

Influence of peat formation conditions on the transformation of peat deposit organic matter

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Abstract. The paper studies the individual composition of n-alkanes, polycycloaromatic hydrocarbons, steroids, bi-, tri-, and pentacyclic terpenoids of two peat deposits of rich fen Kirek located in Western Siberia. Considering the individual n-alkanes concentrations, some indexes were calculated to estimate the humidity during peat formation. It was shown that the pH of peat medium primarily affects steroids, tri- and pentacyclic terpenoids transformations.

1. Introduction

The world's largest wetland systems are situated on the territory of Western Siberia. However, despite many years of wetlands research carried out in the region, this issue is still understudied. n-Alkanes, steroids, bi-, tri- and pentacyclic terpenoids presented in peat are biomarkers. Their composition shows the contribution of different peat-forming plants, peat formation conditions and the processes occurring in peat deposit to the peat composition. The study of individual composition of peat organic compounds allows drawing conclusions about the humidity and the pH impact on the direction of peat organic matter transformation [1].

2. Samples and analysis

Fen Kirek is located in Tomsk region, on the south-eastern shore of lake Kirek. It is a lowland mire, which is supplied by hydrocarbonate groundwater and lake water. Two fen Kirek peat deposits were chosen as the study objects. The first one (sedge peat), being of lake genesis and 6.0 m in depth, was formed by carbonate sapropel deposit, followed by forested grass-sedge floating and fen sedge, grass and sedge-moss peat deposition. Lake waters are alkaline, so peat accumulated in an alkaline environment in constant high humidity conditions. In the lower part of the sedge peat deposit pH is 7.5, decreasing up to 6.9 with depth decrease.

The second deposit (wood-grass peat) is 4.2 m in depth. It was formed due to lake shore paludification, followed by carbonate sapropel deposition, forested sedge floating formation, wood and wood-grass peat deposition accompanied by lake drawdown, with conifers being predominant [2]. Peat was formed in neutral environment with sharp change in water regime. pH values lower from 7.0 to 6.3 with depth decrease in the wood-grass peat deposit.



Peat macrofossil composition was determined by microscopic method. All peat samples were dried and powdered before the analysis. Bitumens were concentrated by extracting with 7% methanol in chloroform at 60°C. Group and individual composition of n-alkanes, polycycloaromatic hydrocarbons, steroids and terpenoids in peat samples were determined by gas chromatography-mass spectrometry (GC-MS). Thermo Scientific gas chromatograph with mass detector fused silica capillary column (30 m in length, 0.25 mm bore, 0.25 µm in film thickness) was used for biomarker molecule analysis. The operating conditions were as follows: temperature was held at 80°C for 2 min ramped to 300°C at 4°C/min, with He acting as carrier gas. The ionization energy of the mass spectrometer was set to 70 eV, with a scanning range being from 50 to 550 amu. The compounds were identified by comparison of their mass spectra with that of reference compounds.

3. Results and discussion

The following groups of organic substances were detected in peat bitumen: n-alkanes, polycycloaromatic hydrocarbons (PAHs), steroids, bi-, tri- and pentacyclic terpenoids. n-Alkanes with the odd homologues C₂₁-C₃₁ base are the main representatives of organic compounds in the studied peat samples. Sedge peat is specified by high relative content of n-C₂₃ alkane, the sample S-1 contains almost equal concentrations of n-C₂₇. The C₂₇ homologue dominates in all samples of wood-grass peat, as well as in wood material from fen Kirek. The molecular mass distributions of n-alkanes in all samples of sedge peat and the sample W-3 of wood-grass peat are shown in figure 1.

