



XV International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov

Spatial distribution of chemical and organic compounds in the water of oligotrophic peatland of Tomsk region (Western Siberia)

O. Naymushina^{a,b*}, S. Shvartsev^{a,b}, O. Serebrennikova^c, K. Ses^a, I. Matveenko^a

^aTomsk Polytechnic University, Lenin ave. 30, Tomsk, 634050, Russia

^bTomsk Department of the Trofimuk Institute of Petroleum-Gas Geology and Geophysics SB RAS, Akademicheskoy ave. 4, Tomsk, 634055, Russia

^cInstitute of Petroleum Chemistry SB RAS, Akademicheskoy ave. 4, Tomsk, 634055, Russia

Abstract

In the central part of Western Siberia a study of the chemical and organic compounds spatial distribution in the water of oligotrophic peatland has been carried out. It was shown that marsh water generally contains exceptionally low total dissolved salinity (TDS), low pH value, high content of organic matter and NH₄, increased content of Fe. The composition of organic matter is characterized by pronounced predominance of organic compounds and the presence of hydrocarbon and oxygen-containing compounds. Features of ionic and organic distribution in water and its ground were investigated.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of Tomsk Polytechnic University

Keywords: marsh water; chemical compounds distribution; organic matter; composition of hydrocarbons

1. Introduction

In Western Siberia marsh water is generally rich in dissolved organic matter, the content of which is several times higher than that of mineral elements^{1,2}. Such water is common for many peatlands of the world³⁻⁹. Meanwhile, the number of studies of ionic and organic distribution in the waters is very few that determines the relevance of the study.

The study area is an isotypical peatland site formed by oligotrophic sedge-sphagnum quagmire of Lake

* Corresponding author. Tel.: +7-961-892-44-08; fax: +7-382-249-2163.

E-mail address: olgnaim@mail.ru.

Murashka, where peat depth varies from 3 to 6 m. Depth of marsh water occurrence reaches 0.3 m on higher points; but on the lower points they flood the ground in between hummocks or form small lakes totaling an area up to first tens of sq. m. Peat deposit hydraulic conductivity values range widely, often between 0.1 – 3.0 m/d¹⁰.

Sampling points are located within undisturbed territory to the North (points ##1-4) and the South (points ##5-8) from Murashka Lake. Water from the lake is taken near the southern shore (Fig. 1).

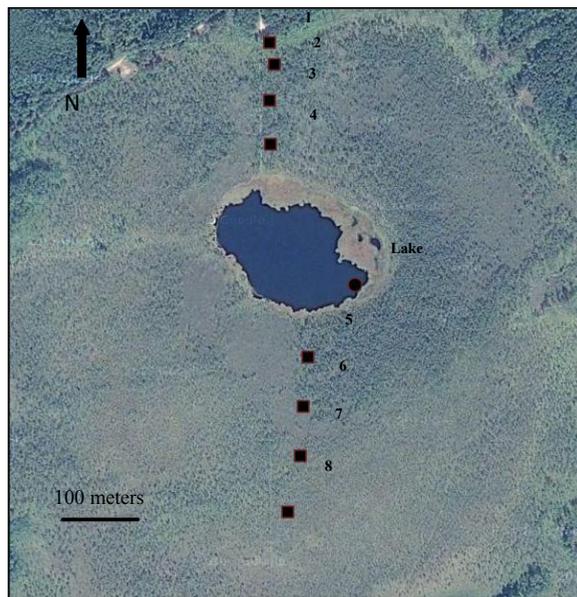


Fig. 1. Location of sampling points based on the Map data © 2014 Google.

2. Methods

The chemical analysis of water was performed at the certified hydrochemical laboratory of Tomsk Polytechnic University using the following methods: potentiometry for pH; titration for Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , Cl^- ; atomic absorption – NH_4^+ , PO_4^{3-} , and Si; polarography for Fe; and spectrometry for Na^+ and K^+ ; photometry for NO_3^- . Part of the samples was conserved and sent to the Institute of Petroleum Chemistry (Siberian Branch of the Russian Academy of Sciences) to conduct a detailed qualitative and quantitative analysis of the organic compounds. Bitumen components were extracted from water with chloroform, and hydrocarbons were concentrated from the extracts by column chromatography with aluminium oxide of level IV activity and elution with hexane. The composition of HC was determined using a NERMAG R-10-10C quadruple mass spectrometer and a Finnigan DFS chromatography–mass spectrometer.

