Organic matter in water and peat of the Ob Fen, Western Siberia

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SUMMARY

The organic material in water and peat collected in March 2021 from the extensive Ob Fen in Western Siberia was analysed using gas chromatography - mass spectrometry (GC-MS). It was shown that the process of formation and subsequent transformation of peat is characterised by the entry into the environment of large amounts of organic substances, whose genesis is currently insufficiently studied. A variety of organic compounds were identified including alkanes, fatty acids, terpenoids, alcohols and aromatics. The concentration of most contaminants decreased significantly with increasing depth of peat deposit. Compounds identified in the water were also found in the peat, indicating active exchange processes in the water-peat system. Recommendations for further study and ecological monitoring of Siberian peatlands are presented.

KEY WORDS: contaminants, diagenesis, GC-MS, peat chemistry, river valley mire

INTRODUCTION

A substantial part of the southern taiga and sub-taiga subzones of Western Siberia is covered by mires which were formed through waterlogging processes during the Cenozoic era, primarily during the Holocene epoch. The presence of peatlands has imposed significant limitations on human lives and economic activity in the waterlogged areas. The area and depth of these peatlands is currently increasing, leading to the replacement of forest phytocenoses by peatlands. There are significant implications for the functioning of natural landscape systems which may impinge on human interests, for example by causing the deformation of engineering systems and structures and reducing the accessibility of the land. Also, peatlands are natural water stores and influence the hydrochemistry and flow regimes of rivers (Savichev 2005), so their expansion may cause significant deterioration of water quality in rivers, lakes and aquifers including water that is used for domestic and drinking purposes (Matukhin 2000, Liss *et al*. 2001, Savichev & Heng 2021). At the same time, huge peat resources remain unexplored and practically unused (Olenin *et al*. 1988, Inisheva *et al*. 1995, 2017).

A fundamental characteristic of peatlands as part of the environment is that they accumulate organic matter rather than decompose it. The composition of the accumulated organic matter is important from the point of view of assessing the influence of peatland ecosystems on regional and global climatic processes (Wagner *et al.* 2005, Gell *et al*. 2023). The distribution of various elements and organic compounds over the depth of the peat deposit is an important characteristic that testifies to the history of the formation and evolution of each peatland (Duchko *et al*. 2013, Serebrennikova *et al*. 2015). The elemental and group composition of peat is an integral characteristic of both the initial composition of the residues of peat-forming plants and the biogeochemical and hydrogeochemical conditions for peat formation and accumulation (Bernatonis *et al*. 2002, Savichev *et al.* 2020a, 2020b). The group composition of peat is important in both the study of peat formation processes and the development of methods for peat use and assessment of its geo-ecological functions. The usual analysis for group composition involves four chemical extractions to distinguish and discover the proportions of: 1) bitumen (organic solvents); 2) water-soluble substances and cellulose (water, often after

hydrolysis in the presence of mineral acids); 3) humic and fulvic acids (alkaline solutions); and 4) lignin (the residue after hydrolysis). For the separation and identification of individual organic compounds, mass spectrometry techniques are often used.

Peatlands can also receive airborne and water-borne chemical contaminants (of anthropogenic origin) including various aromatic compounds, phthalic acid derivatives, antibiotics, hydrocarbons, phenols, pesticides and substances used in household chemicals, as well as inorganic contaminants such as heavy metals (Cu, Zn, Pb, etc.) (Haarstad *et al*. 2012, Savichev *et al*. 2013). Some of these substances tend to accumulate, while others are transformed and/or removed from the system (Haraguchi *et al*. 2002, Savichev *et al*. 2022a, 2022b). A major threat to the environment is posed by water-soluble contaminants that can enter river systems in the runoff water from peatlands. A thorough understanding of the mechanisms of accumulation and removal of such elements and substances (Savichev 2015, Ivanova *et al*. 2020, Savichev *et al.* 2020a, 2020b) will support the improvement of methods for protecting and restoring mire biocoenoses and the ecosystem as a whole. To build this understanding, it is necessary to identify contaminants and to understand their accumulation mechanisms and seasonal variations (Haarstad *et al*. 2012, Savichev 2015, 2023a, 2023b).

For all of the reasons outlined above, it is important to build a comprehensive understanding of the chemical composition of peatland waters (Ivanova *et al*. 2020, Russkikh *et al.* 2020, Serebrennikova *et al.* 2023) and peat (Talbot *et al*. 2016, Steinmuller & Chambers 2019) using modern analytical methods. The purpose of the present study is to identify spatial patterns in the distribution of organic substances (including any contaminants) in the peat and waters of a part of the extensive Ob Fen in Western Siberia where there is no obvious evidence of human influence.

METHODS

Study site

The Ob Fen is located in the southern part of the Tomsk administrative region of the Russian Federation (Figure 1a). It lies at the foot of the Altai-Sayan Mountains in the south-eastern part of the West Siberian Plain, on the left bank of the Ob River which is one of the largest rivers in the world.

The Ob Fen has been described as a pristine river valley mire (Schipper *et al*. 2007). It is about 104 km long and 1.5–7.0 km wide, with an average peat depth

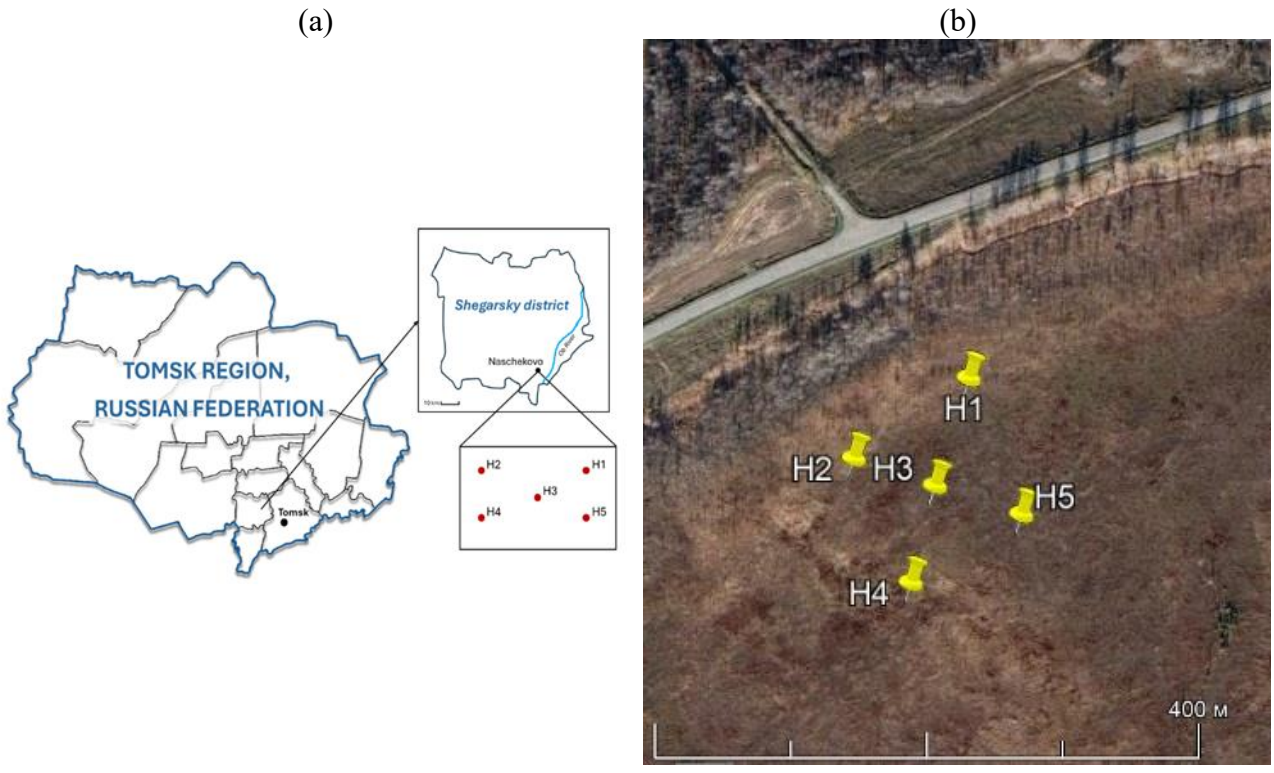

Figure. 1. Schematic diagrams of (a) the location of the site and (b) the research points in the Ob Fen. Geographical co-ordinates of the corners of the research site (H1, H2, H4, H5) are provided in Table 1.

of 3.2 m and a maximum peat depth of 6.0–6.5 m. The peat deposit has been characterised as sedge, sedge-wood, wood, hypnum, sedge-hypnum and lowland reed peat with average degree of decomposition 34 % and ash content 28–29 % (Savichev *et al*. 2013, Savichev *et al*. 2020a, Savichev 2023b).

Collection of samples

The research site near Naschekovo village has been described in detail in previous publications (Schipper *et al*. 2007, Savichev *et al*. 2013, Savichev 2023a, 2023b). It covers a ~100 m square with borehole H3 at its centre, and corners defined by boreholes H1, H2, H4 and H5 (Figure 1b). There are no obvious local sources of anthropogenic pollution and the pollution status is considered to be 'background', based on previous work (Savichev *et al*. 2013, 2020a, 2022a, 2022b; Ivanova *et al*. 2020, Savichev 2023b).

Sampling for this study was conducted on 18 March 2021. Samples of water were collected from the acrotelm at the four corner locations (H1, H2, H4, H5) in specially prepared clean glass bottles. We define the acrotelm (Ingram 1978) as the transitional layer of active water exchange between the peat deposit and the surface formed by either the capitula of bog mosses or a dense mat of vascular plant rhizomes (GOST 19179-73), which was located 0.1–0.3 m above the water table in this case. After water sampling, boreholes were drilled at H2 and H3 with layer-by-layer sampling of peat from 0.25 m below the mire surface down to and including the mineral substratum (Savichev 2023b). Stratigraphy was noted briefly in the field. The water and peat samples were transported to the laboratory for initial processing on the same day.

Laboratory assays

Organic matter composition was studied in four samples of water from the acrotelm at H1, H2, H4 and H5, and in eleven samples of peat from boreholes H2 and H3. The methodology for analysis of water and peat samples is described in detail by Savichev *et al*. (2022a, 2022b), Savichev (2023a, 2023b), GOST R 54332-2011 and GOST 10649-73.

Dissolved organic compounds (excluding fulvo- and humic acids) in the four water samples were determined in chloroform concentrates obtained by three-step chloroform extraction at pH 2, 7 and 11 according to MUK 4.1.663-97 (1997) (Goerlitz & Brown 1984, Soniassy *et al*. 1994).

Aqueous extracts were prepared from the peat samples and the values of pH, EC, Na^+, Cl^- were determined (Savichev 2023a, 2023b), then the peat samples were stored in a freezer at -20 °C until further analysis. After thawing, the samples were weighed then dried, at room temperature for one day then in a desiccator at 40 °C to constant mass. Moisture content was determined by mass loss. Bitumoid was then separated from the samples by extraction with chloroform in a Soxhlet apparatus (see, e.g., Jensen 2007).

