Limnology and Freshwater Biology 2020 (2): 397-404 DOI:10.31951/2658-3518-2020-A-2-397

Original Article

ISSN 2658-3518
LIMNOLOGY FRESHWATER BIOLOGY
www.limnolfwbiol.com

Assessment of water pollution near the deep oil seep in Lake Baikal

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ABSTRACT. Water purity was assessed at the site of a deep oil seepage near Cape Gorevoy Utes (Central Baikal). Polycyclic aromatic hydrocarbons (PAHs) and *n*-alkanes were determined in different types of oil-containing samples collected at this section of Lake Baikal. The set of studied samples included: (i) samples of water from the surface water layer; (ii) samples of water from different depths; (iii) oil on the water surface; (iv) oil from a sediment core. In the surface water layer and the water column, the total concentration of *n*-alkanes ranged from 0.2 to 5.3 µg/L and did not exceed the 0.1 maximum permissible concentration (MPC_{fish} = 50 µg/L) established for hydrocarbons in water bodies of fishery importance. PAHs with carcinogenic properties were less than 0.1 ng/L. The total concentration of PAHs found in the water column did not exceed 110 ng/L; toxic equivalent (TEQ) values ranged from 0.001 to 0.110 ng/L. The distribution of petroleum hydrocarbons from the seepage site was limited, and water pollution was localised. The low level of water pollution is associated with natural mechanisms in the Baikal ecosystem. Microbiological community and phytoplankton make a decisive contribution to the purity of Baikal water, and oil fractionation during deep discharge contributes to the bioavailability of petroleum hydrocarbons.

Keywords: Oil seeps Contamination of water Lake Baikal

1. Introduction

Natural oil seepage in freshwater lakes is associated with rift zones: Lake Tanganyika – with the East African Rift (Simoneit et al., 2000), Lake Chapala – with the Citala Rift (E-W) (Zarate-del Valle et al., 2006), and Lake Baikal – with the Baikal rift. High heat flux in the rift zone of Baikal (76 mW/m^2 on average, Golmshtok et al., 2000) contributes to the heating of sedimentary formations and stimulates the generation of hydrocarbons. According to data on seismic studies, oil and gas may accumulate in the structure of the Cenozoic sedimentary basins in Baikal, with a potential resource of 500 million tons (Kontorovich et al., 2007). The presence of oil is evidenced by natural oil seepage in the form of asphalt that appears along coastal cliffs or comes from depths of 10–15 m to the water surface of the lake approximately 300–500 m from the shore, forming oil slicks from the emerging tar balls with a diameter of up to 1.5 m. In wintertime, oil accumulates under the ice, filling fractures in the ice cover. Examination of this oil indicates that it is an aromatic-naphthenic type, in which there are no normal alkanes, monomethyl alkanes or acyclic isoprenoids. The flow of petroleum hydrocarbons from the bottom of the lake is 0.1–5 tons of heavy oil per year (Kontorovich et al., 2007).

In 2005, a new deep oil seepage was discovered near Cape Gorevoy Utes (Central Baikal). At this site, there were numerous oil slicks with a diameter of up to 1 m. The oil collected at the time of its emergence on the water surface had an extremely high concentration of *n*-alkanes and was identified as non-biodegraded paraffin oil. The oil sampled from the water surface contained a full range of petroleum hydrocarbons: *n*-alkanes, *i*-alkanes, alkyl-cyclohexanes, isoprenoids (pristane and phytane), PAHs and hopanes as well as a complex of unique molecular biomarkers (Gorshkov et al., 2006; Kashirtsev et al., 2006; Khlystov et al., 2007; Kontorovich et al., 2007). In 2008, investigations of the bottom sites near the oil seepage using the MIR deep-sea manned submersibles at depths of 870–920 m revealed structures consisting of paraffin petroleum asphalt, through which oil discharged. At sites with a flat bottom and near these structures, there were accumulations of liquid oil droplets that floated without any periodicity (Khlystov et al., 2009).

According to estimates (Khlystov et al., 2007; Kontorovich et al., 2007), the amount of oil entering Baikal waters at this site does not exceed 4 t/y, which is not comparable to the volumes of industrial oil discharged into the surface waters of the world's oceans during technological disasters (Hazen et al., 2010; Vila

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et al., 2010; Yender and Stanzel, 2011). Nevertheless, constant oil emission, low water temperature and the long replacement period of lake water by tributaries (ca. 330 years) increase the environmental risk of a decline in Baikal water quality. It is also worth noting that natural oil seeps are dynamic systems that develop over time and are characterized by the unpredictability of the emergence of new seeps in time and space.

