants build a distinctive range of n-alkanes. Sphagnum mosses (bog plants) have a higher prevalence of C23 and C25 n-alkanes depending on the species [5]. The rest of the mosses contain longer chain homologues C27, C29. The study of n-alkanes in 10 moss species of the Siberian Arctic wetlands found a significant effect of moisture conditions on the spectrum of n-alkanes in mosses, the difference was observed primarily between xeromesophilic and meso-hygrophilic mosses, i.e. having a dominance of n-alkanes with long (n-C29, n-C31) and intermediate (n-C25) chain lengths, respectively [6]. The spectrum of n-alkanes in dwarf shrubs and lichens is maximized at C25, C27, C29 and C31 [7]. Waxes in leaves of higher vascular plants are dominated by alkanes with uneven numbers of carbon atoms (chains usually containing from 21 to 35 carbon atoms), and the maximum abundance of C27, C29, or C31 alkanes [8].

Phenols are essential components of biological and bioinert systems; they take part in humus formation and pedogenesis in general, being both a product of decomposition of soil humic substances and a substance in humification processes [9]. Phenol can be classified as a labile soil compound that accumulates insignificantly through natural soil formation processes, whereas significant excess of the background content of phenol can be technogenic. On the other hand, it is a highly toxic component...
capable of inhibiting microflora and vegetation; such accumulation can lead to deformation of the soil formation process [10]. Various ecological as well as biological problems associated with the decomposition of plant matter can only be solved if the information about the phenol amount contained in the soil and the nature of their distribution over different soil horizons is available.

This study was aimed at examination of the vertical profile distribution of non-specific organic compounds (NOC) in permafrost peatlands from the tundra zone of Russia; assessment of the historical variability of NOCs accumulation in the active and permafrost peat layers to establish the association between different plant residues and NOCs, and to detect specific NOCs from peats as paleoclimatic markers.

2. Materials and methods

2.1. Objects

The study was conducted at the sites of large clusters of Arctic march ecosystems located in the ecotone of the northern and southern tundra, watershed of the Padimey-Ty-Vis and Korotaikha rivers, the Nenets Autonomous Okrug (NAO) at the continuous and massive-island permafrost sites. The climate, chronology, a detailed description, botanical composition, physical and chemical properties of peatlands 2017-1 and 2017-2 were published earlier in the work [11].

Cross section 2017-1 – Hemic Folic Cryic Histosol. Coordinates: N 68° 02’, E 62° 43’. The section is made on a flat raised peat at the edge part of a flat hummocky bog with a lake complex. The raised peat area is 15×25 m, 0.7–1.5 m high. The micropor replaces of hummocks is as follows: 30–80 cm in diameter, 10–15 cm in height. The depth of the upper permafrost boundary is 33–44 cm, depending on the microrelief features. The inter-hummock spaces are of irregular shape up to 30–50 cm in diameter. The fruticulose level is composed of Ledum, Betula nana, Empetrum, Vaccinium vitis-idaea, Rubus chamaemorus. Subshrubs dominate on the surface and periphery of the raised peat area, including its slopes. The area between hummocks is covered mainly by Polytrichum, Dicranum and various lichen species.

Cross section 2017-2 – Hemic Folic Cryic Histosol (Turbic). The cross section is made 3–4 m from cross section 2017-1 across a triangular raised spot without any vegetation cover. The spot surface has distinct cracks. It rises over the core surface of the peat mound covered by mosses and lichens by 5–6 cm. The diameter of the bare spot is 26 cm, the diameter of its base is 45 cm. The permafrost depth is 43–45 cm.

Cross section 2017-3 – Fibric Floatic Histosol (table 1). The cross section is made in the center of the hollow to the west of a flat hummock. The relief is lowered, the hollow extends 200 m with a maximum width of 20–30 m. The hollows are unenclosed and connected to each other by runoff ravines. The microrelief of the area is almost even without any visible hummock ridges. The area is wet, with peat water level of 15–25 cm up from the peat surface. The vegetation cover is dominated by Sphagnum, Eriophorum, and some Carex species. The permafrost depth is 37 cm.

