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## Natural and Anthropogenic Organic Compounds in Bottom Sediments of Lakes in Southern Siberia

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### Abstract

The distribution of natural and anthropogenic components, and also compounds of mixed origin in sediments of lakes in Southern Siberia, and also Altai steppes and mountains characterised by a varying degree of mineralisation (between 0 and 300 g/dm<sup>3</sup>) was explored by gas chromatography-mass spectrometry. The contribution of the major organic matter sources to the composition of bottom sediments was assessed. Specific oil compounds were determined. As determined, there was the formation of the composition of bottom sediments mainly due to compounds of biogenic and mixed origin. Sections with a high content of pollutants, such as petroleum and pyrogenic hydrocarbons, and also isoalkylbenzenes, *i.e.*, likely degradation products of surfactants, were detected.

**Key words:** lakes, bottom sediments, water, organic compounds, composition, genesis

### INTRODUCTION

Bottom sediments (BS) of water bodies are a natural accumulator of organic and inorganic compounds including the most dangerous and toxic species. However, unlike water, they are less exposed to seasonal fluctuations [1–4]. Papers [5–7] assessed the quality of swamp, lake, and river waters, and also bottom sediments of water bodies of the Siberian region was assessed according to the composition of extractive organic compounds. Research carried out in these works mainly covers the territory of oil production, which is clearly not enough for the huge Siberian region, characterized by developed transport infrastructure. Numerous fresh and salt lakes with unique chemical composition and therapeutic mud are located in the territory of Siberia and Altai, which attracts a large number of tourists. The development of balneology requires the assessment of the current and projected environmental situation to prevent pollution and degradation of recreational water bodies [8].

Research on the composition of organic components of lake sediments in the Siberian region available to date mainly deals with hydrocarbons [5, 7] and especially hazardous pollutants [9]. Single papers have examined the composition of biomolecules in water bodies of Siberia [6, 10–13] and in one of the lakes of Altai Krai [14]. However, the issue of the effect of mineralisation that may have a significant effect on the composition of organic compounds present in water and sediments has not been paid attention to. Therefore, the objective of this research was to determine the effect of mineralisation on the chemical composition of natural organic compounds in BS of water bodies in Siberia and Altai. As these territories are located in the area of anthropogenic impact with an opportunity of oil pollution, research has been carried out to detect specific oil compounds. The paper also analyses mineralisation interlinks of water bodies with the accumulation and distribution of introduced oil components in the water-sediment system.

## RESEARCH MATERIALS AND METHODS

In order to explore the composition of natural organic compounds in BS of water bodies, lakes of southern Siberia, Altai steppes and mountains were selected. The lakes are characterised by varying degrees of mineralisation (between 0 and 300 g/dm<sup>3</sup>): fresh (a mineralisation of less than 1 g/dm<sup>3</sup>), moderately salty (a mineralisation of 4.2 g/dm<sup>3</sup>), slightly salted (8 g/dm<sup>3</sup>), and saline (more than 34 g/dm<sup>3</sup>). Samples of water and BS were selected in some lakes in the territory of Altai Krai (AK), Republic of Khakassia (RK) and Republic of Altai (RA) in June–July of 2010–2018. In case of some lakes, samples were taken from different parts of the water body and in periods differing in the amount of atmospheric precipitation.

The mineralisation of water sampled at a distance of 10–20 cm of the bottom in sampling points of BS was determined according to the value of dry residue [15]. A portion of aqueous samples for the subsequent isolation and analysis of the composition of organic compounds was filtered through a membrane filter with a pore size of 0.45 µm. Liposoluble constituents (lipids) of the aqueous phase were extracted with three 20 cm<sup>3</sup> portions of a 10 % hexane solution in chloroform at ambient temperature, extraction time of 5 minutes. Extract portions were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated with a rotary evaporator. Lipids were extracted from sediments with vapours of a 7 % methanol solution in chloroform.

The quantity of microorganisms in water was determined according to the technique described in [16]. Analysing the group composition and content, and also individual organic compounds (*n*-alkanes, carboxylic acids, their methyl, isopropyl and long-chain esters, aldehydes, alcohols, ketones, tocopherols, steroids, sesquiterpenes, diterpenes, pentacyclic triterpenes (PT), aromatic hydrocarbons, drimanes, cheilanthanes, and also oil steranes and hopanes) in samples of water and BS was carried out using Thermo Scientific DFS GC/MS (Germany). The system was provided by Tomsk Centre for Collective Use SB RAS.

## RESULTS AND DISCUSSION

Table 1 reports the list and the major performance of the samples. Silt (S) and sand-silt (SS) varieties present bottom sediments of the lakes. A strong hydrogen sulphide odour is typical for BS of Solenoye, Tus, Mormyshanskoye, and Gorkoye lakes (Novichikhinskiy district). The waters of all investigated lakes contain heterotrophic bacteria (HB) *Bacillus* and *Pseudomonas*; some waters also have *Micrococcus* and *Sarcina*, the content of which is increased from fresh and slightly salted to highly mineralised ones (see Table 1). The presence of cyanobacteria (*Phormidium Anabaena*, *Gloeocapsa*, and *Oscillatoria*) was determined in salt and hypersalt waters. Sulphate-reducing bacteria (*Desulfobacter* and *Desulfosarcina*) were also detected in Mormyshanskoye Lake.