Lake Baikal is the globally important drinking water source containing 20% of the world's surface freshwater. To assess the purity of water in the area of deep oil seepage near Cape Gorevoy Utes, a natural source of oil hydrocarbons, samples of freshly emitted oil and oil slicks from the water surface as well as the water samples from various layers in the water column were collected. A bottom sediment core was also sampled in the area of deep oil seepage. In all samples of oil, water, and bottom sediments, *n*-alkanes and PAHs were studied. *n*-Alkanes are the dominant components of oil entering the lake in this area. PAHs are a minor component of oil, but this class of substances is among the priority pollutants and subject to constant monitoring in the environment.

2. Materials and methods

Investigations were carried out in 2016 and 2019 at the site of the natural oil seepage near Cape Gorevoy Utes (10 km from the coast, 900 m depth, Central Baikal; coordinates 53°18'33''N 108°23'46'' E). Oil, water from the surface and deep layers, and bottom sediments were sampled on board the research vessel "G. Yu. Vereshchagin" at seven stations, R4 - R10 (Fig. 1). Stations R4, R5, R7 - R10 were located at sites with oil slicks on the surface; station R6 was at a site without oil slicks. Oil slicks were sampled using a sterile beaker and poured into 1 L glass bottles. Water samples were taken using an SBE 32 Carousel Water Sampler from depths of 0, 5, 200, 400, 600, 800, and 860 m and poured into 1 L glass bottles. Fifty mL of dichloromethane was added to each water sample; then the mixture was shaken, covered with a lid with aluminium foil and stored at +5 °C until analysis.

The bottom sediment core was sampled at the VER-16-01 (GC4) station using a gravity corer with a plastic liner. The upper part of the core (from the surface down to 140 cm) contained gas-saturated aleuropelitic muds impregnated with oil; the lower part (from 140 to 310 cm) was clay, in which there were vertical or inclined discharge channels with diameters of up to 5 mm, split and degasification cracks of 1–2 mm, and horizontal aleuro-sandy interlayers also impregnated with oil.

Normal hydrocarbons and PAHs in water samples were determined by liquid-liquid extraction with dichloromethane. Before extraction, 100 μL of PAH solution (a mixture of naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) in acetonitrile with a concentration of 5 ng/μL for each polyarene; 200 μL squalane solution in dichloromethane with a concentration of 330 ng/μL; and 25 mL dichloromethane were added to the water samples. The mixture was shaken for 3 min and moved to a 1 L separatory funnel. After phase separation, the lower dichloromethane layer was separated, and the extraction was repeated with a new 25 mL portion of extractant. The extracts were mixed and concentrated to a volume of ~1 mL. Na_2SO_4 (calcined and chemically