2.2. Methods

The concentration of n-alkanes and phenols was determined in the Chromatography Core Facility Center of the Institute of Biology, Komi Research Center of the Ural Branch of the Russian Academy of Sciences. The extraction of n-alkanes from the soils was made three times on a Dionex™ ASE™ 350 Accelerated Solvent Extractor (Thermo Scientific™, USA) with a mixture of methylene chloride/acetone (1:1) at 100 °C and 1650 psi. The concentration of n-alkanes (C18–C31) was determined by gas-liquid chromatography on a Kristall 2000M gas-liquid chromatograph and a Thermo Electron DSQ Trace Ultra gas chromatograph-mass spectrometer. Phenol was extracted from the soil with a mixture of ethyl alcohol/water (1:1) by means of mechanical shaking for 2 hours. Humic substances as related impurities were removed from the extract on a column with aluminum oxide in the presence of copper (II) sulfate. Preparation of the eluate for phenol mass concentration measurement
includes obtaining its bromine derivative – 2,4,6-tribromophenol, liquid extraction with toluene and a test on a Chromatek Crystal 2000M gas chromatograph with an electron capture detector.

Table 1. Properties of Fibric Floatic Histosol (2017-3).

| Depth, cm | Peat layer | Peat type | Dominant botanical species, % | Degree of decomposition, % | TOC*, % | pHH2O | Ash, % |
|----------|------------|-----------|-------------------------------|---------------------------|---------|-------|-------|
| 0–5      | Hi         | Raised    | Sphagnum lindbergii – 60, Sphagnum jensennii – 40 | 5                       | 47.3    | 4.4   | 3.6   |
| 5–10     | T1         | Raised    | Sphagnum lindbergii – 80, Sphagnum jensennii – 20 | 10                      | 47.5    | 4.6   | 4.3   |
| 10–18    | T2         | Raised    | Sphagnum lindbergii – 80, Sphagnum jensennii – 20 | 15                      | 48.1    | 4.1   | 9.5   |
| 18–30    | T3         | Raised    | Sphagnum lindbergii – 50, Sphagnum jensennii – 10, Scorpidium cossonii – 20, Carex rotundata – 15, Eriophorum – 5 | 25                      | 48.4    | 4.2   | 9.9   |
| 30–37    | T4         | Raised    | Sphagnum lindbergii – 50, Sphagnum jensennii – 20, Scorpidium cossonii – 15, Carex rotundata – 10, Sphagnum balticum – 5 | 25                      | 48.1    | 4.3   | 8.3   |
| 37–60    | T5         | Transitional | Sphagnum lindbergii – 50, Sphagnum jensennii – 10, Scorpidium cossonii – 20, Carex rotundata – 10, Sphagnum riparium – 10 | 20                      | 47.6    | 4.4   | 7.6   |
| 60–74    | T6         | Transitional | Sphagnum lindbergii – 15, Sphagnum jensennii – 15, Carex rotundata – 65, Sphagnum balticum – 5 | 35–40               | 49.5    | 4.7   | 12.4  |
| 74–86    | T7         | Transitional | Sphagnum lindbergii – 15, Sphagnum jensennii – 15, Scorpidium cossonii – 10, Carex rotundata – 30, Sphagnum balticum – 5, Salix – 5, Pinus sylvestris – 5 | 40                      | 51.9    | 5.0   | 11.4  |
| 86–94    | T8         | Transitional | Sphagnum lindbergii – 20, Sphagnum jensennii – 10, Carex rotundata – 35, Eriophorum – 5, Equisetum – 5, Salix – 5, Pinus sylvestris – 10, Betula – 5 | 45–50               | 48.3    | 5.2   | 17.3  |
| 94–108   | T9C        | Transitional | Sphagnum lindbergii – 10, Carex rotundata – 45, Eriophorum – 5, Equisetum – 15, Salix – 5, Pinus sylvestris – 5, Betula – 10, Scorpidium cossonii – 5 | 45–50               | 13.2    | 4.8   | 76.8  |
| 108–127  | C          | –         | –                             | –                       | 2.8     | 5.0   | 94.8  |

* TOC – total organic carbon.