3. Results and discussion

3.1. Hydrochemical data distributed on the area

In terms of chemical composition the marsh water is bicarbonate, less bicarbonate-chloride and bicarbonate-sulfate calcium or calcium-magnesium (Table 1).

In general the anionic composition of the water is homogeneous, except sample #1, wherein the content of bicarbonate, chloride and sulfate ions is considerably higher than in the other samples, the concentration of HCO_3^- exceeds that of other anions.

Table 1. Ionic composition, salinity (mg/L) and pH of marsh and lake water

#	pH	TDS	CO ₂	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Fe _{gen.}	NH ₄ ⁺	NO ₃ ⁻	PO ₄ ³⁻	Si
1	5.8	32.3	82.7	23.2	1.6	1.7	2.5	0.8	1.6	1.0	18.3	0.4	1.2	0.1	8.3
2	3.3	4.2	104.7	3.0	0.4	0.9	1.4	0.3	0.6	0.4	4.0	0.3	0.1	0.1	4.0
3	3.2	6.7	140.8	3.0	1.0	1.6	1.9	0.6	0.8	0.9	4.4	3.6	0.3	0.4	5.3
4	3.2	5.0	140.8	3.0	0.6	0.8	2.2	0.6	0.6	0.3	4.7	1.9	0.1	0.3	5.6
Lake	4.9	8.0	26.4	3.7	1.3	0.7	0.7	0.2	0.5	0.9	0.5	0.4	0.1	0.1	2.9
5	3.1	6.4	122.3	3.0	2.0	0.7	2.2	0.6	0.6	0.4	4.1	1.3	0.1	0.1	3.6
6	3.2	4.9	90.0	3.0	0.6	0.6	2.1	0.6	0.6	0.4	5.0	0.2	0.1	0.1	3.5
7	3.3	3.5	98.0	3.0	0.3	0.6	0.5	0.6	0.5	1.1	7.5	1.6	0.1	0.8	3.8
8	3.4	4.0	98.6	3.0	0.5	0.6	1.0	0.4	0.6	0.9	3.9	1.6	0.1	0.3	3.7

The cationic composition of water is heterogeneous. Basically Ca²⁺ ions prevail except for sample #1 and the lake water, where the content of K⁺ ions dominates over the others.

The marsh water of the isotypical peatland area is mainly acidic, pH ranges within 3.1-4.0, except for sample #1, wherein the pH reaches 6.0. In the lake water pH makes 4.9. From the northern part of the bog to the lake pH varies from 5.8 (sample #1) to 3.0, and then increases slightly (Fig. 2). Thus increased pH value in the lake water can indicate possible groundwater recharge of the lake.

The greatest value of the marsh water salinity exceeding 30 mg/L is recorded in sample #1, that can indicate the change in the recharge type during transition from the high-moor peat bog to the low-moor one which borders are seen in Fig. 1 In this case at changing water and mineral recharge of the bog there is an increase of salinity and pH values. Besides, this sample contains abnormally high value of iron (18.3 mg/L). As a whole in all samples of marsh water the concentration of Fe exceeds several times its Clark concentration in water of the marsh zone, making 0.9 mg/L for the province of moderately humid climate². In lake water the concentration of Fe is minimum (0.5 mg/L). Such specific behavior of iron in marsh water is explained by low ORP and the high content of organic matter.

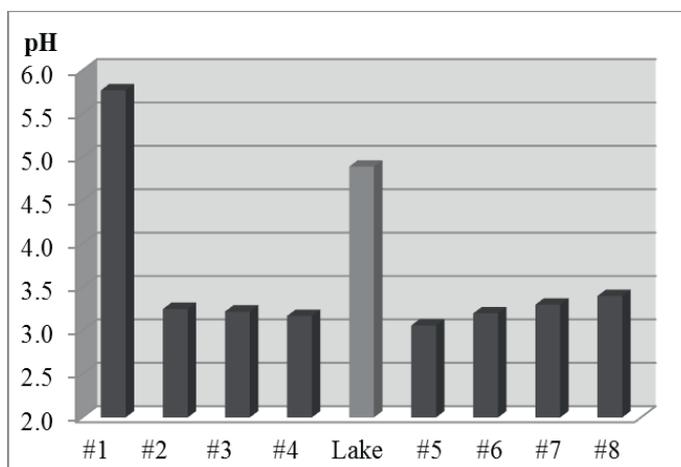


Fig. 2. Spatial distribution of pH values in water.