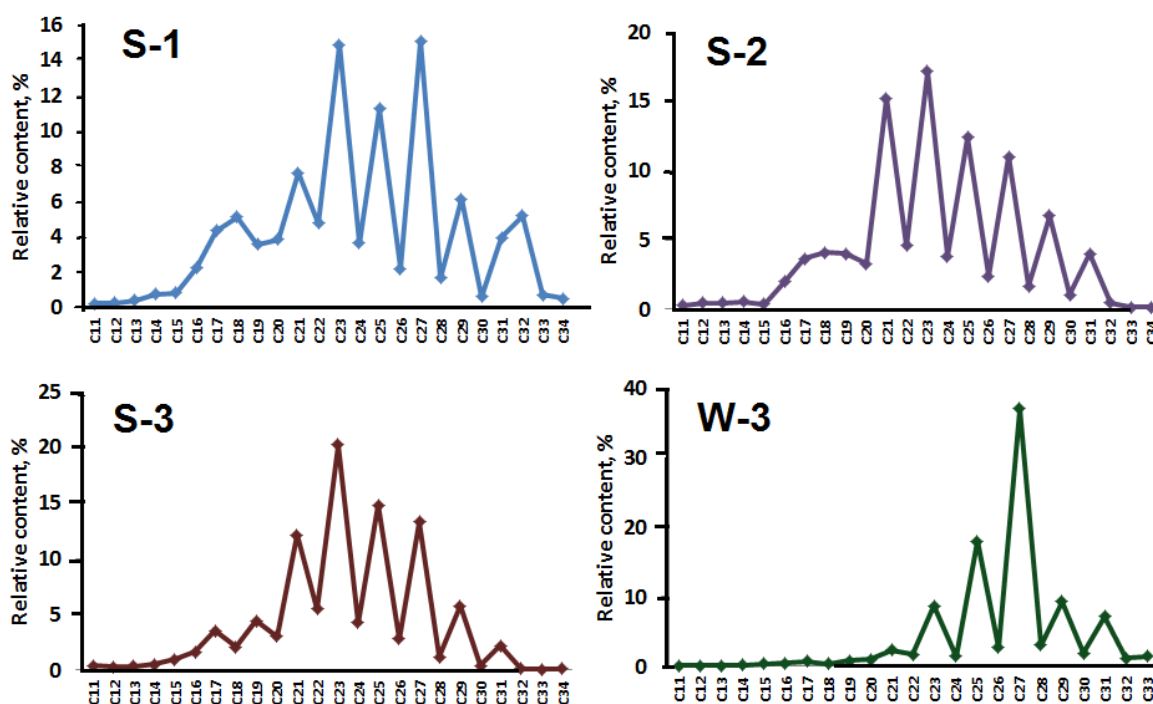


Figure 1. The molecular mass distributions of n-alkanes in samples S-1, S-2, S-3 and W-3.

Considering individual n-alkanes content, one can calculate several indices: Carbon Preference Index (CPI), humidity index (P_{aq}) and the concentrations ratio of n-alkanes, specific for different types of plants.

The predominance degree of molecules with an odd number of carbon atoms can be estimated using index CPI, which is a weight ratio of odd to even homologues [3, 4]. Peat formation conditions can be estimated using the humidity index (P_{aq}) [5, 6]. Considering n-alkanes concentrations ratio, other indices can be calculated to gain more information about mire water balance. Strong relationship

between distribution of plants and humidity conditions allows using the relative content of peat-forming plants biomarkers for mire paleohydrologic history reconstruction [7]. The n-alkanes n-C₂₃/n-C₂₅ concentrations ratio shows the predominance of marsh plants that prefer wet conditions over the plants that grow in dry conditions [8]. The dominant n-alkane, CPI, humidity index (P_{aq}), and the values of the ratio n-C₂₃/n-C₂₅ are presented in table 1.

Table 1. The dominant n-alkane, CPI, P_{aq} and n-C₂₃/n-C₂₅ in fen Kirek peat.

Sampling depth, m	Sample code	Dominant n-alkane	CPI	P _{aq}	n-C ₂₃ /n-C ₂₅
Sedge peat					
0.3	S-1	C ₂₃ , C ₂₇	3.38	0.72	1.32
1.35	S-2	C ₂₃	4.32	0.73	1.38
2.0	S-3	C ₂₃	4.35	0.82	1.37
Wood-grass peat					
0.25	W-1	C ₂₇	7.36	0.77	0.71
1.0	W-2	C ₂₇	6.39	0.83	1.10
1.3	W-3	C ₂₇	6.96	0.62	0.48
1.5	W-4	C ₂₇	21.40	0.88	0.60

CPI values increase with depth and, respectively, peat maturity, which is consistent with the published data [4]. The values of P_{aq} and ratios of n-alkanes n-C₂₃/n-C₂₅ concentrations do not change in sedge peat. The values of these parameters for wood-grass peat change abruptly and correlate with each other well – an increase in n-C₂₃/n-C₂₅ and n-P_{aq} values in the samples W-2 and W-4 might indicate a change of mire water regime due to lake Kirek periodic floods.