TABLE 1

Performance of samples of water and bottom sediments in the investigated lakes

Samples	Lakes (sediment composition and sampling point)	Lake location	Mineralisation, g/dm <sup>3</sup>	pH	Sampling year	HB quantity in water, thousand cl/cm <sup>3</sup>
Itk-12	Iteul (SS, eastern part)	Shirinskiy district, RK	0.24	7.8	2012	2.53
Tus-10	Tus (SS, eastern part)	Same	103	8.0	2010	31.3
Tus-13	Tus (S, eastern part)	»	128.0	8.4	2013	400
Aya-12	Aya (SS, eastern part)	Altai district, RA	0.07	7.4	2012	48.9
Most-16	Mostovoye (SS, western part)	Zavyalovskiy district, AK	0.48	8.4	2016	27
Shel-16	Schelochnoye (SS, northern part)	Same	4.2	9.3	2016	29
Sol-12	Solenoye (S, southern part)	»	116.3	7.6	2012	4200
Sol-16(1)	Solenoye (clay, western part)	»	ND	ND	2016	ND
Sol-16(2)	Solenoye (S, eastern part)	»	34.5	8.1	2016	55
Gor-18*	Gorkoye (SS, western part)	Romanovskiy district, AK	7.8	8.7	2018	2
Morm-12	Mormyshanskoye (S, eastern part)	Same	329.8	7.5	2012	3900
Morm-18*	Same	»	80.2	7.8	2018	1.8
Gor-12N	Gorkoye (SS, south-eastern part)	Novichikhinskiy district, AK	96.8	9.1	2012	18.9

Note. ND is not determined.

\* Samples of BS and water were selected after a period of heavy rains, which led to a decrease in water mineralisation.

**Chemical composition  
of natural organic compounds  
in bottom sediments of lakes**

Acyclic systems represented by *n*-alkanes, alkane acids, and their methyl esters, and also by *n*-alkane-2-ones, *n*-alkanols and *n*-aldehydes are prevailing in the composition of lipids of BS of lakes (Table 2). There is the maximum relative content of acyclic compounds in fresh, relatively deep, and large Lake Itkul (over 94 %), minimum (around 60 %) – in shallow Solenoye Lake. The same lakes are characterised by minimum (1.4 %) and maximum (27–37 %) fractions of cyclic biomolecules, respectively including sesqui- and diterpenes, and also steroids and PT. Fractions of cyclic biomolecules in shallow, well-warmed salt

Tus and Mormyshanskoye lakes are also increased and account for 14 and 20 %, respectively.

Among acyclic structures in all the lakes, regardless of salt content, *n*-alkanes are prevailing. Fatty acids are on the second place according to the occurrence rate. The sapropel in the eastern end of Solenoye Lake also contains *n*-aldehydes in large quantities. This sample is characterised by the maximum relative content of tocopherol. Aliphatic alcohols, *i.e.* *n*-alkanols, in concentrations as high as 150 ng/g are found only in highly mineralised Solenoye and Mormyshanskoye lakes.

In series of  $C_{6(8)}-C_{20(22)}$  carboxylic acids in all BS, even  $C_{12}-C_{18}$  homologues are prevailing and among them, palmitic acid ( $C_{16}$ ). Methyl palmitate is prevailing among carboxylic acids with a formula of  $C_{13}-C_{29(31)}$ . *n*-Aldehydes, *n*-alkane-2-ones,

TABLE 2

Concentration of series of organic compounds in bottom sediments of lakes of Khakassia and Altai, ng/g

Organic comp.	Samples												
	Aya-12	Itk-12	Most-16	Shel-16	Gor-18	Sol-16(1)	Sol-16(2)	Morm-18	Gor-12N	Tus-10	Sol-12	Tus-13	Morm-12
Mineralisation, g/cm <sup>3</sup>	0.1	0.2	0.5	4.2	7.8	–	34.5	80.2	96.8	103	116	128	330
<i>Biological compounds</i>													
Sesquiterpenes	0	0	4	8	0	5	198	0	0	0	0	0	0
Diterpenes	3*	0.3	0	0	0	0	17*	0	2	0	3	0	0.3
PT	83	2	11	12	338	3	1180	1003	106	296	110	100	4
Steroids	34	1	30	20	790	13	3180	1301	109	504	497	31	19
Carboxylic acids	39	40	147	184	2745	147	1480	1925	171	2151	97	94	51
Methyl esters	32	32	56	50	30	46	103	107	26	179	49	57	7
Isopropyl esters	9	4	38	18	10	29	37	11	11	56	7	18	4
<i>n</i> -Alkane-2-ones	27	5	16	4	173	5	659	643	254	94	57	12	12
<i>n</i> -Aldehydes	59	1	0	0	105	0	3276	689	0	0	16	13	4
<i>n</i> -Alkanols	0	0	0	0	0	0	0	127	0	0	145	0	4
Tocopherols	2	0	4	4	18	2	346	83	4	40	19	2	0
<i>Oil compounds</i>													
Steranes	0	1	0	0	0	0	0	0	30	0	7	3	4
Hopanes	2	1	2	0	0	1	0	15	18	1	4	2	3
Cheilanthanes	1	0.4	0	0	0	1	0	0	5	0	5	0	1
Drymanes	0	0	0	0	0	0	0	2	0	157	0	0	0
Cyclohexane	4	1	0	1	2	0.4	0	0	5	9	0	2	2
<i>Mixed genesis compounds</i>													
LAB	14	2	2	0	0	4	0	0	6	45	2	7	2
PAC	6	3	9	7	0	10	51	6	9	282	8	9	2
<i>n</i> -Alkanes	696	162	569	174	4204	191	6366	5377	850	3572	628	575	199
<i>Total</i>	1011	256	888	482	8415	457	16893	11289	1606	7386	1654	925	319
<i>CPI (C<sub>20</sub>-C<sub>32</sub>)</i>	2.8	1.4	2.1	1.4	1.5	1.3	5.0	1.8	3.4	1.5	2.7	1.3	2.8

Note. The dash indicates that no data are available.