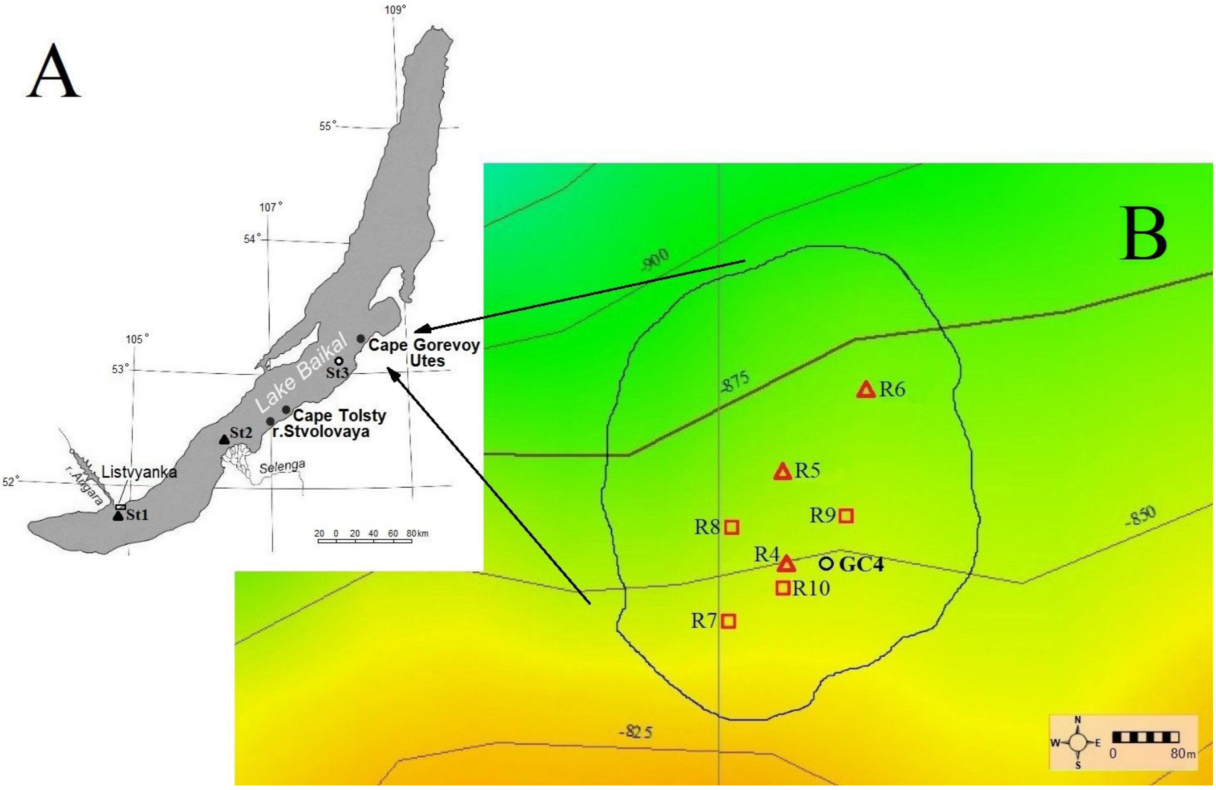

Fig. 1. Map of Lake Baikal: A - ● - sites of oil seeps; ○,▲ – reference stations; B - △, □ - sampling stations.

pure) was added to the concentrate, and the mixture was shaken and centrifuged. The supernatant was transferred to the autosampler vials of the gas chromatography-mass spectrometer. The extracts of water samples containing oil (after chromatography analysis) were dried to constant weight; the resulting residue was weighed. The content of *n*-alkanes and PAHs in these samples was calculated relative to the amount of recovered oil.

To determine *n*-alkanes and PAHs in the bottom sediment core, samples that differed in maximum oil content were taken. The samples were dried at room temperature to constant weight and then homogenised. Two samples (2–3 g) were taken, to which internal standards of 25 μL PAH solution and 50 μL squalane solution were added. PAHs and *n*-alkanes were twice extracted with 15 mL of dichloromethane in an ultrasonic bath, each time for 20 min. The extracts were mixed and centrifuged. The supernatant was taken and concentrated to a volume of ~1 mL; concentrate then was diluted with *n*-hexane in the ratio of methylene chloride: *n*-hexane = 1:10 (v/v); the mixture was kept at +5 °C for 24 h, the sample was centrifuged, and the supernatant was transferred to the flask of the chromatography autosampler and concentrated under an argon flow to a volume of ~ 0.1 mL. The extracts of bottom sediment samples containing oil were dried to constant weight; the resulting residue was weighed. The content of *n*-alkanes and PAHs in these samples was calculated relative to the amount of recovered oil.

In the collected samples, *n*-alkanes and PAHs were determined: *n*-alkanes as homologous series from C_8 to C_{30} and 24 PAH compounds, including 16 priority polyarenes: naphthalene (Nap); 1-methylnaphthalene (1mNa); 2-methylnaphthalene (2mNa); acenaphthylene (Acy); acenaphthene (Ace); fluorene (Fl); phenanthrene (Ph); anthracene (An); 1-metylphenanthrene (1mPh); 2-metylphenanthrene (2mPh); 3-metylphenanthrene (3mPh); 9-metylphenanthrene (9mPh); fluoranthene (Flu); pyrene (Pyr); benzo[a]anthracene (BaA); chrysene (Chr); benzo[b]fluoranthene (BbF); benzo[k]fluoranthene (BkF); benzo[e]pyrene (BeP); benzo[a]pyrene (BaP); perylene (Per); indeno[1,2,3-cd]pyrene (InP); benzo[g,h,i]perylene (BghiP); and dibenzo[a,h]anthracene (DahA).

PAHs and *n*-alkanes in the samples were determined using an Agilent Technologies 7890B GC System 7000C GC-MS Triple Quadrupole Gas Chromatography-mass spectrometer with an OPTIMA® 17 MS capillary column (30 m × 0.25 mm × 0.25 μm). The GC operating parameters were from 50 to 310 °C at a heating rate of 20 °/min, then maintaining the column at the final stage at 310 °C for 35 min. The temperatures of the injector and ion source were 290 °C and 250 °C, respectively; the volume of the injected sample was 2 μL without flow splitting, and the electron impact ionization energy was 70 eV. The chromatograms of sample extracts were recorded in the SCAN mode by scan mass spectrum from 50 to 600 m/z. Peaks were identified using the LIB2NIST v.1.0.0.8 mass spectral data conversion program for 150,000 compounds. For quantification of *n*-alkanes and PAHs, chromatograms of samples were recorded in the SIM mode: the peaks of *n*-alkanes with 57 and 71 m/z; the peaks of PAHs with 128, 136, 142, 152, 154, 164, 166, 178, 188, 192, 202, 228, 240, 252, 264, 276, and 278 m/z. The peaks were identified by relative retention times.