3. Result and discussion

3.1. Distribution and content of n-alkanes

The total content of the sum of n-alkanes in the soils under study is 8–193 µg/g (2017-1), 5–171 µg/g (2017-2) and 21–109 µg/g (2017-3). Regarding the 2017-1 profile we observe an increased mass fraction of n-alkanes in the active layer (AL) T1 (0–5 cm) – T3 (25–30 cm): from 37 µg/g to 119 µg/g (figure 1).

The composition of hydrocarbons is dominated by C23, C25, C27 n-alkanes formed as a result of hypnum and sphagnum transition peat transformation. The moss decomposition degree is 20–35%, however, to the 30-cm depth the proportion of Carex rostrata sedges increases to 20%, which apparently increases the concentration of n-alkanes (mainly C23 and C25) and raises the CPI index from 7.4 to 10.7. In the T4 horizons (30–35 cm) at the boundary of the seasonally thawed layer down to the permafrost T5 (40–50 cm), the sphagnum transition peat also determines the low total concentration of n-alkanes of 41–81 µg/g, with a predominance of C25, C27. In permafrost horizons T6–T8 (50–110 cm) the proportion of woody, shrubby and grassy organic residues increase with an increase in the decomposition degree up to 40%, woody-sedge lowland peat – the mass fraction of the sum of n-alkanes increases from 50 to 90 µg/g. In the underlying permafrost horizons T9–T14 (110–230 cm), the botanical composition constantly contains the remains of sedges and herbaceous plants, remains of moss, while
the qualitative composition of saturated hydrocarbons is dominated by C27, C29 n-alkanes typical for higher plants.

**Figure 1.** Distribution of n-alkanes in peat soils: Hemic Folic Cryic Histosol (A), Hemic Folic Cryic Histosol (Turbic) (B) and Fibric Floatic Histosol (C).
The maximum of hydrocarbons (193 µg/g) and the CPI index (29.8) were recorded in the T13 layer (190–210 cm). In permafrost (PF) from the T14 horizon (210–230 cm) down to the mineral rock G (265–285 cm), the concentration of n-alkanes decreases gradually, the proportion of Menyanthes and Hepatics increases, the C21, C23, C25, C27 components begin to prevail in the composition, while the CPI index falls to 10 units.

The 2017-2 soil is characterized by more intense heating of the surface horizons, a higher degree of decomposition up to 40–50%; so the content of n-alkanes along the profile increases in AL T1 (0–5 cm) – T3 (25–30 cm) from 56 µg/g up to 171 µg/g. Compared to 2017-1, these horizons have higher C29 hydrocarbon content, possibly due to the decomposition of the remains of Salix and Betula nana shrubs (peat type – woody (shrubby) – cotton sedge transitional). Therefore, the CPI indices rise more sharply from 7.6 to 17.1. Up to the AL T4 boundary (30–40 cm) and down to the T14G – G mineral rock (210–240 cm) in PF, the mass fraction of the total n-alkanes ranges from 58 to 114 µg/g, n-alkanes C23, C25, C27 prevail, the CPI indices are 7.6–13.6; the botanical composition is dominated by the remains of sedges, Menyanthes and other herbaceous plants and green mosses. Similarly to 2017-1, the maximum of n-alkanes (120 µg/g) and the CPI index (31.3) are also traced in the permafrost horizon T12 (170–190 cm), and the qualitative composition is dominated by C27 (83 µg/g). d) and C21 (12 µg/g) n-alkanes.