\*Total amount of diterpenes, des-A-triterpenes, and des-A-triterpane.

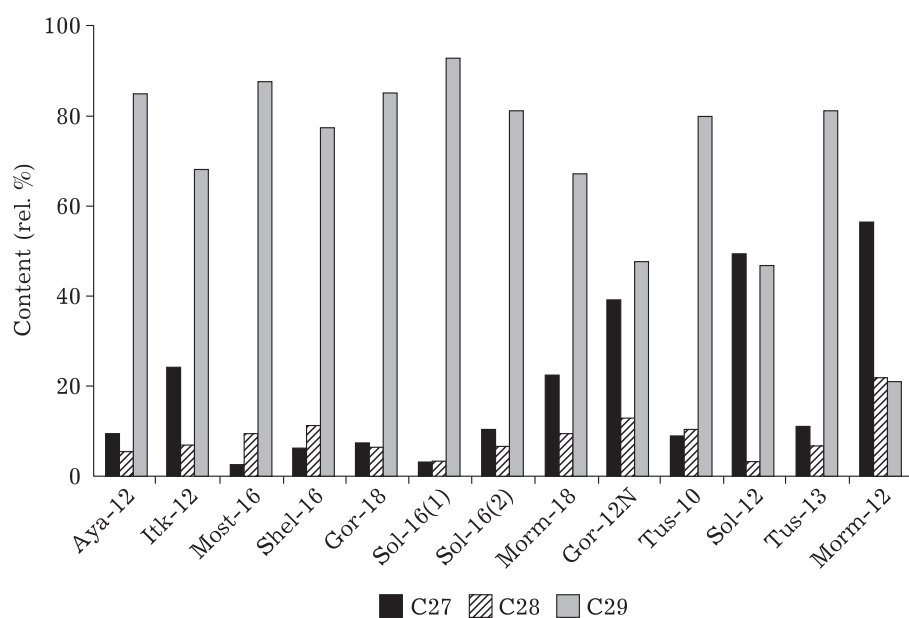


Fig. 1. Relative content of steroid moieties in in bottom sediments of the lakes. Here and in Fig. 2–4, see symbols in Table 1.

and *n*-alkanols are mainly represented by even  $C_{20(22)}-C_{30(32)}$ , uneven  $C_{21}-C_{33}$ , and even  $C_{20(22)}-C_{26(28)}$  homologues, respectively. The  $\alpha$ -configuration is prevailing among tocopherols.

As a rule, steroids are prevailing in the composition of cyclic biomolecules, except for fresh Aya and Itkul lakes, and also silty BS of Tus Lake where the PT content is higher. There is the maximum fraction of steroids in highly mineralised Solenoye and Mormyshanskoye lakes. Derivatives of sitosterol ( $C_{29}$ ) that are typical for vegeta-

tion forms (Fig. 1) are prevailing in most BS of the lakes. The relative content of derivatives of cholesterol ( $C_{27}$ ) is elevated in highly mineralised Solenoye and Mormyshanskoye and also Gorkoye lakes. That may be a consequence of the widespread use of crustaceans *Artemia* in these water bodies. The fraction of derivatives of campesterol ( $C_{28}$ ) is relatively steady and equals to 5–20 % in all samples. Derivatives of lanosterol ( $C_{30}$ ) were found in low concentrations only in the southern part of Solenoye Lake and in the sediments of Schelochnoye

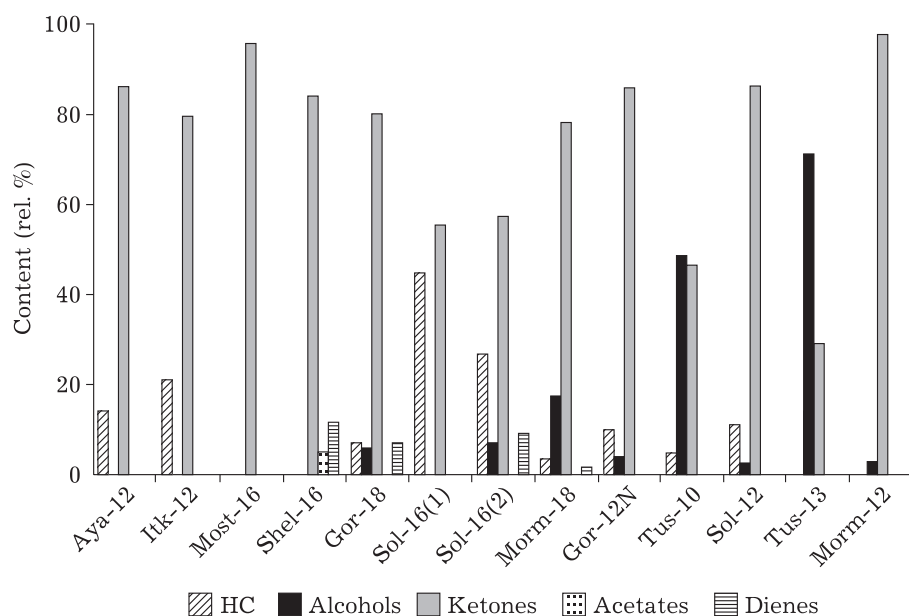


Fig. 2. Functional composition of steroids in bottom sediments of the lakes. Symbols can be seen in Table 1.