Quantification was performed using the internal standard method. The chromatograph was calibrated in the range of the expected PAH and *n*-alkane concentrations in the extracts with the preparation of solutions of PAHs and *n*-alkanes with a concentration of 0.05-50 ng/mL. The calibration solutions were prepared by diluting the certified PAH and *n*-alkane mixture (Supelco, USA) with an *n*-hexane–acetone mixture (1:1, v/v). The concentration of analytes in the samples was calculated as the average value of the results of two determinations in one sample. The PAH and *n*-alkane extraction efficiency were approximately 70% - 80%. Limit of detection (LOD) was calculated as the threefold standard deviation peak area of the PAH and *n*-alkane levels in procedure blanks, in the water: PAH - 0.1-1.0 ng/L, *n*-alkane – 2 ng/L; in the oil: PAH - 1-10 ng/g, *n*-alkane – 100 ng/g. Relative standard deviation (RSDs) for determining PAHs and *n*-alkanes was estimated within a range from 15% to 20% for individual analytes.

Toxic equivalents (TEQ) were calculated according to the following equation:

$$TEQ = C_i \text{ x } TEF_i,$$

where C_i is PAH concentration in ng/L, and TEF_i are the toxicity coefficients for individual PAHs relative to BaP. The following TEFs were used for PAHs from Baikal waters: 0.001 for Na, Acy, Ace, Fl, Ph, Flu, and Pyr; 0.01 for An and Chr; and 0.1 for BbF (Nisbet and LaGoy, 1992).

3. Results and discussion

3.1. *n*-Alkanes and PAHs in oil on the water surface and bottom sediments

n-Alkanes, isoprenoids (pristane and phytane) and PAHs were identified in the composition of freshly emitted oil on the water surface. Moreover, *n*-alkanes were the dominant component in the oil. In the oil slicks, total concentrations of *n*-alkanes (Σ_{alk}) and PAHs (Σ_{PAH}) were low, up to four times lower than in freshly emitted oil (Table 1). In the slicks, *n*-alkanes are represented by homologous series C_{12} - C_{26}. The ratio of light and heavy homologues in this series ($R_{alk} = \Sigma[C_8 - C_{18}]/\Sigma[C_{19} - C_{29}] \geq 0.7$) indicated a partial loss of the light fraction. Records of an unresolved complex mixture (UCM) of branched and cyclic hydrocarbons on chromatograms of slick samples and a decrease in naphthalenes in the PAH fraction confirmed oil deformation on the surface of the lake resulting from evaporation and weathering. PAHs detected in oil on the water surface included 20 compounds. PAH ratios, An/(An+Ph) and Flu/(Flu+Pyr), indicated a petrogenic source of oil (Yunker et al., 2002), and ratios of isoprenoids (pristane/phytane) in oil slicks corresponded to those in the freshly emitted oil.

Table 1. Features of the oil on the water surface

Feature	Freshly emitted oil on the water surface	Oil slicks on the water surface
Homologous series of *n*-alkanes	C_8-C_{29}	C_{13}-C_{26}
Σ_{alk}, %	90	21-24
$R_{alk} = \Sigma[C_8\text{-}C_{18}]/\Sigma[C_{19}\text{-}C_{29}]$	1.0	0.7-0.9
The Pr/Ph ratio	6.7	6.1-6.8
Σ_{PAH}, ppm	1500	530-650
Σ_{naph}, % of total PAHs	32	5.0-25
BaP number, ppm	3.7	5.1-5.6
The An/(An + Ph) ratio	0.09	0.04
The Flu/(Flu + Pyr) ratio	0.34	0.28-0.33

Station R6 (Fig. 1) differed by the lack of surface oil slicks. Nevertheless, *n*-alkanes (C_{12} - C_{26}) and PAHs (14 compounds) were found in surface water samples (Table 2). High molecular weight homologues dominated in the fraction of *n*-alkanes (Σ_{alk} 0.2 – 5.3 µg/L; R_{alk} = 0.7). In the composition of PAHs, unlike that of oil films, there were no high molecular weight PAHs: the content of Per, InP, BghiP, and DahA were below the limit of their quantification (0.1 ng/L); the total concentration of naphthalenes (Σ_{naph}) corresponded to a range from 4.1 to 32 ng/L (30% - 63% of Σ_{PAH}).