Bicyclic (naphthalene and its methyl-, dimethyl-, trimethyl-, tetramethyl derivatives and cadalene), tricyclic (phenanthrene, its methyl, dimethyl, trimethyl and tetramethyl derivatives) and tetracyclic (fluoranthene and pyrene) structures were identified among PAHs in studied samples. Bicyclic PAHs predominate in all samples of sedge peat and in the samples W-2 and W-4 of wood-grass peat, tricyclic – in the samples W-1 and W-3. Tetracyclic PAHs are presented in low concentrations in all peat samples. Trimethylnaphthalenes dominate in the sample S-1 of sedge peat, phenanthrene – in the sample S-2. Cadalene content substantially exceeds the concentration of other PAHs in the sample S-3 as in sedge from fen Kirek [1]. Trimethylphenantrenes prevail in the samples W-1 and W-3 of wood-grass peat, cadalene – in the samples W-2 and W-4. Cadalene has a very stable relic structure and is genetically connected with bicyclic terpenes.

Bicyclic partially unsaturated structures, naphthoaromatic compounds presented by calamenene, α- and β-calacorenes were identified among bicyclic terpenes in fen Kirek peat. All these structures are presented in a wide range of plants (in most conifers) [9]. γ-Cadinene prevails in the sample S-1 of sedge peat, δ-cadinene – in the samples S-2 and S-3, in all samples of wood-grass peat, as well as in sedge and wood material from fen Kirek. The concentrations of cadinene isomers changes slightly with depth decrease. It proves the resistance of these compounds and explains their high content in peat.

The prevalent square of fen Kirek is forested by coniferous trees. That is why tricyclic terpenoids are mainly presented in peat by abietic acid transformation products which are the part of conifers resin, abietic acid monoaromatic analogue, which can be found in pine bark, and 8,13R-epoxylabd-14-ene, distinctive for grass plants and shrubs. Abietic acid derivatives include naphthenic, naphthoaromatic, and aromatic hydrocarbons formed by decarboxylation, hydrogenation, demethylation or dehydrogenation of the parent acid. Table 2 lists relative concentrations of tricyclic terpenoids and pentacyclic terpenoids groups in the investigated peat.

Table 2. The content of tricyclic terpenoids and pentacyclic terpenoids groups in the peat of fen Kirek, % rel.

Sampling depth, m	Sedge peat			Wood-grass peat			
	0.3	1.35	2	0.25	1	1.3	1.5
Sample code	S-1	S-2	S-3	W-1	W-2	W-3	W-4
Tricyclic terpenoids							
18-Norabietane	52.17	89.66	76.71	81.99	92.29	88.33	39.32
18-Norabieta-8,11,13-triene	3.19	2.36	6.51	5.08	4.55	3.56	5.7
Abieta-8,11,13-triene	0.43	0.28	0.39	0.28	0.19	0.15	0.32
10,18-Bisnorabieta-5,7,9(10),11,13-pentaene	2.54	1.75	8.25	5.16	1.27	3.16	28.6
Methyl-6,8,11,13-abietatetraene-18-oat	0.12	0.18	0.1	0.05	0.04	0.1	0.04
Methyl-8,11,13-abietatriene-18-oat	0.37	0.27	0.53	0.28	0	0.12	0.37
Abieta-8,11,13-triene-18-ol	0	0	0	0.07	0	0.02	0.08
Dehydroabietic acid	0	0	0	0.11	0	0.98	3.92
8,13 R -Epoxyabd-14-ene	38.2	3.06	4.32	1.22	0.78	0.63	0.86
Retene	3	2.44	3.18	5.75	0.88	2.94	20.8
Pentacyclic terpenoids							
Unsaturated structures	92.23	89.65	59.7	86.99	75.47	83.9	98.64
Saturated structures	7.77	10.36	40.3	13	24.54	16.1	1.37
Hydrocarbons	39.41	22.75	82.09	27.06	62.84	54.84	20.41
Ketones	60.59	77.26	17.91	61.31	37.17	24.34	28.96
Alcohols	0	0	0	11.62	0	20.82	50.64