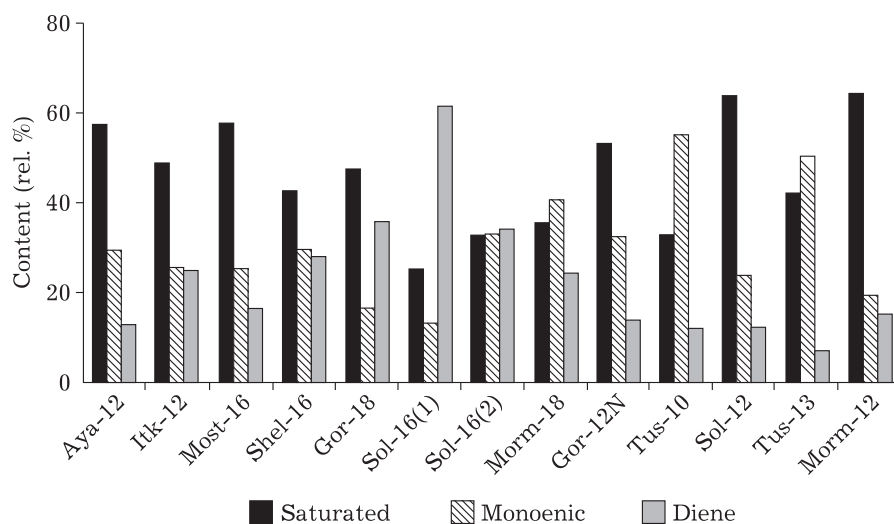


Fig. 3. Degree of hydrogen unsaturation for steroids in bottom sediments of lakes. Symbols can be seen in Table 1.

Lake; 24-methylenecycloartane-3-one ( $C_{31}$ ) was detected only in BS of the east end of Solenoye Lake.

For the most part, steroids are presented by compounds with the ketone functionality, such as stanone and stenone derivatives. In the first place, that is referred to fresh lakes (Fig. 2), in BS of which stanones are prevailing like in most other lakes.

There are close concentrations of stanones and stenones in BS to the east of Solenoye Lake. There is an increased fraction of hydrocarbons (HC), such as sterenes, in clay sediments. The presence of dienes and acetates is typical for BS in moderately salted and slightly salted lakes. Alcohols (sterols) also appear in weakly salted lakes and are the main group of steroids in highly mineralized Tus Lake.

According to the degree of the hydrogen unsaturation in the composition of steroids in most BS, saturated compounds are prevailing (Fig. 3). Steroids with two double bonds are prevalent in clay sediments of Solenoye Lake, whereas mono-unsaturated systems – in BS of Tus Lake.

The PT compounds that are prevailing among terpenoids of all investigated lakes are presented by mono- and di-unsaturated perhydropicenes ( $C_{30}$ ) and cyclopentaperhydrochrysene compounds ( $C_{27}$ – $C_{30}$ ), HC systems, ketones, alcohols, and acetates. Perhydropicenes with prevailing ketones are prevalent in all lakes. Among cyclopentaperhydrochrysene compounds, in most BS the concentration of lupene derivatives with alcohol or keto-moieties is maximum. Hopenes are prevalent in fresh lakes Mostovoye and Aya, whereas keto-substituted hopane compounds are prevailing in silt deposits of Mormyshanskoye, Solenoye, and

Gorkoye lakes (Novichikhinskiy district). Sesqui- and diterpenes are sporadically distributed in the lakes. These species were recorded at the maximum amount in BS near the east coast of Solenoye Lake covered with heavy vegetation. Sesquiterpenes are presented here widely and diversely, whereas des-A-triterpenes and des-A-triterpane are added to diterpene (retene). The origin of triterpane derivatives is linked to higher terrestrial vegetation [17]. The same compounds are also present at lower concentrations in the BS of the fresh lake Aya surrounded by luxuriant vegetation along the entire perimeter.

The presence of *n*-alkanes in natural objects is usually linked to their production by biological systems or pollution with oil components, which is indicated by the nature of the molecular mass distribution (MMD) of these compounds. The prevalence of homologues with an uneven number of carbon atoms over even ones is typical for plants and contemporary sediments. The former is levelled in oil and petroleum products. There is the complex nature of MMD (Fig. 4) for *n*-alkanes in BS.

The values of odd CPI (carbon preferences index) coefficients, *i.e.*, the ratio of molecules with an odd number of carbon atoms to even ones, in the  $C_{20}$ – $C_{32}$  range lie in the interval of 1.3–5.0. As it is known, CPI values for biogenic *n*-alkanes may reach 6 and over, whereas the former are close for oil species. Hence, the content of *n*-alkanes indicates and the presence of oil components in definite quantities, in addition to biogenic moieties, in BS. The maximum MMD for *n*-alkanes in the low-molecular-mass region falls on  $C_{17}$  in all lakes;  $C_{25}$ – $C_{31}$  are prevailing in the high-molecular-mass