The chloroform-bitumoid extracts obtained were analysed by gas chromatography - mass spectrometry (GC-MS). For more detailed analysis, the samples were separated into polar and non-polar fractions by column chromatography (Agilent polymer cartridges). The GC-MS analysis was performed on an Agilent 7890B (GC)-Agilent Q-TOF 7200 (MS) instrument on a DB-5ms quartz capillary column, length 30 m, inner diameter 0.25 mm, layer thickness 0.25 μm. The evaporator inlet temperature was 300 °C and the initial temperature of the column thermostat oven was 40 °C, followed by heating at a rate of 5 °C min^{-1} to 150 °C then at 3 °C min^{-1} to 310 °C and holding at 310 °C for 20 min. The carrier gas (helium) flow rate was 1.1 mL min^{-1}. Both total ion current (TIC) and selected individual ions (SIM) were measured. Appropriate standards were used to quantify the components. To subtract laboratory background, blank experiments were performed.

RESULTS

Water

The organic matter in the water samples collected on 18 March 2021 is characterised in Table 1, where mean values obtained for samples collected on 26 November 2018 (from Ivanova *et al*. 2020) are shown for comparison. The water collected in 2021 contained significant amounts of alkanes, esters, alcohols and a number of other compounds at significantly higher levels (5–25 times) than were found in 2018. However, there was noticeable heterogeneity in the values obtained even though the samples were collected from locations no farther than 100 m from one another.

Contaminants identified in the composition of the water are listed in Table 2. The most common contaminants are phthalates, concentrated at boreholes H2 and H5 (~348 and ~510 ng L^{-1} respectively). Various other contaminants containing phenolic groups and esters were also detected. These are chemical industry products and household chemicals including products of the cosmetic and/or pharmaceutical industries (marked with asterisks in Table 2).

Peat

The stratigraphical characteristics of peat sampled from boreholes H2 and H3 that were noted in the field are shown in Table 3, and details of the eleven peat samples used for determination of organic matter content can be found in Table 4. The organic matter identified in the peat samples included alkane hydrocarbons, alcohols, fatty acids, terpene hydrocarbons, aromatic compounds and a number of other substances. The n-alkanes are mainly represented by C_{14} to C_{36} compounds (in which the number of carbon atoms ranges from 14 to 36), fatty n-acids (FA) by compounds ranging from C_8 to C_{20}, and n-alcohols by C_{12}–C_{22} compounds. The distributions of these three compound classes are shown in Tables A1–A3 in the Appendix, and a summary is provided in Table 5. Various geochemical indices calculated from the data for n-alkanes are shown in Table 6.

The distribution of n-alkanes found in the peat bitumoids across the depth of the peat deposit is uneven, with a marked concentration in the layer below the acrotelm followed by a decrease towards the mineral substratum (Tables 5 and A1). The n-alkanes are mainly represented by high molecular

Table 1. Concentrations (μg dm^{-3}) of organic compounds in water samples collected on 18 March 2021 at boreholes H1, H2, H4 and H5. For the summarisation of data (Shvartsev *et al*. 1996, Turov *et al*. 1998), A = arithmetic mean; $\delta_A \approx \frac{\sigma}{\sqrt{N}}$ = error in determination of arithmetic mean where σ = mean square deviation; N = sample volume (dm^3); and values in (parentheses) are for samples collected in the Ob Fen near the village of Naschekovo on 26 November 2018, from Ivanova *et al*. (2020). n.d. indicates no analytical data.

Substance		H1	H2	H4	H5	Summarisation of data	
		56° 30.905' N 84° 1.571' E	56° 30.864' N 84° 1.504' E	56° 30.822' N 84° 1.564' E	56° 30.858' N 84° 1.630' E	A	δ_A
n-Alkanes	total	201.44	666.07	112.00	196.96	328.39 (30.48)	157.03 (6.39)
	hexadecane	8.12	18.09	7.51	8.32	n.d.[1]	n.d.
	docosane	29.17	40.98	7.15	25.47	n.d.	n.d.
	tetracosane	19.98	23.95	7.31	23.95	n.d.	n.d.
	octacosane	18.23	16.12	10.56	26.79	n.d.	n.d.
aliphatic alcohols		361.14	522.12	188.09	559.88	164.93 (53.81)	91.07 (8.23)
compounds with phenolic OH- group		336.63	303.08	15.63	n.d.	n.d.	n.d.
esters and other O-containing compounds		1667.09	2578.77	1035.68	2570.64	271.41 (136.34)	111.65 (26.34)
hydrocarbons except alkanes		353.56	439.96	11.09	747.54	n.d.	n.d.
aromatics		19.73	96.18	5.62	n.d.	32.29 (7.90)	27.38 (4.29)
fatty acids		52.42	676.69	452.27	747.54	n.d.	n.d.
terpenoids		12.74	251.69	355.74	633.84	n.d.	n.d.
steroids		91.33	523.79	252.31	374.82	n.d.	n.d.
alkaloids		9.99	n.d.	n.d.	n.d.	n.d.	n.d.
phosphates		n.d.	40.19	21.38	119.62	n.d.	n.d.
sulfur-containing compounds		n.d.	n.d.	4.26	n.d.	n.d.	n.d.
nitrogen-containing compounds		n.d.	n.d.	61.24	159.53	n.d.	n.d.

Table 2. Characterisation of the main contaminants found in the water samples. Asterisks (*) identify products of the cosmetic and/or pharmaceutical industries (see text). n.d. indicates no analytically significant signal.

Compounds	Concentration (ng L^{-1})			
	H1	H2	H4	H5
2-(Isobutoxycarbonyl)benzoic acid	7.02	13.48	6.92	11.85
Phthalic acid, butyl 2-propylpentyl ester	13.34	n.d.[1]	n.d.	n.d.
Phthalic acid, 3,3-dimethylbut-2-yl isobutyl ester	25.89	27.24	12.50	n.d.
Phthalic acid, di(oct-3-yl) ester	n.d.	n.d.	n.d.	51.61
Dimethyl phthalate	7.00	n.d.	n.d.	n.d.
Diethyl phthalate	21.10	37.15	14.49	n.d.
Diisobutyl phthalate	38.31	53.32	28.99	40.67
Dibutyl phthalate (DBP)	7.77	13.80	7.06	11.70
Benzyl butyl phthalate	24.30	30.31	20.99	26.19
Bis(2-ethylhexyl) phthalate (DEHP)	70.90	172.81	31.71	368.01
Total phthalate in the acrotelm layer of the borehole	*215.63*	*348.11*	*122.66*	*510.03*
Phenol, 2-(1,1-dimethylethyl)-4-methyl-	4.30	n.d.	n.d.	n.d.
Durohydroquinone	7.10	n.d.	n.d.	n.d.
6-tert-Butyl-2,4-dimethylphenol	n.d.	12.73	n.d.	n.d.
Butylated Hydroxytoluene	292.10	210.23	15.62	n.d.
Phenol, 2,4,6-tris(1-methylethyl)-	n.d.	14.88	n.d.	n.d.
Hexanedioic acid, bis(2-ethylhexyl) ester	n.d.	35.83	n.d.	n.d.
*Octadecyl octanoate	55.77	84.38	79.10	84.42
*Octocrylene	34.61	51.09	n.d.	31.13
*Cetyl palmitate	18.65	n.d.	n.d.	n.d.
*Octadecyl hexadecanoate	10.76	n.d.	n.d.	n.d.
*Isopropyl myristate	19.60	24.78	14.47	29.97
*Isopropyl palmitate	23.24	30.05	13.85	n.d.
*Glycerol tricaprylate	n.d.	30.09	19.91	49.95
*Octadecyl stearate	n.d.	19.28	n.d.	92.48
Octinoxate	n.d.	n.d.	n.d.	369.74
Diethyltoluamide (N,N-Diethylmethylbenzamide)	n.d.	n.d.	n.d.	26.67

Table 3. Peat depths at the boreholes, with brief descriptions of the physical condition of basal layers of the peat deposit and the transition to mineral substratum.

Borehole	Peat depth (m)	Depth of layer (m)	Description
H1	5.00	3.75–4.00	whitish coloured sediments
		4.50–5.00	strongly waterlogged peat
		5.00–5.25	organic-mineral sediments
		5.25–5.50	mineral soil (loam)
H2	up to 5.75	4.00–4.25	strongly waterlogged peat
		4.50–4.75	strongly compacted black peat (possibly resulting from fire), mineral soil (loam)
		4.75–5.75	strongly waterlogged peat
H4	up to 4.75	4.00–4.25	black peat with wood residues
		4.75–5.00	mineral soil (loam)
H5	up to 5.00	3.50–3.75	heavily waterlogged peat
		4.25–5.00	black peat with well-preserved wood remains
		5.25–6.00	mineral soil (loam)

Table 4. Characterisation of peat samples for the determination of organic matter content. dw = dry weight.

Borehole	Sample code	Sampling depth (m)	Yield of chloroform bitumoid (% of dw)	Moisture content (% of dw)
H2	H2-23	0.00–0.25	8.32	92.38
	H2-24	0.25–0.50	17.35	90.15
	H2-25	0.50–0.75	10.22	82.73
	H2-33	2.50–2.75	4.92	78.57
	H2-45-46	5.50–6.00	1.29	30.62
H3	H3-67	0.00–0.25	14.07	84.85
	H3-68	0.25–0.50	8.79	89.33
	H3-69	0.50–0.75	3.68	89.21
	H3-77	2.50–2.75	6.48	81.46
	H3-85	4.50–4.75	0.79	63.19
	H3-86	4.75–5.00	1.57	28.48

Table 5. Concentrations of the n-alkanes, n-fatty acids and n-alcohols in the peat samples. The FA/A index is calculated as the quotient of the gravimetric contents of n-fatty acids to n-alkanes, and characterises the degree of diagenetic transformation of organic matter.

Borehole	Sample	Depth (m)	Concentration (dry mass basis; mg g^{-1})			FA/A
			n-alkanes (m/z = 57, 71)	n-fatty acids (m/z = 60, 73)	n-alcohols (m/z = 83, 111)	
H2	H2-23	0.00-0.25	4.47	14.07	3.10	3.15
	H2-24	0.25-0.50	10.24	6.07	3.47	0.59
	H2-25	0.50-0.75	8.68	6.13	2.35	0.71
	H2-33	2.50-2.75	4.43	5.75	1.87	1.30
	H2-45-46	5.50-6.00	1.29	0.81	0.54	0.63
H3	H3-67	0.00-0.25	6.19	11.21	5.21	1.81
	H3-68	0.25-0.50	6.86	8.32	2.55	1.21
	H3-69	0.50-0.75	2.57	3.19	1.18	1.24
	H3-77	2.50-2.75	7.12	8.09	2.33	1.14
	H3-85	4.50-4.75	1.00	0.53	0.28	0.53
	H3-86	4.75-5.00	1.37	1.20	0.75	0.88

weight (C_{19}–C_{33}) homologues. Based on the (lowest) values of the SVR index, the largest contributions of terrestrial plants to the organic matter are observed in samples H2-24, H2-45-46 and H3-86 (Table 6). The n-alcohols are mainly represented by compounds with alkyl chain lengths from C_{12} to C_{24} (Table A2) and even-numbered alcohols predominate. The maximum in the distribution is usually at C_{16} and C_{18}. Fatty n-acids are mainly represented by C_8–C_{26} compounds with a maximum at C_{16}–C_{18} (Table A3), which is generally characteristic of vegetation dominated by higher (vascular) plants. In the lower peat layers at H2 and H3, the amount of C_{18}–C_{26} n-fatty acids is less than in the upper layers, which is probably related to diagenetic processing of long-chain acids. In general (except in the 2.50–2.75 m layer), the concentrations of n-fatty acids and n-alcohols decrease with increasing depth, probably due to the processing of organic matter that originated predominantly from plants.