The samples S-2 and S-3 are specified by a significant predominance of saturated hydrocarbon – 18-norabietane, which dominates also in the sample S-1. The content of 8,13R-epoxyabd-14-ene is also rather high in this sample. 18-Norabietane prevails in all samples of wood-grass peat while high concentrations of 10,18-bisnorabieta-5,7,9(10),11,13-pentaene and retene were found in the sample W-4.

The content of 18-norabietane, reduction product of molecular biological source, increases whereas the concentration of bi- and triaromatic diterpene hydrocarbons, dehydrogenation product of initial biomolecules declines with depth decrease in sedge and wood-grass peat profiles. pH of the peat medium changes in the same way [10].

Monoaromatic dehydroabietic acid is absent in sedge peat while its methyl ester (methyl-8,11,13-abietatrien-18-oat) was detected in all samples. The acid content is low in wood-grass peat, it declines with depth decrease. Low concentration of dehydroabietic acid in the upper part of the peat profile can be explained by its rapid esterification. The small amount of free protons in fen Kirek bottom waters made it possible to preserve diterpenic acid and prevented its esterification. The content of methyl-8,11,13-abietatrien-18-oat in wood-grass peat varies similarly.

Triterpenoids are presented by hopane, oleanane, ursane and lupane derivatives with different lateral substituents and unsaturated bond positions in molecules. Structural analogues of oleanane and lupane include C₃₀ ketones and alcohols with one or two unsaturated bonds in the molecule. Only urs-12-ene-3-one was identified in the sample W-4 of wood-grass peat among ursane derivatives. The distribution of oleanane, lupane and hopane derivatives in fen Kirek peat is presented in Figure 2A.

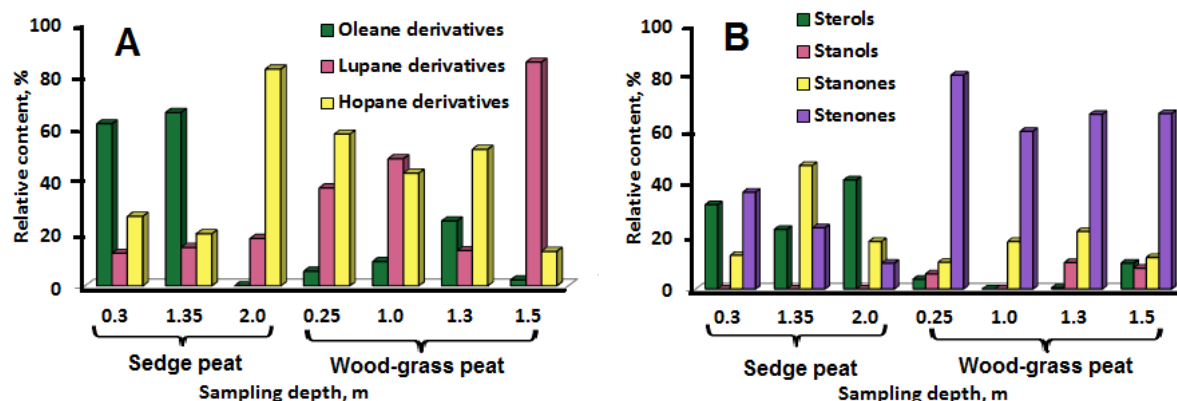


Figure 2. The content of pentacyclic terpenoids structural (A) and steroid (B) groups in fen Kirek peat, % rel.