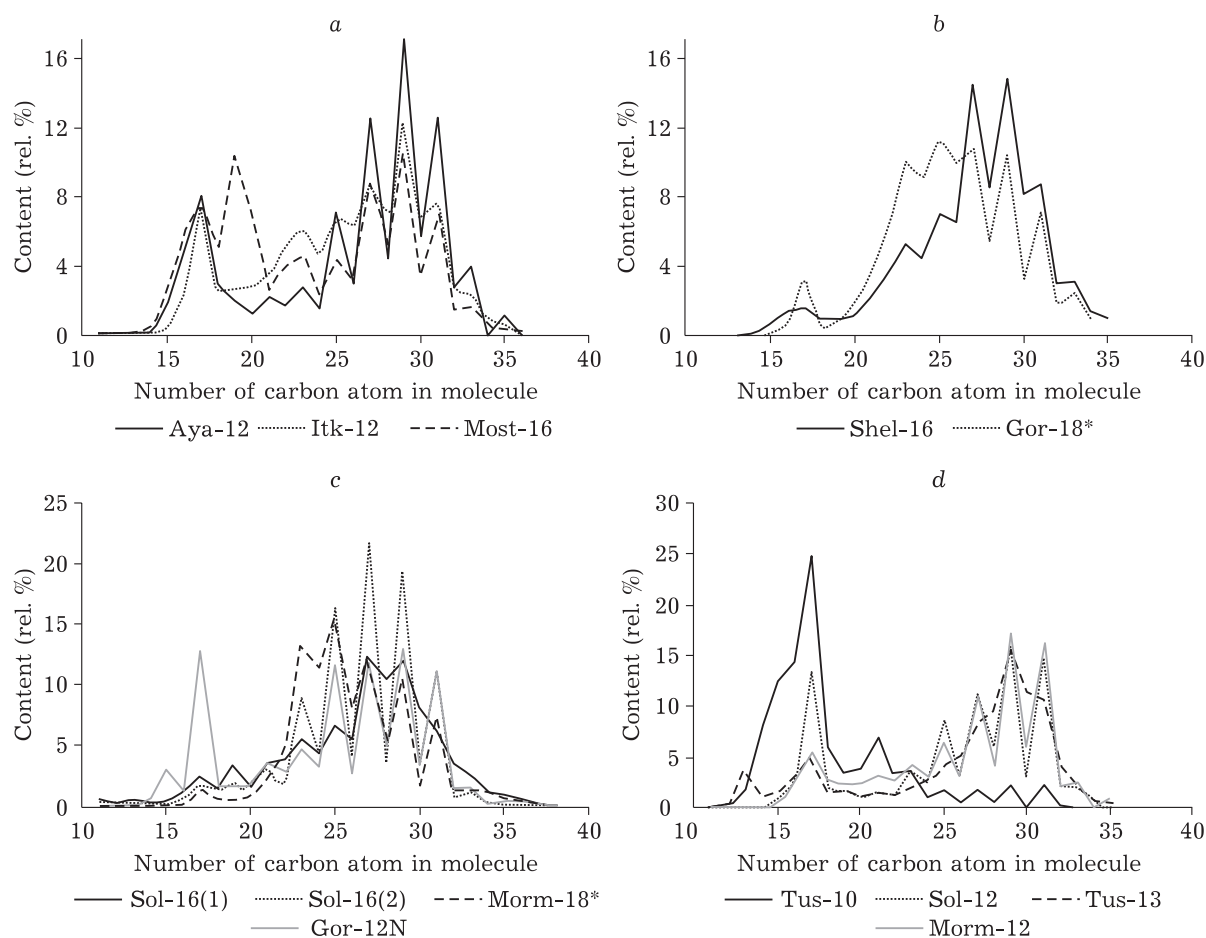


Fig. 4. Molecular mass distribution of *n*-alkanes in lake bottom sediments: *a* – fresh lakes, *b* – moderately salted and slightly salted, *c* – weakly saline (between 34 and 100 g/dm<sup>3</sup>), and *d* – strongly saline (from 100 g/dm<sup>3</sup> and higher).

region. The prevalence of uneven C<sub>27</sub>–C<sub>31</sub> homologues in the high-molecular-mass region is typical for terrestrial vegetation [18]. The content of C<sub>23</sub> and C<sub>25</sub> species is indicative of the contribution of aquatic plants [19] into the sediment. Contributing is maximum in the BS of the eastern portion of Solenoye Lake (Fig. 5).

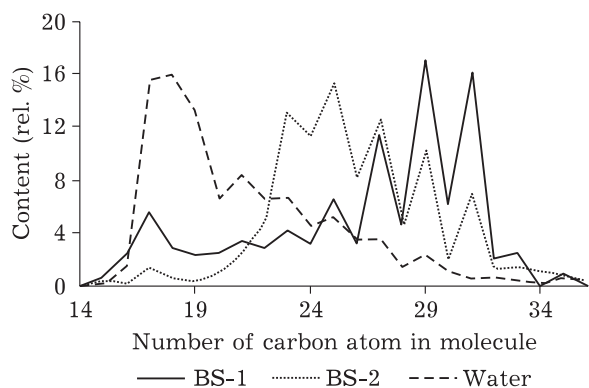


Fig. 5. Molecular mass distribution of *n*-alkanes in bottom sediments and desalted water of Mormyshanskoye Lake.

Mono-, bi-, tri-, and tetracyclic compounds were detected among aromatic HC systems in the investigated waters (Table 3). There were found no aromatic compounds in Gorkoye Lake (Romanovskiy district). There are monoaromatic compounds in BS; they are comprised of the so-called linear alkylbenzene (LAB) species. The latter are C<sub>18</sub>–C<sub>19</sub> benzene compounds with alkyl substituents branched at the  $\alpha$ -atom of the alkyl chain. Linear alkyl-substituted benzene compounds were determined in 9 lakes. The maximum fraction (as high as 70 %) of these species as a part of aromatic HC was determined in the fresh Aya Lake. The relative content of LAB in the remaining lakes is 13–55 %. The origin of these systems is usually linked to the environmental addition of surfactants. The latter may be transferred with wind and fall into the lake together with fallen atmospheric precipitation [20].