In the fractures and interlayers of the bottom sediment core, the amount of oil was minimal, up to 2.9% of the core mass, and the Σ_{alk} concentration varied from 0.10 to 1.4% (Table 3). In the oil from upper layers of the core (samples from 0.40 and 50 cm layers) high molecular weight paraffins dominated, apparently resulting from the migration of the light fraction to the lake water. The oil composition in the core sample from a deep layer (274 cm) showed an equal ratio of light and high molecular homologues of *n*-alkanes (a series from C_{13} to C_{29}). PAHs identified in the oil from the core contained 24 compounds (Σ_{PAH} 400-1400 ppm), including high molecular weight polyarenes at a level of $^{<}$ 0.1–10 ppm. The amount of BaP in the core samples did not exceed 3.2–9.8 ppm. The PAH composition and ratio of indicator polyarenes corresponded to those in the freshly emitted oil on the water surface.

3.2. *n*-Alkanes and PAHs in the water column

In the water column (5–860 m at stations R4, R5, R7 – R10), normal hydrocarbons are identified as homologous series from C_{12} to C_{27}, with the Σ_{alk} concentration ranging from 0.2 to 4.5 µg/L (Table 2). The average value Σ_{alk} concentration is 1.6 µg/L, and 1.5 times higher than the median value, indicating a heterogeneous distribution of alkanes in the water column. At station R6 (station distinguished by the lack of surface oil slicks), the Σ_{alk} content in water samples from the 5–860 m layer corresponded to a narrow range of values, from 0.2 to 0.9 µg/L; low molecular weight homologues dominated most of the samples. At station R4, layers of 200, 600, and 800 m had a significant content of high homologues (Fig. 2).

The PAH fraction in the water column (5–800 m layer at stations R4 – R10) had a narrow series of low molecular weight polyarenes, including Na, Ace, Fl, Ph, Flu, and Pyr. In single samples, there were Acy, Chr, BbF, and BeP. The total number of naphthalenes (Σ_{naph}) had a maximum proportion (up to 85%) in the total Σ_{PAH} concentration, which was within the range from 1.0 to 110 ng/L (Table 2). At station R6, the content of PAHs in water samples differed in a narrow range of detected concentrations, from 3.9 to 15 ng/L.

It is worth noting that extreme concentrations of *n*-alkanes and PAHs were detected in the water sample from the 200 m layer at station R4, in which the Σ_{alk} concentration reached 330 µg/L, and Σ_{PAH} concentration reached 100 ng/L. Normal hydrocarbons were represented by a series from C_{13} to C_{29}, with a dominance of high molecular weight homologues, similar to the *n*-alkane content in samples from the upper layers of the core. The PAH concentration in this sample was also higher than in the samples from other layers of the water column (by an order of magnitude), and the content of naphthalenes in the fraction was estimated at the maximum level, up to 85% of the Σ_{PAH} concentration.

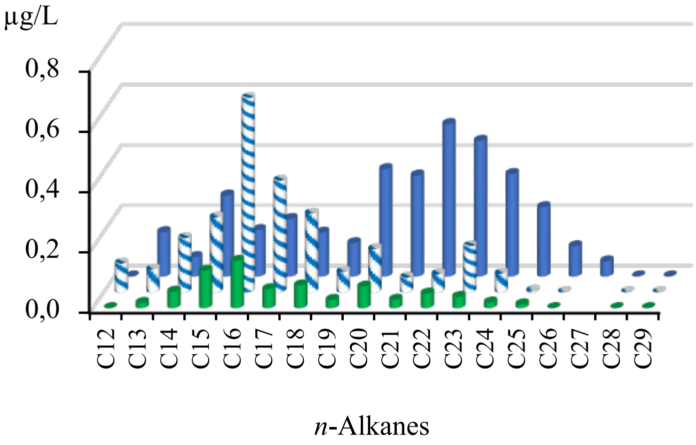

Fig. 2. A ratio of homologues of n-alkanes in water extracts from the 600 m layer:

🟦 - station R4; Σalk = 3.4 µg/L; Ralk = 0.4;

▨ - station R5 (Σalk = 2.4 µg/L; Ralk = 3.5.