Aromatic hydrocarbons are mainly represented by alkylbenzenes, naphthalenes and phenanthrenes, although pyrene and dibenzothiophene were also detected (Russkikh *et al.* 2020). Figure 2a shows the

Table 6. Geochemical indices calculated on the basis of molecular weight distribution of n-alkanes.

Borehole	Sample number	CPI	E/O	Pr/Ph	C_{23}	C_{27}	C_{29}	C_{31}	K_{df}	P_{aq}	ACL	SVR
H2	H2-23	3.17	0.46	0.47	11.40	12.78	13.25	5.60	0.50	0.56	26.94	0.86
	H2-24	4.88	0.25	0.65	4.74	7.31	15.70	24.79	0.20	0.19	29.20	0.30
	H2-25	3.21	0.41	0.49	9.97	12.42	8.96	10.41	0.51	0.53	27.13	1.11
	H2-33	3.25	0.44	0.58	7.72	11.45	13.72	11.50	0.36	0.42	27.57	0.56
	H2-45–46	3.16	0.46	0.53	5.66	13.10	16.68	13.57	0.25	0.32	27.82	0.34
H3	H3-67	2.91	0.41	0.24	7.24	12.47	15.86	12.96	0.32	0.39	27.75	0.46
	H3-68	3.42	0.45	0.37	11.25	11.59	10.91	5.63	0.56	0.59	26.73	1.03
	H3-69	3.74	0.42	0.37	11.17	11.35	10.72	7.61	0.54	0.57	26.78	1.04
	H3-77	3.24	0.41	0.47	10.78	12.80	10.60	7.76	0.52	0.56	27.09	1.02
	H3-85	3.43	0.40	0.55	8.77	14.85	16.23	9.42	0.38	0.42	27.39	0.93
	H3-86	3.20	0.45	0.33	7.65	12.11	18.40	8.80	0.33	0.38	27.64	0.42

Explanations of the indices:

CPI: Index of oddness, which characterises the contribution of higher plants to organic matter.

E/O (Even/Odd): Parity factor, which is the ratio of even n-alkanes to odd n-alkanes. This factor characterises the contribution of even n-alkanes, the source of which, in addition to plant matter, is largely microbiota.

Pr/Ph (Pristane to Phytane quotient): This coefficient characterises the redox environment of sedimentation. Values ≥ 3 are characteristic of an oxidative sedimentation environment (Peters *et al*. 2005).

C_{23}: The relative content of n-alkane C_{23} (% of the sum of all n-alkanes), a marker for *Sphagnum* moss.

C_{27}: The relative content of n-alkane C_{27} (% rel), predominant in *Scheuchzeria*.

C_{29}: The relative content of n-alkane C_{29} (% rel), predominant in *Sedge*, *Carex*.

C_{31}: The relative content of n-alkane C_{31} (% rel), marker for *Puszyca (Eriophorum)*.

K_{df}: Peat dryness factor, $K_{df} = (C_{21}+C_{23})/(C_{21}+C_{23}+C_{29}+C_{31})$.

P_{aq}: A coefficient representing the contribution made by terrestrial and aquatic plants; $P_{aq} = (C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})$.

ACL: A coefficient that characterises average chain length;
$ACL = (23\cdot C_{23}+25\cdot C_{25}+27\cdot C_{27}+29\cdot C_{29}+31\cdot C_{31}+33\cdot C_{33})/(C_{23}+C_{25}+C_{27}+C_{29}+C_{31}+C_{33})$ (Duchko 2016).

SVR: (*Sphagnum*/vascular quotient): A coefficient that characterises the content of *Sphagnum* relative to vascular plants in the composition of the organic matter (Duchko 2016).

variation of aromatic hydrocarbon concentrations with depth in the two cores. At H2, the concentration profile of alkylbenzenes does not follow the trend in chloroform bitumen yield (CBY; reflecting the total amount of organic matter in the peat) and the uppermost layer of peat contained more dienzothiophene than was present at H3. At H3 the distributions of naphthalenes, phenanthrenes, pyrene and dibesothiophene do not follow the trend in CBY but, at the same time, show similarities amongst themselves. The presence of biphenyl was recorded in borehole H3 only, with maxima in the surface and 2.50–2.75 m layers.

Compounds of known anthropogenic origin that were identified in the peat are listed in Table 7 (borehole H2) and Table 8 (borehole H3). These Tables include all identified compounds belonging to the phthalate group along with some polycyclo-aromatic compounds and other contaminants. The total concentration of aromatic series contaminants (excluding phthalates) is 1083.06 ng kg^{-1} in borehole H3 and 387.04 ng kg^{-1} in borehole H2. This means that there are 2.8 times more aromatic series contaminants in the peat at H3.

The main contaminants are various phthalates (i.e., derivatives of phthalic acid), the most common being dibutyl phthalate, diisobutyl phthalate, diethyl phthalate, butyl isobutyl phthalate, bis(2-ethylhexyl) phthalate and di-sec-butyl phthalate. Figure 2b shows the distribution of phthalates by depth in boreholes H2 and H3. As the depth of sampling increases, the amount of phthalates in both boreholes decreases.

In addition to phthalates, octinoxate and diethyltoluolamide were also found as contaminants in borehole H2 only, where octinoxate was found in the upper horizon. Dibenzothiophene was found in both boreholes, at concentrations that generally decreased with increasing depth in the cores.

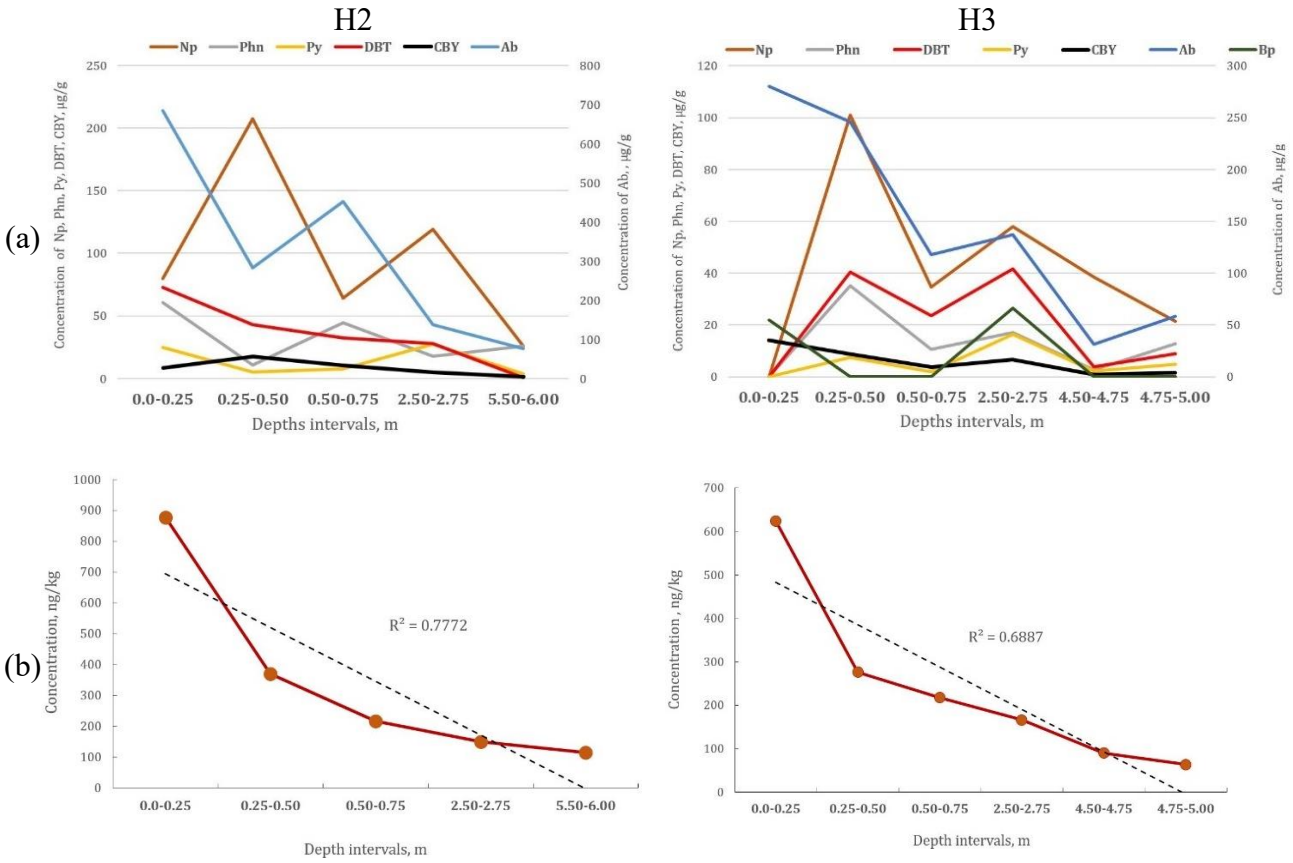

Figure 2. Changes with depth in the peat cores from boreholes H2 (left) and H3 (right) in the concentrations of (a) aromatic hydrocarbons: Np = naphthalenes, Phn = phenanthrenes, Py = pyrene, DBT = dibenzothiophene, CBY = chloroform bitumen yield, Ab = alkylbenzenes, Bp = biphenyl; and (b) total phthalates (dry mass basis; μg g^{-1}).

Table 7. Dry mass concentrations (Conc.; ng kg^{-1}) of the main contaminants in the peat samples from borehole H2. m/z is the mass-to-charge ratio of the characteristic ion (when processed by GC-MS); n.d. indicates no analytically significant signal.

Depth range	0.00–0.25 m		0.25–0.50 m		0.50–0.75 m		2.50–2.75 m		4.75–5.00 m	
Sample number	H2-23		H2-24		H2-25		H2-33		H2-45-46	
	m/z	Conc.	m/z	Conc.	m/z	Conc.	m/z	Conc.	m/z	Conc.
Phthalates										
Di-sec-butyl phthalate	121, 150, 167	345.76	121, 150, 167	156.50	121, 150, 167	n.d.	121, 150, 167	n.d.	121, 150, 167	n.d.
Dibutyl phthalate	149, 223	340.16	149, 223	169.22	149, 223	n.d.	149, 223	43.50	149, 223	n.d.
Phthalic acid, di(2-propylpentyl) ester	267, 91	n.d.	149, 167	43.81	149, 167	n.d.	149, 167	n.d.	149, 167	n.d.
Diisobutyl phthalate	149, 223	190.22	149, 167	n.d.	149, 167	n.d.	149, 167	n.d.	149, 167	58.63
Bis(2-ethylhexyl) phthalate	149, 167	n.d.	149, 177	n.d.	149, 177	216.60	149, 177	n.d.	149, 177	39.42
Diethyl phthalate	149, 177	n.d.	149, 150	n.d.	149, 150	n.d.	149, 150	8.70	149, 150	17.44
Butyl isobutyl phthalate	149, 150	n.d.	149, 167	n.d.	149, 167	n.d.	149, 167	33.39	149, 167	n.d.
Phthalic acid, di(oct-3-yl) ester	149, 167	n.d.	149, 143	n.d.	149, 143	n.d.	149, 143	28.70	149, 143	n.d.
Dihexyl phthalate	149, 143	n.d.	149, 223	n.d.	149, 223	n.d.	149, 223	35.90	149, 223	n.d.
Other aromatic hydrocarbons										
Dibenzothiophene	184	72.80	184	42.81	184	32.51	184	28.00	184	0.82
Unknown aromatic hydrocarbon	259, 456	n.d.	259, 456	n.d.	259, 456	n.d.	259, 456	210.10	259, 456	n.d.
Other contaminants										
Octinoxate	178, 161	276.21	178, 161	n.d.	178, 161	n.d.	178, 161	n.d.	178, 161	n.d.
Diethyltoluamide	119, 91	69.05	119, 91	n.d.	119, 91	n.d.	119, 91	n.d.	119, 91	n.d.