3.2. Organic compounds distributed in the area

In swamp water the content of organic substances exceeds that of mineral substances. The composition of organic matter is characterized by pronounced predominance of humic matter and the presence of hydrocarbon and oxygen-containing compounds (Table 2).

Table 2. Composition of organic matter of marsh and lake waters

#	C _{org} mg/L	Aquabiten	Hydrocarbons (HC) mkg/L	Oxygen-organic compounds (OOC)	HC/OOC
1	70.3	0.03	2.95	0.97	3.0
2	88.1	0.04	1.7	0.81	2.1
3	120.6	0.08	19.4	19.6	1.0
4	119.4	0.06	6.52	6.33	1.0
Lake	14.9	0.05	6.17	1.56	4.0
5	98.5	0.05	10.7	7.16	1.5
6	102.8	0.07	10.9	7.04	1.6
7	88.4	0.07	25.9	13.3	1.9
8	74.6	0.06	16.1	8.08	2.0

If moving from the northern part of the bog to the lake (from the sample #1 to sample #4), the relative content of hydrocarbons in the marsh waters decreases, but in the lake it is higher than in all the examined marsh water (Fig. 3). At further movement to the south from the lake the relative content of HC increases slightly.

The main hydrocarbons in the studied water are n-alkanes (83-97% of the total HC). In all marsh waters there are pentacyclic terpenes and squalene. They are not found only in lake water, where HC are presented by alkanes solely (Table 3). The rest of the HCs are observed only in the part of marsh water.

Bicyclic and tricyclic terpanes as well as steranes and arenas are absent in water of the northern part of the bog (#1 and 2). This part is characterized by the lowest values in all other groups of hydrocarbon concentration in water.

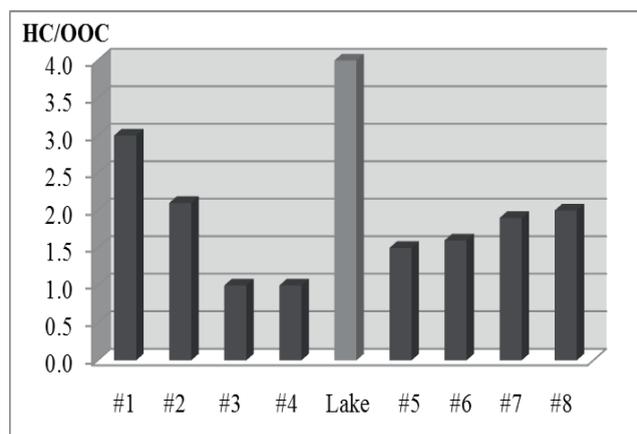


Fig. 3. Spatial distribution of the relations of HC sum content to the OOC sum content in water.

Table 3. Concentration of particular hydrocarbon groups in the waters (mkg/L)

Hydrocarbon group	1	2	3	4	Lake	5	6	7	8
n-alkanes	2.87	1.66	15.8	5.73	6.17	8.75	9.72	24.93	15.18
Squalene	0.009	0.012	0.27	0.12	0	0.14	0.19	0.02	0.22
Bicyclic terpanes	0	0	1.38	0.26	0	0.21	0.36	0.44	0.28
Tetracyclic terpanes	0	0	0.25	0.03	0	0.05	0.08	0.07	0.02
Pentacyclic terpanes	0.07	0.03	0.71	0.11	0	0.36	0.15	0.11	0.28
Steranes (typicaly oil)	0	0	0.11	0.21	0	0.32	0.28	0	0.05
Aromatic hydrocarbons	0	0	0.11	0.06	0	0.09	0.16	0.35	0.11

The water of sample #3 is characterized by the maximum concentration of cyclic saturated (except steranes) HC. Marsh water samples taken near the northern and southern shore of the lake are rich in steranes. When moving from the lake to the south and to the north the sterane concentration in water decreases. To the southern and northern direction from the lake the relative content of aromatic structures in the hydrocarbon mixture is also reduced.

Among OOC in marsh water fatty acids dominate (Table 4) of C₇-C₂₀ structure with prevalence of palmitic acid, whereas in water sample #4 located near the northern shore of the lake caprylic acid dominates.