As it is known, di- and triaromatic compounds may be of both natural and anthropogenic genesis [21, 22]. According to existing views, aromatic

TABLE 3

Concentration of aromatic compounds in bottom sediments of Khakassia and Altai lakes, ng/g

Aromatics comp.	Samples												
	Aya-12	Itk-12	Most-16	Shel-16	Gor-18	Sol-16(1)	Sol-16(2)	Morm-18	Gor-12N	Tus-10	Sol-12	Tus-13	Morm-12
Mineralisation, g/cm <sup>3</sup>	0.1	0.2	0.5	4.2	7.8	–	34.5	80.2	96.8	103	116	128	330
<b>Monoaromatics (LAB)</b>	<b>13.5</b>	<b>1.9</b>	<b>1.7</b>	<b>0</b>	<b>0</b>	<b>3.7</b>	<b>0</b>	<b>0</b>	<b>5.9</b>	<b>45.1</b>	<b>2.1</b>	<b>7.1</b>	<b>1.8</b>
<b>Biaromatic species</b>	<b>3.7</b>	<b>0</b>	<b>3.6</b>	<b>2.4</b>	<b>0</b>	<b>3.4</b>	<b>50.8</b>	<b>6.0</b>	<b>3.0</b>	<b>242.6</b>	<b>4.0</b>	<b>6.8</b>	<b>0.3</b>
Naphtaline compounds	0	0	0.8	0	0	0.5	0	0	0	0	0	0.4	0
Methylnaphthalene compounds	0	0	0.5	0.4	0	0.9	0	0	0	28.8	0	1.5	0
Dimethylnaphthalene compounds	0.5	0	0.8	0.8	0	1.1	46.4	6.0	1.5	114.5	1.4	3.4	0
Trimethylnaphthalene compounds	3.2	0	1.1	1.2	0	0.5	4.4	0	1.6	99.3	2.6	1.3	0.3
Biphenyl	0	0	0.4	0	0	0.4	0	0	0	0	0	0.2	0
<b>Triaromatic</b>	<b>1.7</b>	<b>3.0</b>	<b>4.3</b>	<b>4.0</b>	<b>0</b>	<b>5.7</b>	<b>0</b>	<b>0</b>	<b>2.8</b>	<b>35.2</b>	<b>0.2</b>	<b>1.4</b>	<b>0.4</b>
Phenanthrene	0	0.8	3.0	2.1	0	0	0	0	2.5	20.4	0	1.2	0.4
Methylphenanthrene compounds	1.4	0.8	1.1	0.9	0	2.2	0	0	0	12.9	0	0	0
Dimethylphenanthrene compounds	0	1.1	0.0	1.0	0	1.9	0	0	0	0	0	0	0
Trimethylphenanthrenes	0	0.3	0	0	0	1.3	0	0	0.0	0	0	0	0
Fluorene	0.2	0	0.2	0	0	0.4	0	0	0.3	1.9	0.2	0.2	0
<b>Tetraaromatic species</b>	<b>0.5</b>	<b>0.2</b>	<b>0.7</b>	<b>0.5</b>	<b>0</b>	<b>0.8</b>	<b>0</b>	<b>0</b>	<b>2.8</b>	<b>4.4</b>	<b>3.8</b>	<b>0.6</b>	<b>0.8</b>
Fluoranthene	0.2	0.1	0.3	0.5	0	0.4	0	0	1.7	4.4	2.3	0.3	0.5
Pyrene	0.2	0.1	0.4	0	0	0.3	0	0	1.1	0	1.5	0.3	0.3

Note. The dash indicates that no data are available.

HC systems are not synthesised by living organisms but are generated from organic compounds contained therein during the transformation of organic matter resulting from biochemical and thermochemical reactions. Aromatic systems discovered in nature are bound with lignins, pigments, and essential oils [18, 23, and 24]. Likely precursors of mono, bi-, and triaromatic compounds are carotenoids, terpenoids, and alkaloids [18].

For example, potential precursors of alkyl-substituted naphthalene compounds may be cyclic sesquiterpenoid systems contained in essential oils of

many plants. Anthropogenic sources of aromatic compounds of lake waters, in particular, polymethyl-substituted compounds may be oil and petroleum products, and also indirectly plants that accumulate these systems from aqueous solutions, air, and soil [25]. Pyrene and fluoranthene derivatives are contained in oils in low concentrations [18], represent coal combustion products, and are transferred with wind. Therefore the indicated species are referred to pyrogenic HC compounds [26].

Dimethyl- and trimethyl-substituted naphthalene compounds typical for oil are prevailing

TABLE 4

Fraction of typical oil components in the composition of organic compounds of bottom sediments, rel. %

Oil components	Samples												
	Aya-12	Itk-12	Most-16	Shel-16	Gor-18	Sol-16(1)	Sol-16(2)	Morm-18	Gor-12N	Tus-10	Sol-12	Tus-13	Morm-12
Steranes	0	0.5	0	0	0	0	0	0	1.9	0	0.5	0.3	1.2
Hopanes	0.2	0.2	0.2	0	0	0.1	0	0.1	1.1	0.02	0.2	0.2	0.9
Cheilanthanes	0.1	0.1	0	0	0	0	0	0	0.3	0	0.3	0	0.3
Drimanes	0	0	0	0	0	0	0	0.01	0	2.3	0	0	0
Cyclohexane	0	1.6	0.7	0	0	0.1	0	0	0.3	0.1	0.3	0	0.5
<i>Total amount</i>	0.3	2.4	0.9	0	0	0.2	0	0.1	3.6	2.5	1.3	0.5	2.9

in series of diaromatic HC derivatives. Those systems were found in maximum fractions in Solenoye and Tus lakes. Phenanthrene and its methyl-substituted homologues (see Table 3) are prevailing among triaromatic HC derivatives. On the contrary, tetracyclic aromatic HC compounds are presented by unsubstituted fluoranthene and pyrene. Hence, aromatic HC compounds in the investigated BS are mainly of anthropogenic origin.