Table 8. Dry mass concentrations (Conc.; ng·kg^{-1}) of the main contaminants in the peat samples from borehole H3. m/z is the mass-to-charge ratio of the characteristic ion (when processed by GC-MS); n.d. indicates no analytically significant signal.

Depth range	0.00–0.25 m		0.25–0.50 m		0.50–0.75 m		2.50–2.75 m		4.50–4.75 m		4.75–5.00 m	
Sample number	H3-67		H3-68		H3-69		H3-77		H3-85		H3-86	
	m/z	Conc.	m/z	Conc.	m/z	Conc.	m/z	Conc.	m/z	Conc.	m/z	Conc.
Phthalates												
Di-sec-butyl phthalate	149	267.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dibutyl phthalate	149	238.90	n.d.	n.d.	149	13.40	149	30.40	149	55.22	149	8.01
Phthalic acid, 2-ethylbutyl octyl ester	149,167	117.71	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diisobutyl phthalate	149, 223	n.d.	149, 223	204.40	149, 223	n.d.	149, 223	n.d.	149, 223	n.d.	149, 223	n.d.
Bis(2-ethylhexyl) phthalate	149, 167	n.d.	149, 167	71.76	149, 167	n.d.	149, 167	n.d.	149, 167	n.d.	149, 167	n.d.
Diethyl phthalate	149, 143	n.d.	149, 143	n.d.	149, 143	3.71	149, 143	21.41	149, 143	2.96	149, 143	2.46
Butyl isobutyl phthalate	149, 150	n.d.	149, 150	n.d.	149, 150	140.42	149, 150	66.82	149, 150	13.02	149, 150	43.80
Phthalic acid, di(oct-3-yl) ester	149, 167	n.d.	149, 167	n.d.	149,167	59.71	149, 167	38.82	149,167	18.60	149,167	9.03
Dihexyl phthalate	149, 143	n.d.	149, 143	n.d.	149, 143	n.d.	149, 143	8.64	149, 143	n.d.	149, 143	n.d.
Other aromatic hydrocarbons												
Biphenyl	154	54.70	154	n.d.	154	n.d.	154	66.02	154	n.d.	154	n.d.
Dibenzothiophene	184	n.d.	184	40.30	184	23.50	184	41.50	184	3.76	184	8.80
Anthra[2,3-b]furan-4,11-dione, 2,3-dihydro-3,6-dimethyl-	207, 263, 278	n.d.	207, 263, 278	261.01	207, 263, 278	n.d.	207, 263, 278		207, 263, 278	n.d.	207, 263, 278	n.d.
2-Benzylnaphthalene	202, 218	n.d.	202, 218	575.27	202, 218	n.d.	202, 218	n.d.	202, 218	n.d.	202, 218	n.d.
Unknown aromatic contaminant	149, 191, 234	n.d.	149, 191, 234	n.d.	149, 191, 234	n.d.	149, 191, 234	n.d.	149, 191, 234	8.20	149, 191, 234	n.d.
Other contaminants												
Tridecyl decanoate	173, 57	n.d.	173, 57	160.05	173, 57	n.d.	173, 57	n.d.	173, 57	n.d.	173, 57	n.d.
2-Pentacosanone	59, 58	n.d.	59, 58	1165.07	59, 58	606.11	59, 58	n.d.	59, 58	n.d.	59, 58	n.d.
Diethyltoluamide	119, 190, 91	n.d.	119, 190, 91	7.86	119, 190, 91	n.d.	119, 190, 91	n.d.	119, 190, 91	n.d.	119, 190, 91	n.d.

DISCUSSION

Organic content of water

Compared to the (March 2021) water samples reported here, the water samples collected in November 2018 by Ivanova *et al.* (2020) had approximately the same pH values, but significantly higher values of specific electrical conductivity (EC) and content of major ions due to the input of groundwater under pressure upwelling from Paleogene sediments (Savichev 2023a, 2023b). Given the absence of external anthropogenic factors and the use of the same sampling and analysis techniques for the determination of organic matter in 2018 and 2021, we suggest that the differences observed are related to the processes of organic matter transformation in the peat deposit during the winter period in the absence of new plant residues and with limited access to oxygen. The significant heterogeneity in the distribution of organic matter over short distances across the surface of the peatland is also an interesting result. This heterogeneity is noticeable during visual inspection of the peat and analysis of the distribution of major ion contents (Savichev 2023a, 2023b). This phenomenon might be explained by the combination of initially heterogeneous conditions (waterlogging according to the scheme: formation of a floodplain reservoir, its subsequent eutrophication, formation of a lowland mire and, at the same time, waterlogging of adjacent territories) and related heterogeneous conditions of interaction between peat and groundwater - "breakthrough" of pressurised water through the thickness of colmatised (i.e., clogged with fine particles) organic-mineral sediments and mineral soils at the bottom of the peat layer, taking into account the heterogeneity and non-stationarity of their composition and filtration properties.

The levels of phthalates present in water and peat are typical for lowland peatlands located near urbanised settlements. Some phthalates can be recycled in peat sediments (Muller & Kordel 1993, Patel *et al*. 2020, Xing *et al*. 2022).

In general, most of the compounds enter the peat water in precipitation along with runoff from fields and the road. The water collected at points H2 and H5 contained higher concentrations of phthalates compared to points H1 and H4. In the case of H2, this may be related to its location close to the edge of the peatland where the influence of the nearby road is greater than at the other boreholes. In the case of borehole H5, there may be a slope and hydrochemical underflow.

Organic components of peat

The odd n-alkanes C_{25}, C_{27}, C_{29}, C_{31}, C_{33}, which are markers of higher plants (Peters *et al*. 2005), naturally dominate the composition of n-alkanes in all of the peat samples. The large contributions of terrestrial plants in samples H2-24, H2-45-46 and H3-86 indirectly indicate the occurrence of changes in climate and, consequently, in conditions for peat formation including those related to microbiological processes, both during the modern period and during the Holocene as a whole. It is also interesting to note that elemental sulfur was detected in sample H2-45-46 (depth 5.50–6.00 m) with a rather high content of dry residue (5.15 mg g^{-1}). Only traces of sulfur (0.0038 mg g^{-1}) were found in the lower horizon at borehole H3. This fact correlates well with the conclusion of Savichev *et al*. (2020b) that hydroxide mineral forms predominate in the upper part of the peat deposit, and sulfide in the lower part where a reducing geochemical barrier is formed. Besides, it is necessary to note the discrete conditions of interaction between peatland water and pressurised waters in mineral aquifers underlying the peat (Savichev *et al*. 2022a, 2022b). This is explained by both local changes in the filtration properties of soils and the heterogeneity of initial conditions, since the peatland probably started to form about 9,500–8,000 years ago within a waterlogged former channel of the Ob River. Perhaps some of the boreholes hit the channel edge or its bank while others fell within the old riverbed. This is evidenced indirectly by the increased CPI value and minimum P_{aq} values for sample H2-24, collected from the near-surface layer at borehole H2.

Of the aromatic hydrocarbons detected, phenanthrenes, naphthalenes and alkylbenzenes mainly originate from natural sources such as the decomposition of plants and woody residues (lignin). Pyrene may accumulate as a result of fires. Differences in the distribution of aromatic hydrocarbons between boreholes H2 and H3 (see Figure 2) indicate different mechanisms of organic matter accumulation at these two sites (Pastukhov *et al.* 2021, Neves *et al.* 2022, Gabov *et al.* 2025).

Most phthalates are plasticisers in plastics (Luo *et al*. 2018). The highest concentrations of phthalates are found in the upper horizons of the boreholes. Furthermore, a steep decline in phthalate content is evident when transitioning from upper to lower peat layers in both boreholes (Figure 2b). This may indicate transboundary transport of phthalates, i.e., that they enter the peat from the atmosphere with aerosols or precipitation. Total phthalate content is

slightly (~1.2 times) higher in borehole H2 than in borehole H3. This difference may be due to the fact that H2 is located close to a convexity of the peatland boundary (see Figure 1) and this area may act as a geochemical barrier and accumulator of various contaminants, especially in view of the technogenic influence of the nearby road. In addition to atmospheric transport, phthalates can enter the environment through runoff from fields (Muller & Kordel 1993, Luo *et al*. 2018). They can also leach from plastics into water and accumulate in soil. Phthalates are not safe for the environment and human health because they might induce adverse estrogenic effects on human beings and some of them are potentially carcinogenic (e.g., dibutyl phthalate; Luo *et al*. 2018, Xing *et al*. 2022). The reduction of phthalate concentrations with increasing depth in both boreholes suggests that the peatland acts as a filter, retaining contaminants and thus preventing them from entering the underlying horizons.

2-Benzylnaphthalene appears to form as a result of fuel combustion (Lima *et al*. 2007, Patel *et al*. 2020). Octinoxate is used as a UV filter in various types of cosmetics (Cahova *et al*. 2023) and diethyltoluolamide is one of the active ingredients in repellents, insecticides and pesticides (Dorman 1990). Tridecyl decanoate and 2-pentacosanone can be found in household chemicals and cosmetics. However, 2-pentacosanone is also present in the plant species *Solanum tuberosum*, as well as in other plants (Jamatia *et al*. 2024, Chu *et al*. 2025). It is likely that dibenzothiophene is formed as a result of fuel combustion, including through exposure to the nearby road. Its concentration in borehole H2 decreases with increasing depth, which aligns with our assumptions regarding the filtering properties of the peatland.

Concluding remarks

From our results it is clear that the process of peat formation and subsequent transformation is characterised by the introduction of a large amount of organic matter into the environment, the origin of which is currently poorly understood. A number of the component organic compounds are likely to be identified as substances of anthropogenic origin, although anthropogenic influence is either undetectable or extremely weak with respect to the inorganic content of both peatland waters and peat (Savichev *et al.* 2020a, 2020b; Savichev & Heng 2021; Savichev 2023a, 2023b). The time of sampling is likely to be important. During the growing season and at the beginning of the winter low-water period, when there are enough poorly decomposed plant residues in the peat deposit, the concentrations of a number of organic substances are lower than at the end of the winter low-water period under conditions of restricted oxygen access. In view of this it is advisable, firstly, to continue a comprehensive study of the processes of organic matter transformation in peatlands, including simultaneous studies of the composition of inorganic and organic matter as well as the microflora. Secondly, it is already necessary to differentiate the results of environmental monitoring of economic activities in peatlands (especially oil and gas production) in terms of the phases of the peatland water regime.