The 2017-3 botanic composition down to 18 cm deep is dominated by mosses Sphagnum jensenii, Sphagnum lindbergii, the peat is highland sphagnum-hollow one, the degree of peat decomposition is also reduced to 5–15%, AL is characterized by excessive moisture, therefore the concentration of the sum of n-alkanes is low and amounts to 34–60 µg/g, with a predominance of C23, C25 hydrocarbons. CPI indices are 6.8–8.3. In T3–T5 horizons (18–60 cm), Scorpidium cossonii mosses and Carex rotundata sedges appear in the botanical composition, the type of peat changes to the transitional sphagnum one, the mass fraction of saturated hydrocarbons (with a predominance of C21, C23, C25,) increases to 88–108 µg/g. At the same time, the proportion of even components in the qualitative composition of n-alkanes increases, which lowers the CPI indices to 3.1–6.3 in 18–37 cm STL. The botanical composition of 60–108 cm permafrost horizons features sedge and woody-sedge transitional types of peat, the sum of n-alkanes decreases to 21–54 µg/g due to higher proportion of C23, C25 hydrocarbons and, to a lesser extent, C27 hydrocarbons; the CPI indices increase to 5.3–9.3.

3.2. Distribution of phenols
The total content of water-soluble phenol in peatlands is 0.6–97.9 µg/g (2017-1), 4.7–98.1 µg/g (2017-2), 0.6–41.2 µg/g (2017-3) (figure 2). The vertical distribution of phenol along the peatland profile has similar patterns; AL and the AL-PF boundary feature a small mass fraction of phenol, layers of permafrost 50–70 cm (70–90 cm) deep close to the seasonal thawing layer boundary demonstrate a slight increase in its mass fraction, and there is a significant increase of it in deeper horizons 110–265 cm (110–190 cm) formed during the periods of the Holocene climatic optimum. In AL, both natural and, possibly, technogenic phenols are more susceptible to chemical and biochemical transformation, which determines their lower concentrations. On the contrary, the profile of the 2017-3 excessively moistened soil displays a relatively high mass fraction of phenol in AL and at the AL-PF boundary and its significant decrease in the PF horizons. It should be noted that the profile distribution of phenols correlates with the content of structurally related aromatic compounds (r = 0.61–0.71) – PAHs, which are also a decomposition product and a starting substance for humification. This indicates a predominantly natural origin of phenol formed in past periods through decomposition of the remains of moss vegetation prevailing at that time and conserved in the permafrost layer. Some authors [12] emphasize the sensitivity of surface peat to climatic changes and the groundwater level, thus phenolic compounds stabilized in deep water-saturated peat horizons and decomposed in unsaturated and seasonally saturated layers.

The 2017-1 and 2017-2 low profile peat 265–285 cm (190–240 cm) is dominated by meso-eutrophic and eutrophic plant species: grasses (Menyanthes trifoliata, Carex rostrata, Equisetum) (40–85%), tree remains (Pinus sylvestris) (up to 35%) and hypnum mosses (15–25%).
Figure 2. Distribution of phenol in peat soils: Hemic Folic Cryic Histosol (A), Hemic Folic Cryic Histosol (Turbic) (B) and Fibric Floatic Histosol (C).
As a result, at the initial stage of wetland formation under the conditions of the Holocene I climatic optimum, the phenols being formed were subject to chemical and biochemical transformation – the mass fractions of phenol were 0.3–4.7 µg/g. The next stage of peat accumulation II (130–265 cm for 2017-1 and 110–190 for 2017-2) is characterized by an abrupt change in hydrological conditions towards intense watering; Sphagnum riparium, Sphagnum teres, Calliergon sp. indicating swamp areas or channels start dominating. Under the conditions of excessive moisture, significant amounts of phenol were formed and conserved in the permafrost horizons of the studied peatlands – the mass fraction of phenol was 51–98 µg/g. Some researchers [13] suggest that decomposition of phenolic components of peat occurs mainly above the groundwater level and decreases to a large extent in deeper water-saturated oxygen-free peat horizons.