#### *Distribution and composition of oil components in lake bottom sediments*

Cyclohexane derivatives with long alkyl substituents that are typical oil compounds not found in living nature. These compounds were found in BS of seven of the investigated lake areas. There are no these systems only in the south and east of the Solenoye Lake, the west of the Mostovoye Lake and in the BS of Mormyshanskoye Lake. The lakes were selected after a period of heavy rains, which caused a decrease in the mineralisation of this lake (Table 4).

Bicyclic HC, such as drimanes, that become more concentrated in light fractions of oil are present in significant concentrations within sand-silt sediments of Tus Lake and BS of Mormyshanskoye Lake that were selected after a period of heavy rains.

Tricyclic cheilanthanes and pentacyclic hopanes are typical for more high boiling oil fractions. Here-with, hopanes are almost not exposed to weathering processes [27]. Cheilanthanes are present in BS of a half of the lakes investigated (see Table 4). Hopanes that are prevailing among the majority of the investigated BS are more widely spread in these lakes. These systems were not detected only near the eastern steep bank of the Solenoye Lake and the wide beach of the Schelochnoye Lake, to which there is no opportunity to get closer by transport means, and also in the Gorkoye Lake (Romanovskiy district), in which BS were selected after intense rains that had an effect on an increase in the level and a decrease in the mineralisation of lake water.

Steranes that are presented by the regular and rearranged configuration are present in muddy sediments of highly mineralised Mormyshanskoye Lake and the southern tip of Solenoye Lake, and sand-silt sediments of Gorkoye (Novichikhinskiy district) and Itkul Lake. Steranes in silty deposits of Tus Lake include regular configurations only; in the rest ones, a ratio of diasteranes to regular ones is changed between 0.1

and 0.5 in the BS of Solenoye Lake and Gorkoye Lake, correspondingly. As demonstrated by the analysis of the location of sampling points of BS containing an increased amount of oil components, the latter are located near car roads or shores equipped with campings.

#### *Mineralisation effect on the distribution of natural and oil organic compounds in the water-sediment system*

Changing the content of organic compounds in BS when lake water is diluted with intense rainfall and, as a result, upon a decrease in its mineralisation between 330 g/dm<sup>3</sup> (BS-1) and 80 g/dm<sup>3</sup> (BS-2), and also the composition of organic components in the desalinated aqueous phase have been analysed as exemplified by Mormyshanskoye Lake (Table 5).

A decrease of mineralisation in the lake is accompanied by changing the content of certain classes of organic compounds in BS. Oil steranes and cyclohexane derivatives vanish; the content of hopanes is decreased due to the loss of homohopanes. The relative content of *n*-alkanes is decreased; the appearance of their molecular mass distribution is changed, in other words, the fraction of C<sub>16</sub>-C<sub>21</sub> and C<sub>29</sub>-C<sub>33</sub> homologues is reduced (see Fig. 5). The fraction of *n*-alkanes as a part of organic components of the aqueous phase is higher compared to BS; C<sub>17</sub>-C<sub>19</sub> are prevailing among them.

TABLE 5

Relative content of certain groups of organic compounds in bottom sediments and water of Mormyshanskoye Lake, rel. %

Groups of compounds	BS-1	BS-2	Water
Steroids	5.96	11.52	0.03
Pentacyclic triterpenes	1.25	8.88	0.13
Carboxylic acid	16.00	17.05	2.02
Methyl esters	2.20	0.95	0
Isopropyl esters	1.25	0.10	0
<i>n</i> -Alkan-2-ones	3.76	5.70	0
<i>n</i> -Aldehydes	1.25	6.10	0
<i>n</i> -Alkanol	1.41	1.12	0
Tocopherols	0.10	0.74	0
Steranes	1.25	0	1.03
Hopanes	0.94	0.13	0.54
Cheilanthanes	0.31	0	0
Cyclohexane	0.63	0	0.52
Aromatic HC	1.25	0.05	0
<i>n</i> -Alkanes	62.42	47.63	95.74



TABLE 6

Relative content of certain groups of organic compounds in sediments and water of Gorkoye Lake, rel. %

Groups of compounds	Bottom sediments	Water
Steroids	9.4	1
Pentacyclic triterpenes	4	1.5
Carboxylic acid	32.6	68
Methyl esters	0.4	0
Isopropyl esters	0.1	0
Long-chain esters	0	22.4
<i>n</i> -Alkan-2-ones	2.1	0.8
<i>n</i> -Aldehydes	1.3	0
Tocopherols	0.2	1.7
<i>n</i> -Alkanes	50	4.6

The fraction of polar oxygeneous acyclic (aldehydes and ketones) and cyclic compounds (steroids, PT compounds, and tocopherols) is increased due to a decrease in the relative content of *n*-alkanes as a part of organic components of BS-2.

In addition to *n*-alkanes, water contains carboxylic acids, and also steroids and PT systems in trace amounts, and also representatives of oil compounds, such as sterane and cyclohexane derivatives, not detected in BS after basin desalination. Homohopanes vanished from the composition of BS-2 were also detected in the aqueous phase. Thus, the disappearance of sterane and cyclohexane derivatives from BS, and also a decrease in the content of hopanes and *n*-alkanes is likely to be the consequence of their washing out with desalinated water from the sediment.

There are no carboxylic acid esters and aldehydes that are present in BS both in water of Gorkoye Lake and Mormyshanskoye Lake with a

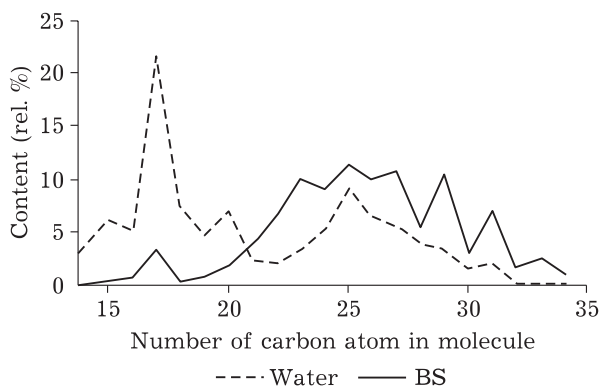


Fig. 6. Molecular mass distribution of *n*-alkanes in water and bottom sediments of Gorkoye Lake.

mineralisation of 7.8 and 80 g/dm<sup>3</sup>, respectively (Table 6).