The study of contaminants in the water of the acrotelm seems to be an important task as it characterises the water–peat exchange processes (Ivanova *et al*. 2020, Inisheva *et al*. 2021). The main contaminants found in the sampled water and peat are phthalates and certain aromatic compounds. These include dibenzothiophene, 2-benzylnaphthalene and biphenyl, which are produced during the processing or combustion of petroleum products. However, several other contaminants have been identified, including various esters, octocrylene and diethyltoluamide. Also, some phthalates may occur naturally. Distinguishing between sources requires further research (Thiemann 2021). Other compounds containing phenolic groups (e.g. 6-tert-butyl-2,4-dimethylphenol, butylated hydroxy-toluene, etc.) and various esters (e.g., octadecyl octanoate, isopropyl palmitate, etc.) found in peatland waters originate from products of industrial synthetic chemistry. The peat layer acts as a filter, preventing the penetration of some contaminants into the lower horizons. The concentrations of all contaminants found in the sampled water and peat are typical of background areas of lowland peatlands in close proximity to urban settlements. It was also noted that the acrotelm water contains many compounds of peat origin, which indicates active exchange processes in the water-peat system.

Thus, peatland is an important environment for the accumulation of a variety of significant organic compounds including alkanes, fatty acids, alcohols, terpenoids, steroids, esters and others.

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AUTHOR CONTRIBUTIONS

AAG: initiation and organisation of work, performance of analyses, processing of results, manuscript writing, data curation; OGS: data interpretation, manuscript writing; TVC: work with peat samples, methodological support, collection of analytical data; YuAM: visualisation; EVG: organisation, administrative support and coordination of work.

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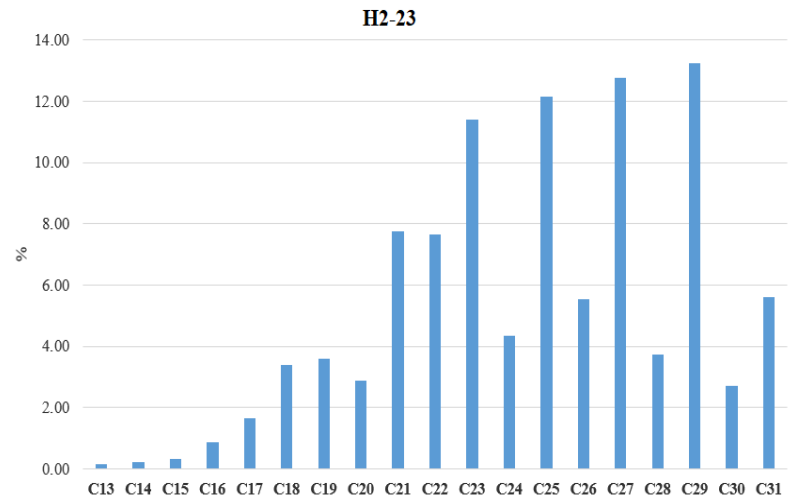
Appendix

Table A1. Molecular weight distribution of n-alkanes in peat samples.

BOREHOLE H2



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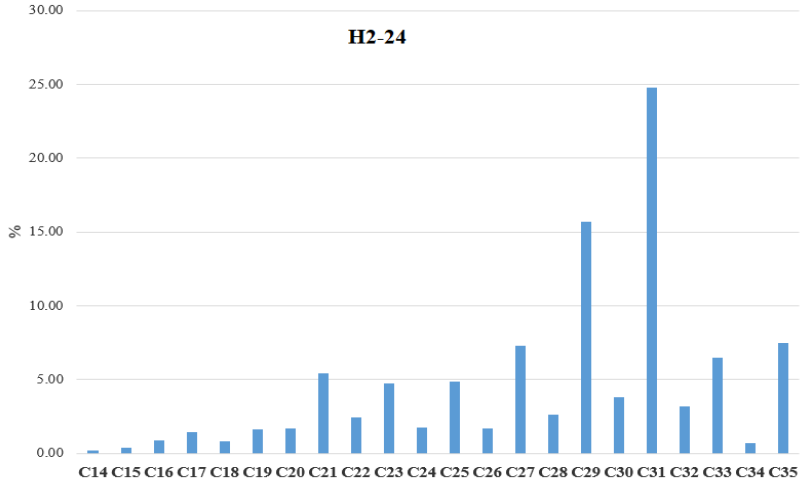
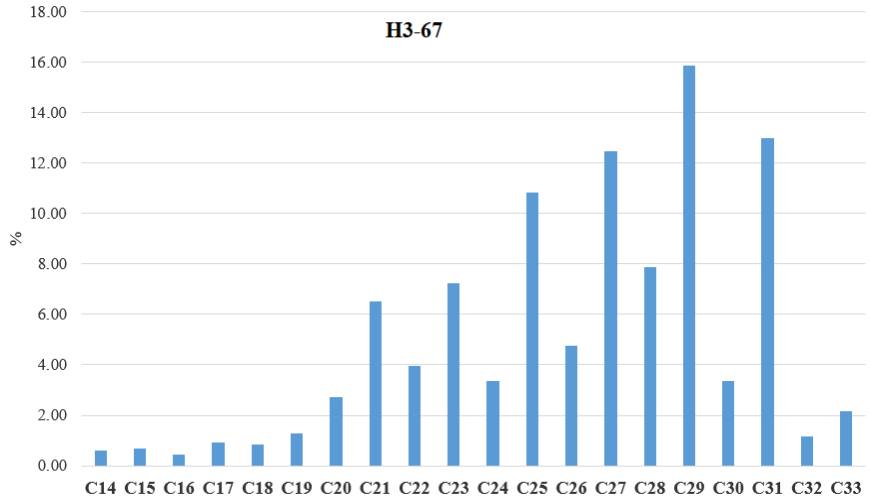
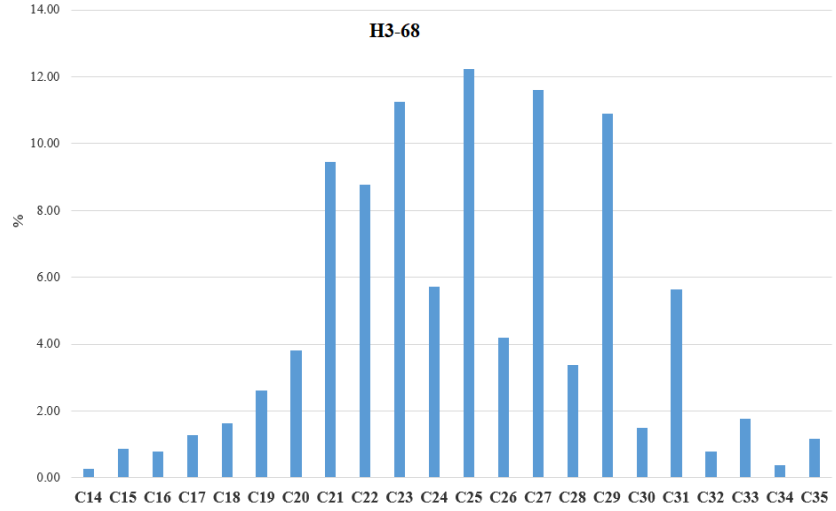


Depth 0.25–0.50 m

BOREHOLE H3





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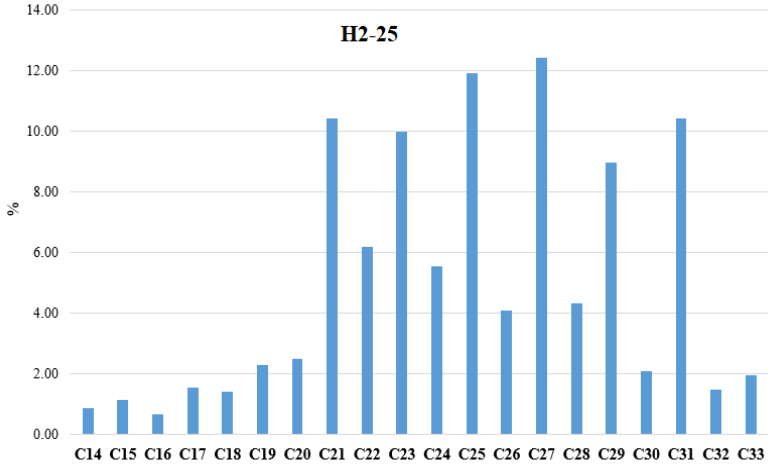

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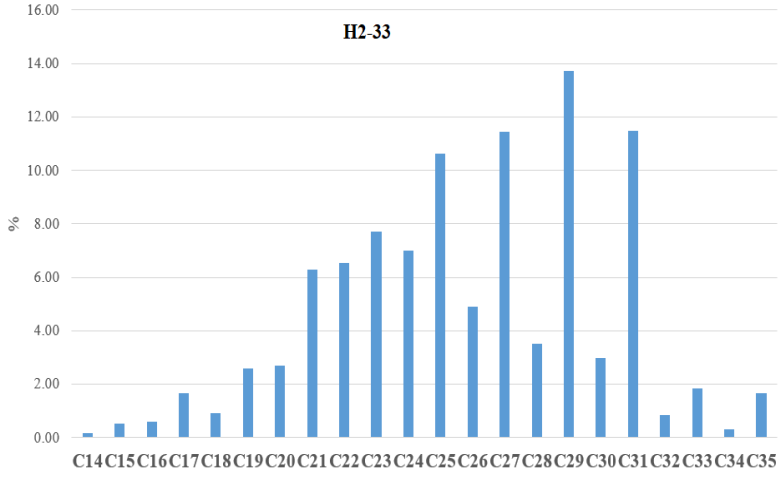
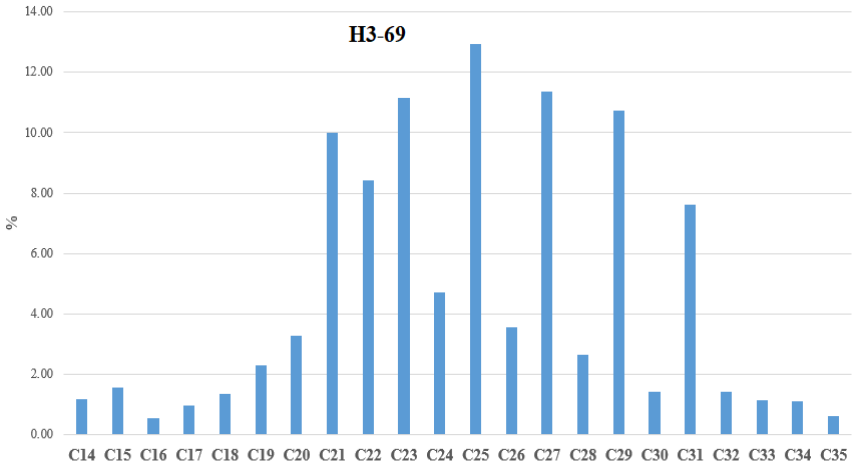
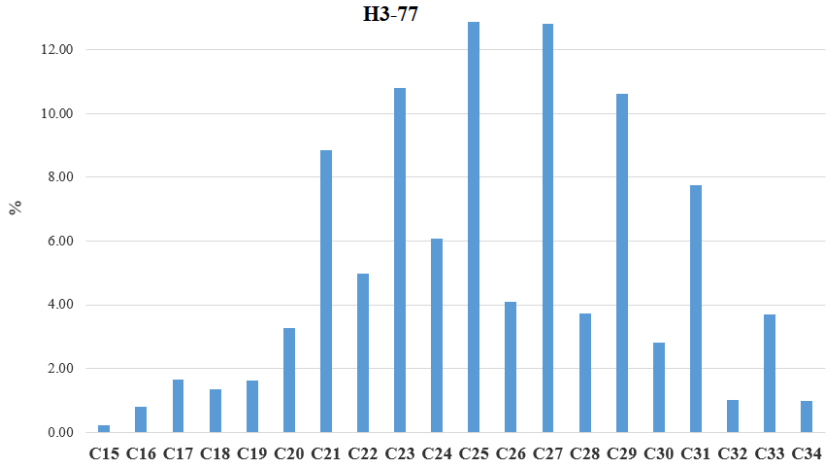