At stage III (Atlantic climatic optimum of Holocene II), a large proportion of grassy and woody remains with a high degree of decomposition (R = 40%) was identified in the botanical composition of peat at 50–110 cm deep, while the proportion of mosses is low; thus, in drier conditions the equilibrium shifts towards a greater transformation of phenols, their accumulation in the peat horizons decreases to 13–38 µg/g. At the same time, there are low extremes of the phenol content 35–38 µg/g in the T6 50–70 cm (2017-1) and T7 70–90 cm (2017-2) horizons apparently to indicate periods of excessive moisturing (the proportion of Calliergon sp. mosses increases). The revealed trends highlight the predominantly natural origin of phenol formed in the past periods through decomposition of the remains of the vegetation prevailing at that time and transformation of high-molecular humic substances [14] and conserved in PF.

At stage IV (transition) the two sections described down from 50cm deep are dominated in terms of their botanical composition by meso-eutrophic and eutrophic sphagnum mosses and shrubs. Later, in Middle and Late Subboreal the climate cooled significantly and humidification decreased. At the stage of Late Subboreal (SB3) – Early Subatlantic (SA1), permafrost was aggradated and vegetation was formed by oligotrophic communities. 20 cm of the peat surface (stages V, VI) are composed of dicrotanum (Dicranum elongatum), hypnum (Warnstorfia sp.) and polytrichum (Polytrichum sp.) green mosses, Eriophorum, and fruticose (Ledum). These stages are not found in the 2017-2 soil section, since its upper layer was destroyed by frost and wind erosion. In the seasonally thawing and transitional horizons close to the seasonal thawing layer boundary, as a result of increased aeration of peat, the formed phenols are decomposed decreasing their content in the 0–50 cm horizons to 6–14 µg/g.

The 2017-3 botanical composition data show significant differences from the botanical composition of peat hummocks. At foundation of the peat area, the grassy layer is dominated by Carex rotundata and Equisetum with some woody remains of Pinus sylvestris and Betula; the amounts of phenol are minimal of up to 0.6–1.0 µg/g. The 75–118 cm layer (stage I) of peat is characterized by a high degree of decomposition – 40–50%. Down from 90 cm there is a decrease in wood residues and an increase in the proportion of Carex rotundata sedges, which is caused by depleted mineral nutrition, which results in the mass fraction of phenol in the 56–94 cm horizons increasing to 6–10 µg/g. The water content of the biotope increases significantly; the proportion of hygro- and hydrophilic oligotrophic mosses Sphagnum lindbergii and Sphagnum jensenii increases in the 25–56 cm horizons, which leads to an increase of the phenol content in them to 14–20 µg/g. The botanical composition of the upper 0–18 cm AL of hollows is formed completely by Sphagnum lindbergii and Sphagnum jensenii mosses; the level of peat waters is 15–25 cm above the surface, which creates favorable conditions for phenol production and its maximum accumulation (27–41 µg/g). A number of lower maximum amounts of phenol in the soil of hollows compared to the soils of hummocks are probably explained by the fact that a significant proportion of phenol is also contained in the aqueous phase.

4. Conclusion
The spectra of nonspecific organic compounds (n-alkanes, phenol) were identified, and the regularities of their vertical distribution in the tundra peatlands of the European Arctic zone were detected. The composition of n-alkanes in peatlands is mainly determined by the vegetation composition and is represented by the C18–C31 homologous series, with a noticeable predominance of long-chain
homologues (> C21) with an odd number of carbon atoms. Seasonally thawing peat layers subject to aeration show lower n-alkane accumulation through decomposition of moss vegetation. Local maxima of n-alkanes have been found in permafrost layers formed through transformation of high molecular-weight organic compounds following decomposition of woody and grassy vegetation that used to dominate during the Holocene climatic optimum. The maximum content of phenol in the soils of hummocky peatlands is found in deep permafrost layers, which indicates the stages of peat accumulation under excessive moisture conditions and is associated with certain groups of plant residues, mainly mosses (Sphagnum). During climatic optima, owing to an increase of woody and grassy species in the botanical composition and higher aeration of peat, phenols got transformed and their mass fraction decreased significantly. The highest rate of phenol accumulation in the highland soil of hollows was observed in AL due to maximum water content. Thus, the NOC composition is a paleoclimatic marker and reflects changes both in the paleovegetation stages and the peat decomposition degree.

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