The fraction of polar steroids and PT is higher in slightly salted water in Gorkoye Lake unlike more mineralised water in Mormyshanskoye Lake. Carboxylic acids are prevailing; there are *n*-alkane-2-ones and tocopherols; the relative content of non-polar *n*-alkanes, among which the C<sub>17</sub> homologue is prevalent, is decreased (Fig. 6).

There are no oil components both in BS and water. In the water of Gorkoye Lake, long-chain esters that are absent in BS of this lake, and also in the water of more mineralised Mormyshanskoye Lake have been detected in a relatively high concentration. They involve C<sub>26</sub>-C<sub>34</sub> homologues with the prevalence of C<sub>28</sub> and C<sub>30</sub>. Moreover, each of them is presented by several isomers.

Waters of both lakes are different from the corresponding BS by a decreased ratio of steroid content to PT (0.2-0.7 and 1.3-2.3 in water and

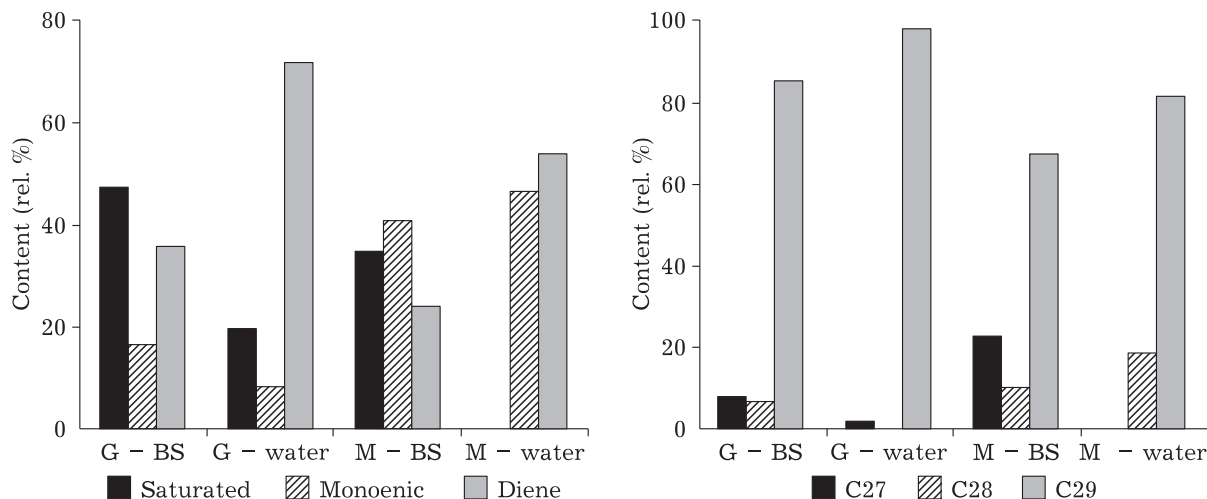


Fig. 7. Relative content of steroid moieties in water and bottom sediments of Gorkoye (G) and Mormyshanskoye (M) lakes.

BS, respectively), a greater degree of unsaturation of steroid structures and a higher fraction of C<sub>29</sub> compounds (Fig. 7).

Thus, the composition of organic compounds in lake bottom sediments (BS) largely depends on aqueous-phase mineralisation. A decrease of the latter leads to washing out primarily non-polar and then some oxygenous species.

## CONCLUSION

As demonstrated by the results of the research, lake waters of the southern Siberia and Altai are characterised by a mineralisation degree between 0.1 and 300 g/dm<sup>3</sup>, the presence of mainly heterotrophic bacteria *Bacillus* and *Pseudomonas*, rarely also *Micrococcus* and *Sarcina*, the number of which (2–4200 k cl./mL) is drastically increased in highly mineralized waters.

The presence of components of biogenic and anthropogenic origin has been found in the composition of the identified organic compounds of bottom sediments (BS) and water. Biogenic sesqui- and diterpenes are present in BS only near the forested shores of the lakes. Steroids and triterpenoids are prevailing among cyclic compounds in salt lakes and fresh water bodies, respectively.

There are no clearly apparent peculiarities in the composition of acyclic biogenic compounds (carboxylic acids and their esters, *n*-aldehydes and *n*-alkane-2-ones) of fresh and salt lakes. However, *n*-aldehydes have been detected only in highly mineralised lakes. The composition of *n*-alkanes and aromatic hydrocarbons (HC) indicates the probable presence of oil components in a certain quantity within BS along with biogenic constituents.

Cyclic compounds (steranes, hopanes, and cheilanthanes) typical for oil, and also cyclohexane derivatives and alkylated polycyclic aromatic hydrocarbons) have been determined and identified in BS near car roads and coasts equipped with campings.

A reduction in mineralisation due to diluting lake water with intense rain precipitation leads to the disappearance of oil steranes and cyclohexane derivatives that enrich the aqueous phase from BS. There is also a decrease in the content of oil hopanes, among which homohopanes detected in the aqueous phase vanish.

The acquired results may be used to predict the distribution of certain oil components within the water-sediment system in water bodies polluted with oil products.

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