Depth 2.50–2.75 m

BOREHOLE H3





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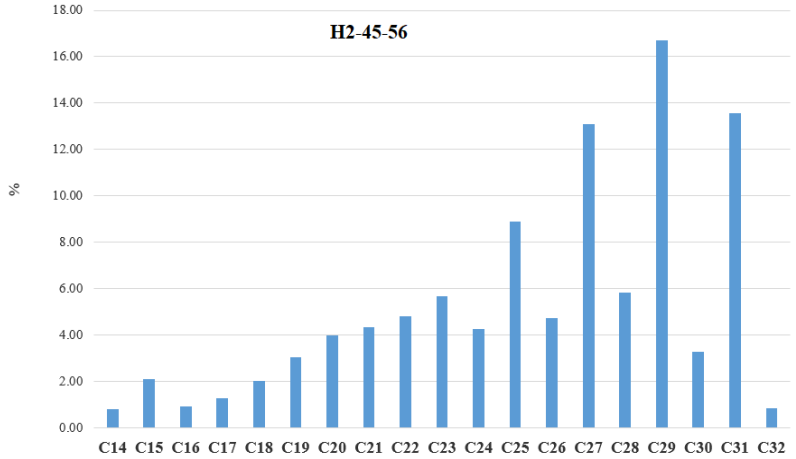
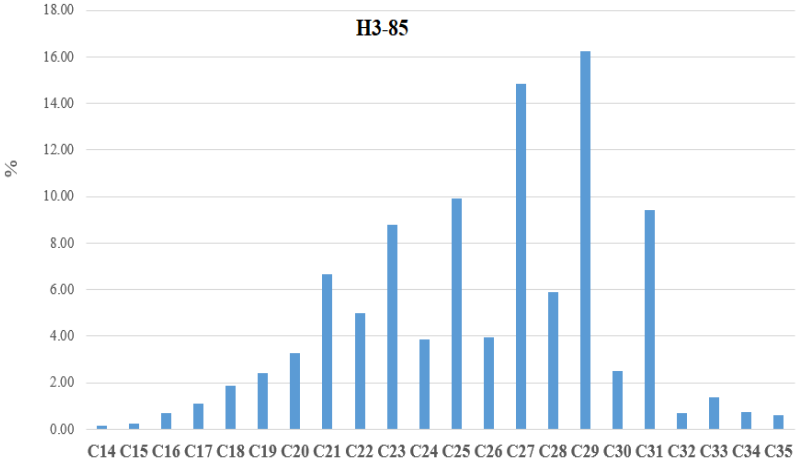


Depth 5.50–6.00 m

BOREHOLE H3

Depth 4.50–4.75 m



Depth 4.75–5.00 m

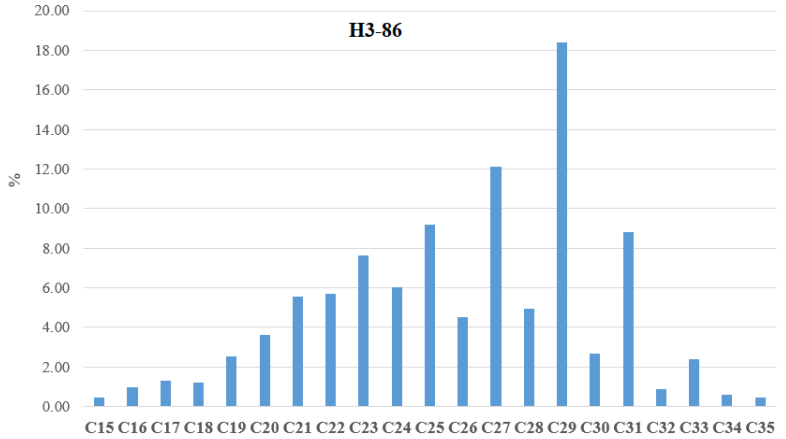
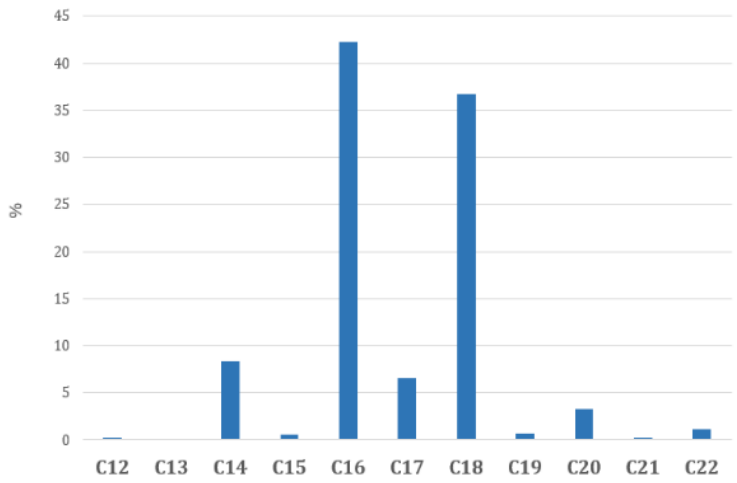


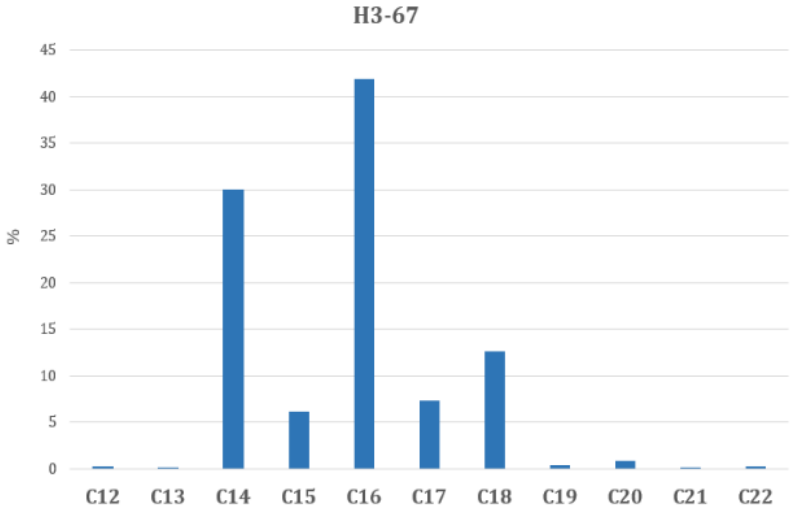
Table A2. Molecular weight distribution of n-alcohols in peat samples.

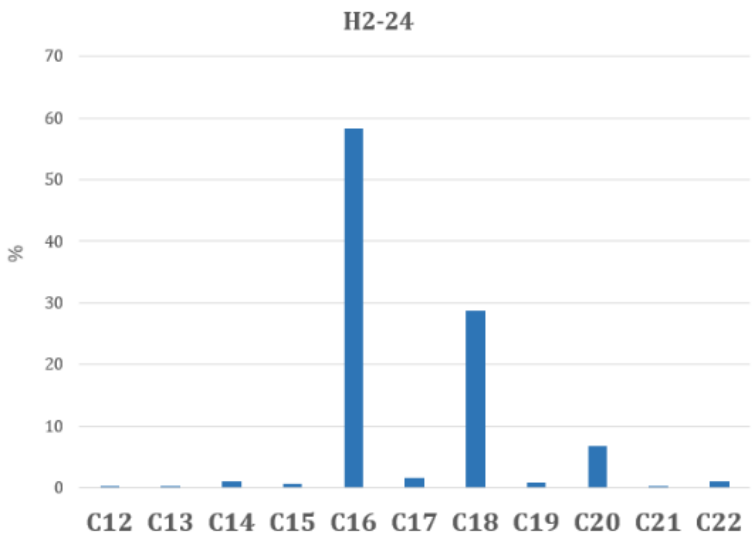
BOREHOLE H2



Depth 0.00–0.25 m

BOREHOLE H3





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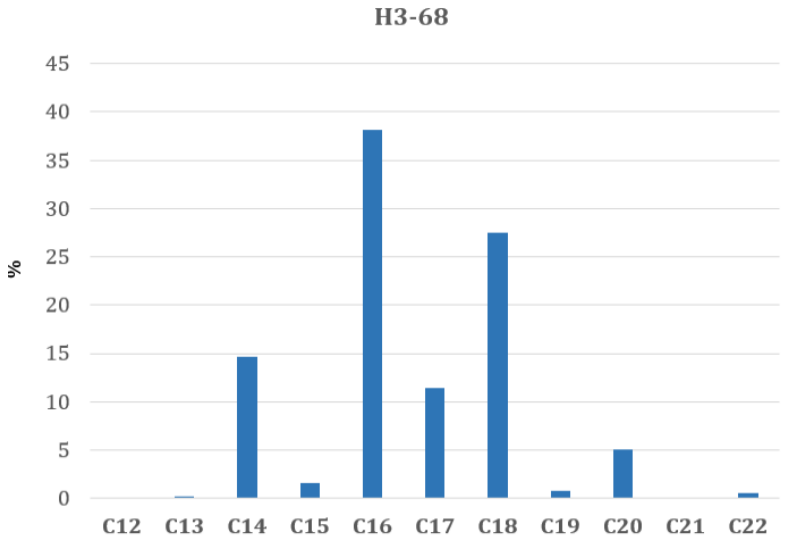
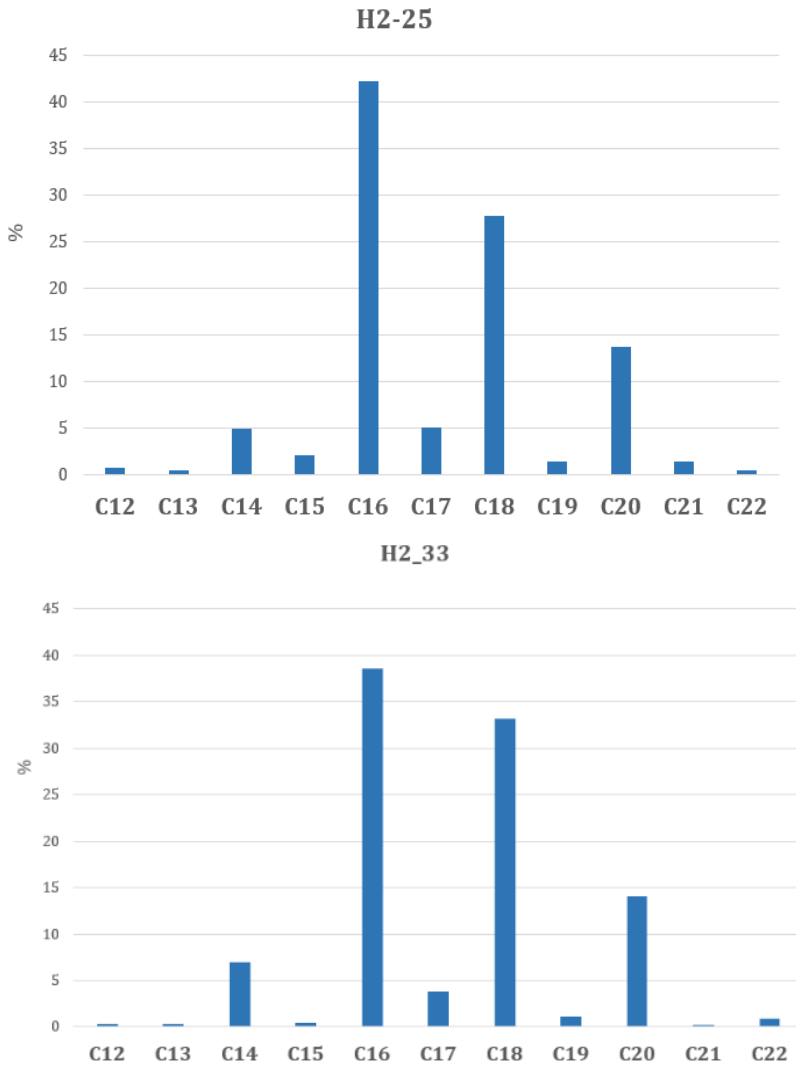