Table 4. Composition of oxygenated organic compounds in waters (mkg/L)

Group of compounds	1	2	3	4	Lake	5	6	7	8
Fat acids	0.7	0.45	4.17	3.38	0.64	3.13	2.21	8.03	3.18
Methyl esters	0.003	0.007	0.02	0.02	0.04	0.09	0.03	0	0.02
Ethyl esters	0.18	0.22	0.27	0.32	0.74	0.2	0.14	0.03	0.24
Isopropyl ester	0.02	0.01	0.04	0.04	0.02	0.07	0.05	0	0.03
n-alkanones	0.03	0.05	6.06	1.68	0.12	1.3	1.38	4.63	1.01
i-alkanones	0.06	0.04	1.21	0.34	0	0.4	0.3	0.9	0.33
Tocopherols	0	0	0.62	0.12	0	0.13	0.1	0.04	0.07
n-aldehydes	0.18	0.08	2.49	0.53	0	0.38	0.61	3.53	1.07
Terpinoides	0	0	4.48	0.12	0	1.47	1.49	0.27	0.81
-alkohole	0	0	1.95	0.07	0	0.71	0.79	0.11	0.37
-ketones	0	0	2.53	0.05	0	0.76	0.7	0.16	0.44
Steroid	0.02	0.04	4.2	0.39	0	1.12	1.57	0.41	1.76
-alkohole	0.02	0.04	3.05	0.36	0	0.9	1.32	0.28	1.52
-ketones	0	0	1.16	0.03	0	0.22	0.25	0.13	0.25

Only in the lake water fat acids are presented mostly by palmitic acid, and the main compounds of OOC are ethyl esters among which palmitate dominate sharply. In marsh water among ethyl esters, along with palmitate prevailing, the concentration of cerotic acid ester is rather high.

From the northern part of the bog to the lake shore the concentration of ethyl esters of fat acids increases, reaching its maximum in the lake water, then again decreases in the southward. Methyl esters show a trend to concentration change, but their content in the lake water is lower than in the marsh waters near the southern coast.

The contents of all other groups of OOC as well as the concentration of the majority of HC groups are maximum in water sample #3. In the northern part of the bog in marsh water ketones, tocopherols and triterpenoids are absent.

4. Conclusion

According to the data obtained the most probable reasons for the differences in the composition and distribution of chemical and individual organic compounds in the studied waters are the structure of peat deposits, species composition of bioproducers (mosses, bacteria, and vegetation), the terms of organic matter deposition as well as the type of water-mineral recharge of the bog¹¹.

Peat deposits can be a source of not only humic and mineral compounds entering the marsh water, but also organic compounds of specific class (aromatic, cyclic hydrocarbons, oxygenated organic compounds, etc.), indicating similarity of the initial organic products and allows for tracing the transformation of substances in these natural sites.

References

1. Vernadskii V.I. History of Natural Waters. Moscow: Nauka; 2003 [in Russian].
2. Shvartsev S.L. Geochemistry of fresh groundwater in the main landscape zones of the Earth, *Geochem. Int.* 2008; **46**: 13, p. 1285–1398.
3. Schnitzer M. Soil Organic Matter. Amsterdam: Elsevier; 1978.
4. Magdi Selim H. Competitive Sorption and Transport of Heavy Metals in Soils and Geological Media. CRC Press; 2012.
5. Inisheva L.I., Zemtsov A.A., Novikov S.M. Vasyugan Mire. Natural Conditions, Structure and Functioning. Tomsk: Tomsk State Pedagogical University Press; 2011.
6. Buckingham S, Tipping E, Hamilton-Taylor J. Concentrations and fluxes of dissolved organic carbon in UK topsoils. *Sci Total Environ.* 2008; **407**: 460–470.
7. Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Hogasen T, et al. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature.* 2007; **450**: 537–541.
8. Tipping E, Woolf C. Humic substances in acid organic soils – modeling their release to the soil solution in terms of humic charge. *J Soil Sci.* 1990; **41**: 573–586.
9. Lars Rosenqvist, Dan B. Kleja, Maj-Britt Johansson. Concentrations and fluxes of dissolved organic carbon and nitrogen in a *Picea abies* chronosequence on former arable land in Sweden. *Forest Ec. and Man.* 2010; **259**: 275–285.
10. Shvartsev S.L., Serebrennikova O.V., Zdvizhkov M.A., Savichev O.G., Naymushina O.S. Geochemistry of wetland waters from the lower Tom basin, Southern Tomsk oblast. *Geochem. Int.* 2012; **50**: 4: 367–380.
11. Serebrennikova O.V., Kadychagov P.B., Gulaya E.V., Preis Yu.I. Hydrocarbon composition of the organic matter of peats in the south of Western Siberia, *Solid Fuel Chemistry.* 2010; **44**: 5, p. 324-334.