🟩 - station R6 (Σalk = 0.73 µg/L; Ralk = 2.0

Table 2. Content of *n*-alkanes and PAHs in the water column in 2016 and 2019

Feature	Water layer, m						
	0	5	200	400	600	800	860
	Stations R6						
Σ_{alk}, µg l^{-1}	0.2 – 5.3	0.7	0.2 - 0.7	0.7	0.2 - 0.7	0.3 - 0.9	0.2 - 0.4
R_{alk}	0.7 – 0.8	3.3	1.7 - 2.9	2.1	0.7 - 2.0	1.4 - 3.0	1.0 - 4.3
Σ_{PAH}, ng l^{-1}	14 - 51	5.4	4.7	10	15	14	3.9
$\Sigma_{naph.}$, ng l^{-1}	4.1 - 32	3.1	3.0	9.0	5.0	4.1	3.1
R_{PAH}^{**}	0.6	0.7	1.0	0.7	0.6	0.6	0.7
Feature	**Stations R4, R5, R7 – R10**						
Σ_{alk}, µg l^{-1}	-	1.3 - 4.5	0.2 – 2.8 (330*)	0.8 - 4.0	0.2 -3.4	0.3 - 2.6	0.2 – 3.7
R_{alk}^{1}	-	1.3 - 2.1	0.6 – 1.2	0.9 - 1.7	0.4 -3.2	0.6 – 5.8	1.0 – 3.2
Σ_{PAH}, ng l^{-1}	-	18 - 90	18 – 100	14 – 59	7.2 – 62	5.2 - 47	12 – 110
$\Sigma_{naph.}$, ng l^{-1}	-	5.7 – 67	13 -87	3.2 - 7.9	5.1 -54	3.3 – 32	6.2 – 83
R_{PAH}^{**}	-	0.6	0.6	0.6	0.5	0.6	0.6

Note: * – the extreme concentration of *n*-alkanes; ** – the ratio of the Flu/(Flu + Pyr) concentrations

Table 3. Features of the bottom sediment core, VER-16-01, GC.4

Feature	Core layer, cm							
	0	10-15	40	50	100	200	250	274
Moisture, %	70	60	61	63	60	46	40	40
Total carbon content, %	5.1	5.1	7.7	7.5	5.6	2.7	2.9	2.6
Oil content, %	0.47	0.64	2.5	2.9	0.20	0.18	0.36	0.34
Σ_{alk} in oil, ppm	1400	1700	780	1200	1500	920	3300	1400
$R_{alk} = \Sigma[C_8\text{-}C_{18}]/\Sigma[C_{19}\text{-}C_{29}]$	0.52	-	0.35	0.33	-	-	-	1.1
Σ_{PAH} in oil, ppm	400	460	510	550	890	870	1100	1400
Σ_{naph} in oil, ppm	44	58	12	9.0	74	56	180	250
Σ_{phen} in oil, ppm	230	270	450	370	590	580	530	760
BaP in oil, ppm	8.5	6.7	9.7	9.2	5.3	3.2	9.3	9.8
The An/(An + Ph) ratio	0.26	0.34	0.12	0.11	0.12	0.11	0.12	0.10
The Flu/(Flu + Pyr) ratio	-	-	0.23	0.21	0.32	0.31	0.32	0.30

3.3. Assessment of Baikal water pollution near the deep oil seep

The area of the water surface covered with oil slicks at the site of the oil seepage near Cape Gorevoy Utes in 2016 and 2019 did not change in comparison with the 2005 data (Khlystov et al., 2007) and was ~1 km^2. In the surface water layer (without oil slicks), the Σ_{alk} concentration almost has not changed over 15 years since the discovery of this phenomena and ranges from 0.3 to 8.3 µg/L, with an average value of 3.6 µg/L and median of 3.0 µg/L (Fig. 3). Except for some samples, for example, from the 200 m layer at station R4, the concentration of the detected *n*-alkanes does not exceed the maximum permissible concentration (MPC_{fish} = 50 µg/L) established for monitoring petroleum hydrocarbons in water bodies of fishery importance (The list of fishery standards…, 1999) and is 25 to 40 times lower than the concentration of aliphatic hydrocarbons in the waters of the Atlantic and Southern oceans (Nemirovskaya, 2004).

Oil can enter the water column from different channels, such as asphalt structures resulting from oil fractionation at the water-bottom interface (Gorshkov et al., 2020), cracks and faults at the bottom of the lake, emitting separate oil balls at the bottom of the lake (Khlystov et al., 2009). In the latter case, the oil may enter the water column with minimal fractionation. The detection of extreme concentrations of *n*-alkanes and PAHs in the sample from the 200 m layer (station R4) may be the result of a similar oil discharge to lake waters and inclusion into the sample of water hydrocarbon plume that ascended through the water column to the surface of the lake.