Oleanane derivatives, reflecting angiosperms contribution in peat formation, dominate in the samples S-1 and S-2 of sedge peat. It was detected that D-friedoolean-14-en-3-one has the highest concentration. Oleanane derivatives completely disappear in the sample S-3 while hopanes begin to dominate. It may indicate high degree of peat bacterial processing.

The content of pentacyclic structures with double bonds is significantly higher than the one in saturated compounds. The contribution of triterpenic saturated structures grows with depth decrease in the wood-grass peat deposit alongside reducing pH values. The content of saturated structures declines with depth decrease in the sedge peat deposit.

The concentration of ketonic derivatives of pentacyclic terpenoids increases with depth decrease in both peat profiles alongside the transition to a more acidic environment during peat formation. The alcohol content decreases while the concentration of hydrocarbons increases with depth decrease in wood-grass peat. Alcohol derivatives are completely absent in sedge peat while hydrocarbons content reduces with depth decrease.

Steroids in fen Kirek peat are presented by the set of cholestane, ergostane, stigmastane and cycloartane derivatives. Total concentrations of these compounds are presented in table 3. Stigmastane derivatives with C₂₉ composition dominate among the steroids in all studied peat samples. Stigmast-4-ene-3-one prevails in the sample S-1 of sedge peat, α -stigmastan-3-one – in the sample S-2. Stigmast-4,6-dien-3-ol was detected in high concentrations at these depths. It dominates in the sample S-3. Stigmast-4-ene-3-one prevails in the samples W-1 and W-2 of wood-grass peat, stigmast-5-en-3-ol (sitosterol) – in the samples of W-3 and W-4.

Table 3. The content of steroid groups in fen Kirek peat, % rel.

Sampling depth, m	Sample code	Cholestane derivatives	Ergostane derivatives	Stigmastane derivatives	Cycloartane derivatives
Sedge peat					
0.3	S-1	0.94	4.47	93.47	1.12
1.35	S-2	0	12.1	87.89	0
2.0	S-3	2.24	5.23	88.8	3.73
Wood-grass peat					
0.25	W-1	2.68	5.65	90.63	1.05
1.0	W-2	0	6.2	93.96	0
1.3	W-3	0	3.04	96.97	0
1.5	W-4	3.91	2.79	87.86	5.42

Cholesterol and its derivatives (C₂₇), reflecting microalgae contribution in peat formation, were found in the upper and lower part of both peat profiles in low concentrations. The distribution of sterols, stanols, stanones and stenones in fen Kirek peat is presented in Figure 2B. Stenones prevail in the sample S-1 of sedge peat, stanones – in the sample S-2, sterols – in the sample S-3. High relative content of sterols in the sedge peat deposit might be explained by their good preservation in alkaline conditions. Stenones prevail in all samples of wood-grass peat. Low concentrations of sterols in this peat deposit may be related to the specific composition of the original plants which often contain saturated sterol derivatives.

4. Conclusion

n-Alkanes with dominance of the odd homologues C₂₁-C₃₁, bi-, tri- and tetracyclic aromatic hydrocarbons, partially unsaturated bicyclic and naphthenoaromatic compounds, tricyclic transformation products of abietic acid and also 8,13R-epoxylabd-14-ene were identified in the studied samples of fen Kirek peat. Pentacyclic terpenoids are presented by hopane, oleanane, ursane and lupane structural analogues, steroids – by a set of cholestane, ergostane, stigmastane and cycloartane derivatives with various lateral substituents and unsaturated bond positions in molecules. The studied peat largely inherits the composition of initial peat-forming plants.

It was found that the pH of the medium affects to the greatest extent the transformation of steroids, tri- and pentacyclic terpenoids during peat formation. The content of ketonic derivatives of pentacyclic terpenoids and 18-norabietane increases with depth decrease in sedge and wood-grass peat profiles whereas the content of bi- and triaromatic diterpene hydrocarbons declines alongside pH of the peat medium. The small amount of free protons in the wood-grass deposit bottom waters prevents diterpenic acid esterification.

Thus, it was shown that peat formation conditions have a significant impact on the conversion of peat deposits organic matter. Therefore, considering detailed data about the individual composition of organic compounds, the rough reconstruction of peat formation conditions can be carried out.

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