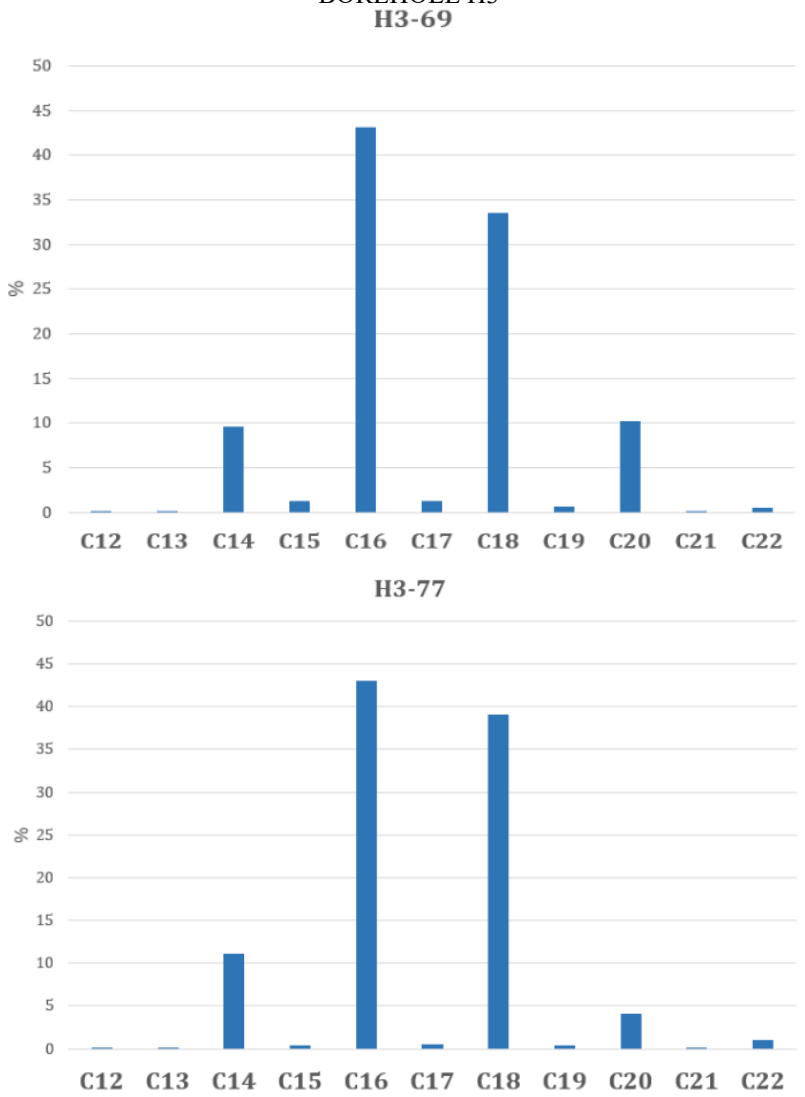
BOREHOLE H2



Depth 0.50–0.75 m

Depth 2.50–2.75 m

BOREHOLE H3



BOREHOLE H2

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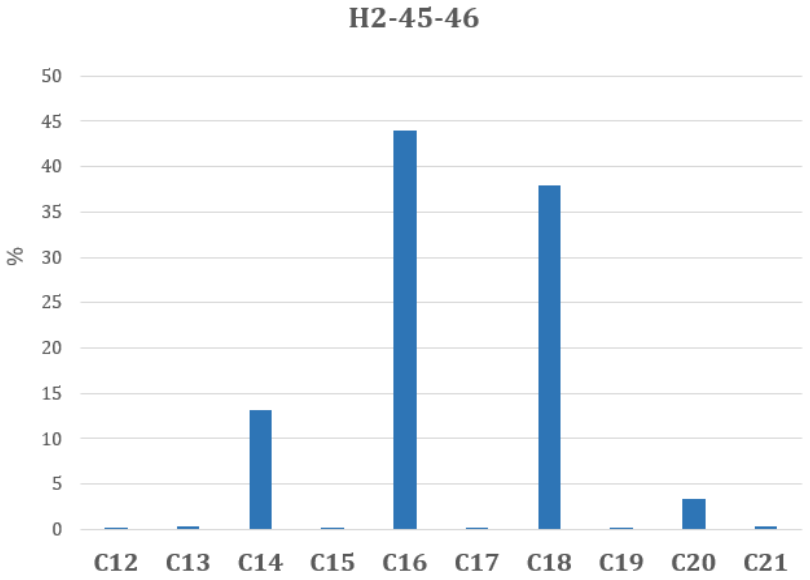

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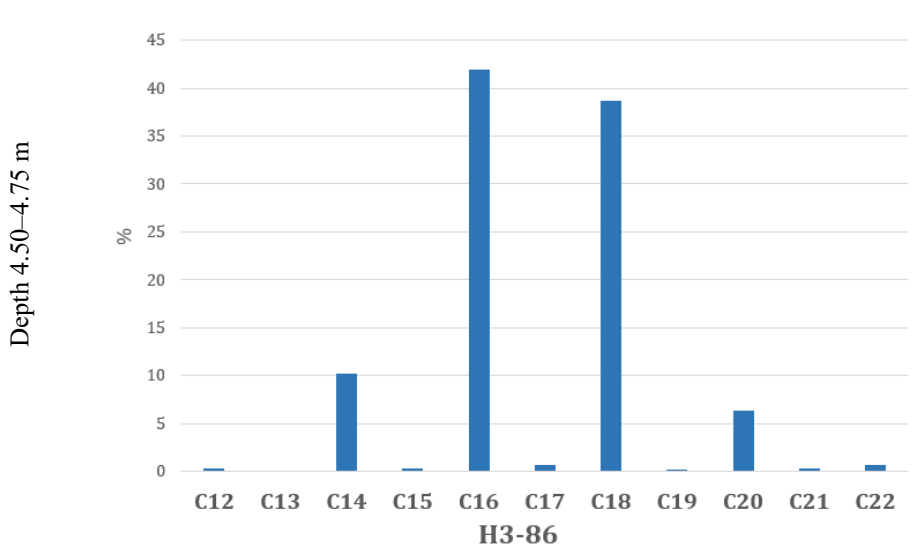


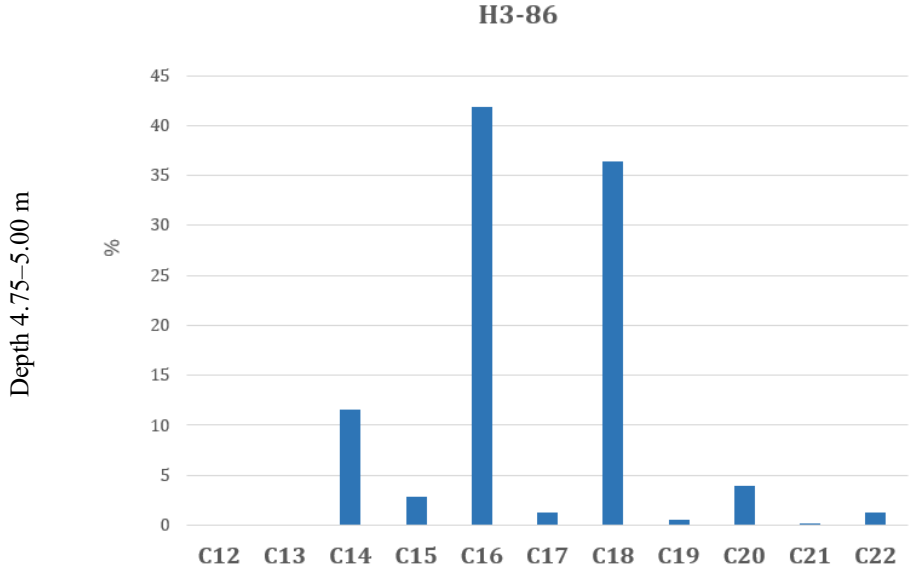
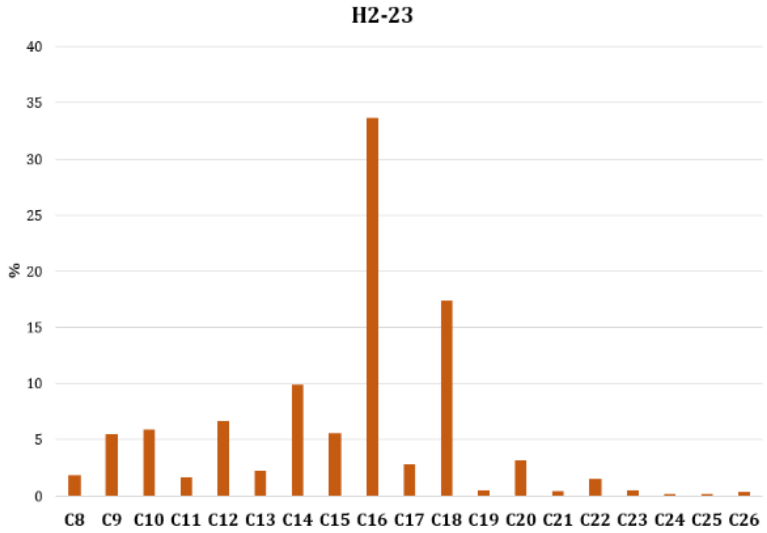


Table A3. Molecular weight distribution of n-fatty acids in peat samples.