The fraction of PAHs in the water column did not contain high molecular weight polyarenes with carcinogenic properties (BaP and DahA). In particular, BaP was not identified above the 0.02 MPC, which is established for this pollutant in drinking water: MPC_{EU} BaP = 10 ng/L (Council Directive 98/83/EC, 1988); MPC_{RUSSIA} BaP = 5 ng/L (SanPIN 2.1.4.1074-01.2001, 2002).

For PAHs found in the water column, total toxic equivalent (ΣTEQ) values ranged from 0.004 to 0.110 ng/L (Fig. 4). The maximum ΣTEQ values were observed for the PAH fraction in the bottom water layer (860 m), in which naphthalenes dominated. Contribution of naphthalenes to ΣTEQ is rated at 50-60%. The presence of An, Chr and BbF in water, which have relatively high toxicity coefficients (TEFs), also significantly contribute to the total TEQ of PAHs in this water layer. On a water surface covered with oil slicks, the toxicity of PAHs reaches a total TEQ of 100-200 ng/L. In the water of the upper water layer (5 m), ΣTEQ does not exceed 0.110 ng/L. Deep water (R4, 400 m) is characterised by a minimum level of total TEQ (0.004 ng/L), which is comparable to the toxicity assessment of PAHs in water samples collected at the reference station in the Baikal pelagic zone. In the absence of oil slicks on the water surface (station R6, 0 m), the ΣTEQ of PAHs is 0.055 ng/L. (St.3; Fig. 1).

The distribution of petroleum hydrocarbons in Baikal water from the site of deep seepage is limited, and water pollution is localised. The total concentrations of *n*-alkanes at the reference station (St.1, $\Sigma_{alk} \leq 0.15$ μg/L; Russell and Rosell-Mele, 2005; Gorshkov et al., 2010) are up to 35 times lower than the maximum Σalk concentrations found in the water column and on the water surface near Cape Gorevoy Utes. PAH concentrations in the surface water layer at sites without oil slicks on the surface and deep layers are comparable with Σ_{PAH} concentrations at reference stations and in the pelagic zone (7.0–36 ng/L; Gorshkov et al., 2018).

The low level of water pollution due to petroleum hydrocarbons near deep oil seepage sites is associated with natural mechanisms in the Baikal ecosystem. Microorganisms and phytoplankton make a decisive contribution to the purity of Baikal water, and oil fractionation during deep discharge contributes to the bioavailability of petroleum hydrocarbons. Model experiments indicated that during the cultivation of Baikal microorganisms in the presence of oil as a carbon source, *n*-alkanes and PAHs effectively degrade. Moreover, diatoms *Synedra acus* subsp. *radians*, the dominant species of Baikal phytoplankton, accumulate PAHs in their lipid bodies (Pavlova et al., 2005; 2012; Shishlyannikov et al., 2017; Gorshkov et al., 2020).

In the model experiments on oil degradation, there was no selective destruction of *n*-alkanes, and conversion of the fraction of normal hydrocarbons showed a simultaneous decrease in the content of all homologues. Therefore, the dominance of light *n*-alkanes in the water at sites with oil seepage is likely to be the result of oil fractionation at the bottom-water interface.

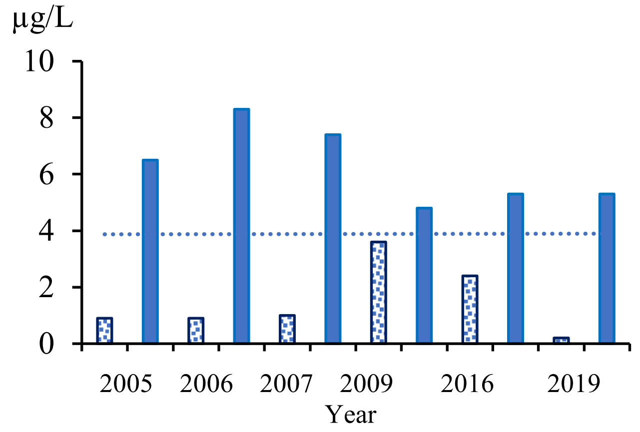

Fig.3. The trend of the content of n-alkanes in the surface water layer (without oil slicks) near the oil seep in 2005 – 2019, minimum ▨ and maximum 🟦 Σ_{alk} concentrations, MPCfish = 50 μg/L