BOREHOLE H2



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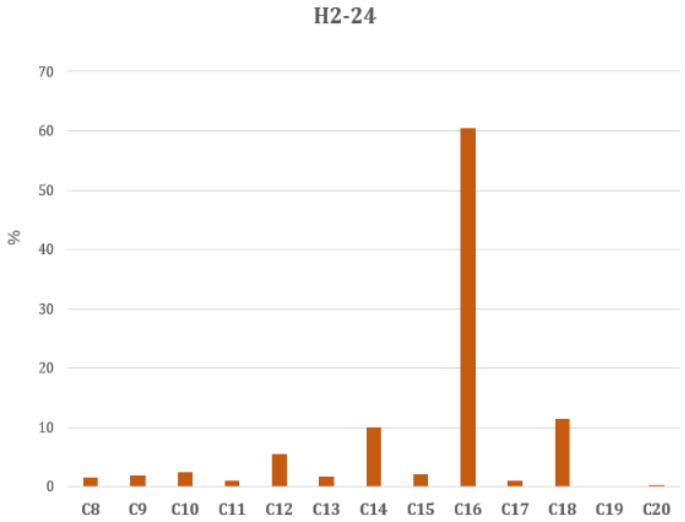

Depth 0.25–0.50 m

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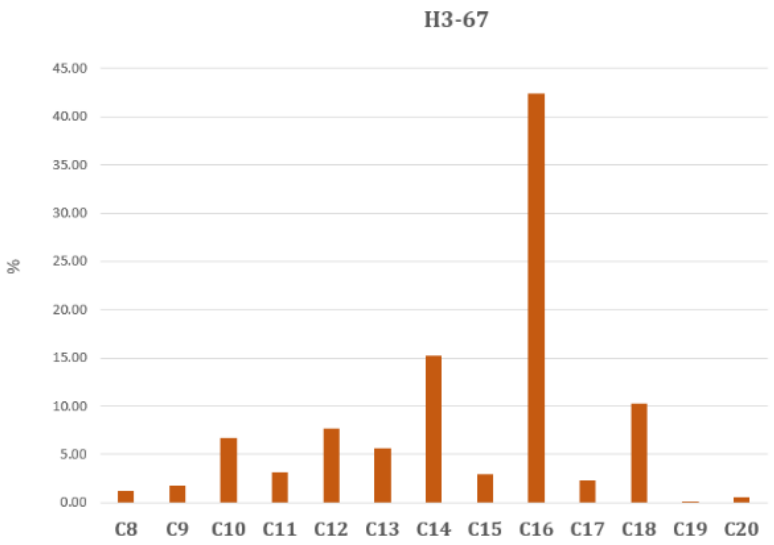

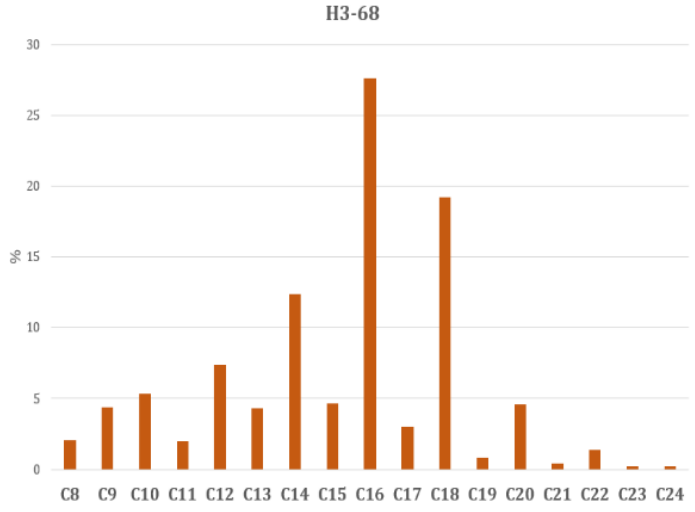

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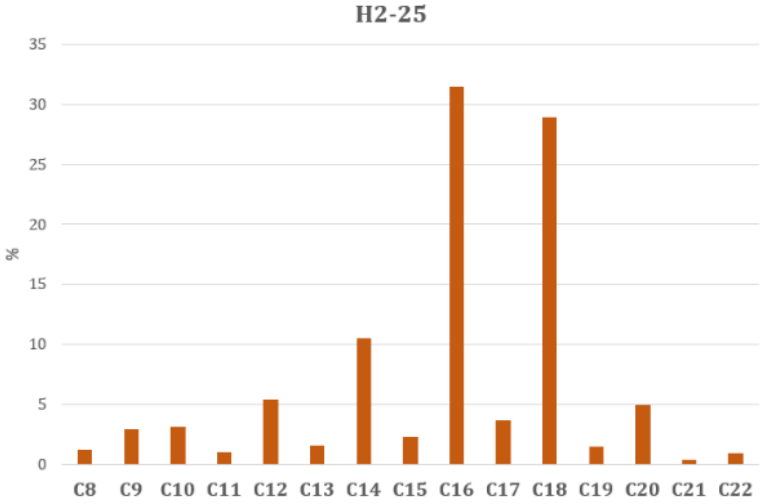
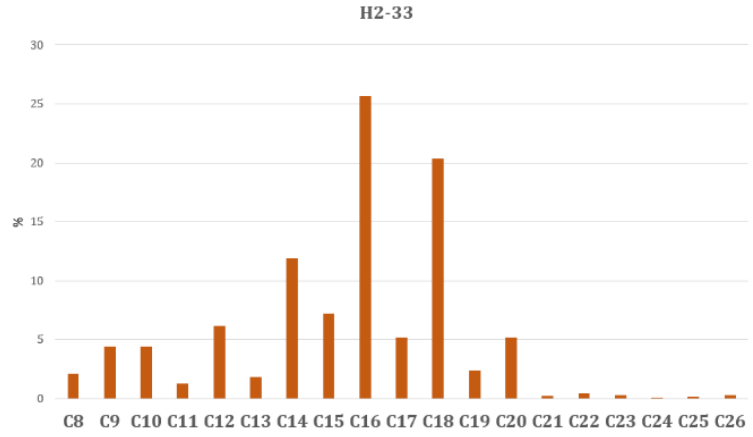


Depth 0.50–0.75 m



Depth 2.50–2.75 m

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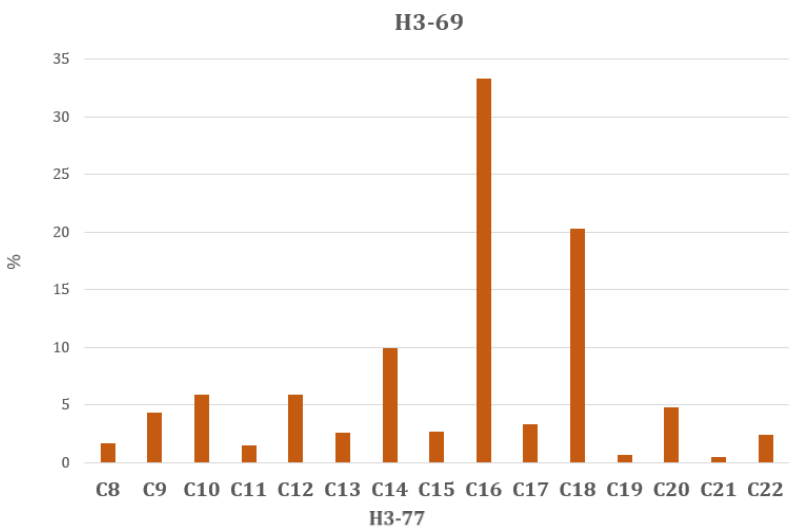

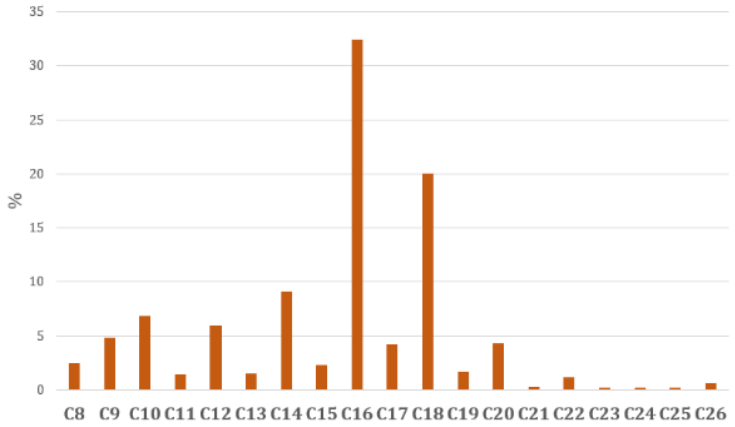

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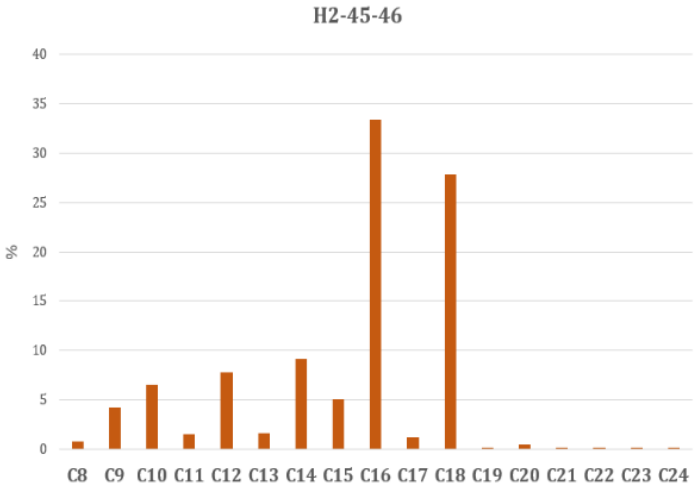
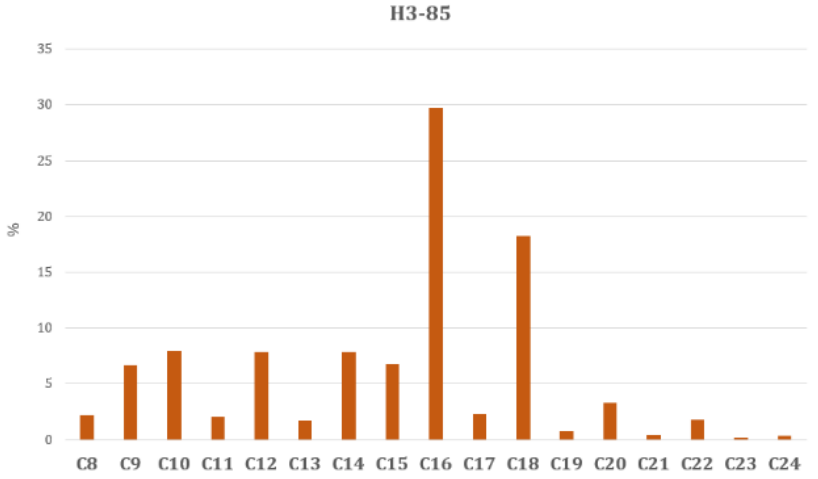


Depth 5.50–6.00 m

BOREHOLE H3

Depth 4.50–4.75 m



Depth 4.75–5.00 m