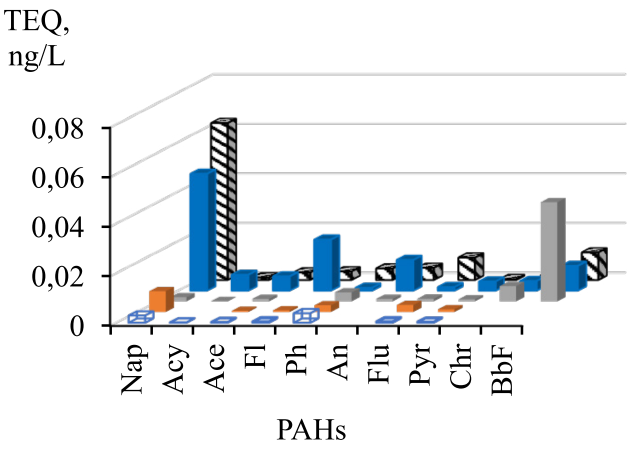

Fig. 4. Toxicity assessment of PAHs in the water column at the site of the oil seepage near Cape Gorevoy Utes:

▯ - station R4, 400 m: Σ_{PAH} 14 ng/L, ΣTEQ 0.004;
🟧 - station R6, 0 m: Σ_{PAH} 14 ng/L, ΣTEQ 0.055;
▮ - station R10, 5 m: Σ_{PAH} 90 ng/L, ΣTEQ 0.113;
🟦 - station R7, 860 m: Σ_{PAH} 100 ng/L, ΣTEQ 0.100
▧ - station St.3, 5-1500 m (reference station in the Lake Baikal pelagic zone): Σ_{PAH} 10-27 ng/L, ΣTEQ 0.013-0.018

Perhaps, the ability to degrade hydrocarbons is fixed in the genomes of Baikal microorganisms inhabiting areas of natural oil seepage (Likhoshvay et al., 2013; Lomakina et al., 2014), because, owing to geological processes, oil and its deformation products are permanent components in the ecosystem of the east coast of the Central Baikal basin. Additionally, Baikal microorganisms synthesise surfactants (Pavlova et al., 2010); hence, biosurfactants can contribute to the sorption of hydrocarbons on suspended particles in Baikal water and subsequent deposition on the lake bottom.

The presence of *n*-alkanes and PAHs in Baikal water is due to not only natural sources but also technogenic sources, i.e. surface runoff, emissions from vessels of the Baikal fleet, and emissions into the atmosphere from industrial enterprises along the coast. In the latter case, the Σ_{PAH} concentration in the surface water layer near the Listvyanka settlement can reach 160 ng/L, and in the Selenga River delta, the total concentration of petroleum hydrocarbons was 16–78 μg/L (St.1, St.2; Gorshkov et al., 2010).

4. Conclusion

The oil concentrates mainly on the water surface in the form of oil slicks. The area of the lake covered with oil slicks is ~1 km^2, and it almost has not changed since the discovery of oil seep in 2005. From 2005 to 2019, the concentration of *n*-alkanes in the surface water ranged between 0.2 and 8.3 μg/L, with an average value of 3.6 μg/L. The concentration of *n*-alkanes does not exceed 0.1 MPC_{fish} (MPC_{fish} = 50 μg/L), which was established for monitoring petroleum hydrocarbons in water bodies of fishery importance. The Σ_{PAH} concentration was within the range from 1.0 to 110 ng/L, and the fraction of PAHs detected there had no carcinogens. In particular, BaP was not identified above the 0.01–0.02 MPC, which had been established for this pollutant in drinking water (MPC_{EU} BaP = 10 ng/L, MPC_{RUSSIA} BaP = 5 ng/L). The toxicity of PAHs in oil slicks on the water surface had the TEQ value from 100 to 200 ng/L. For the PAHs found in the water column, TEQ values ranged from 0.004 to 0.110 ng/L. Deep water (400 m) is characterised by a minimum level of total TEQ, which is comparable to the assessment of the toxicity of PAHs in water samples collected at the reference station in the Baikal pelagic zone. The distribution of petroleum hydrocarbons in Baikal water from the site of deep seepage is limited, and water pollution is localised. At reference stations in the Baikal pelagic zone, the total concentrations of *n*-alkanes in the surface water layer are up to 35 times lower than that at the seepage site. The concentrations of PAHs in the surface water layer and deep layers in the pelagic zone of Lake Baikal range from 7.0 to 36 ng/L.

Acknowledgments

This work was conducted within the framework of the State Task, projects No. 0345–2019–0007 (*AAAA-A16-116122110064-7*) and No. 0345–2019–0008 (*AAAA-A16-116122110065-4*). The chromato-mass-spectrometric analysis was conducted at the Collective Instrumental Centre “Ultramicroanalysis”.

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