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Wildfires as a Source of PAHs in Surface Waters of Background Areas (Lake Baikal, Russia)

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) were detected in different types of PAH-containing samples collected in Lake Baikal during wildfires in the adjacent areas. The set of studied samples included the following: (i) water from the upper layer (5 m); (ii) water from the surface microlayer; (iii) water from the lake tributaries; (iv) water from deep layers (400 m); and (v) aerosol from the near-water layer. Ten PAHs were detected in the water samples: naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, and chrysene. The total PAH concentrations (Σ PAHs) were detected in a wide range from 9.3 to 160 ng/L, characterizing by seasonal, intersessional, and spatial variability. In September 2016, the Σ PAH concentration in the southern basin of the lake reached 610 ng/L in the upper water layer due to an increase in fluorene, phenanthrene, fluoranthene, and pyrene in the composition of the PAHs. In June 2019, Σ PAHs in the water from the northern basin of the lake reached 290 ng/L, with the naphthalene and phenanthrene concentrations up to 170 ng/L and 92 ng/L, respectively. The calculation of back trajectories of the atmospheric transport near Lake Baikal, satellite images, and Σ PAH concentrations in the surface water microlayer of 150 to 960 ng/L confirm the impact of wildfires on Lake Baikal, with which the seasonal increase in the Σ PAH concentrations was associated in 2016 and 2019. The toxicity of PAHs detected in the water of the lake in extreme situations was characterized by the total value of the toxic equivalent for PAHs ranging from 0.17 to 0.22 ng/L, and a possible ecological risk of the impact on biota was assessed as moderate.

Keywords: wildfires; PAHs; water of Lake Baikal; ecological risk



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1. Introduction

The water crisis, a decline in the quality and quantity of water on the planet, is a global problem of our time [1]. Wildfires are one of the main causes of the water crisis [2–5] because they lead to hydrological and structural changes in the landscape [6,7] and to a change in the composition of surface and ground waters [8–10]. An increase in the number and intensity of wildfires, as well as in the areas of their distribution, seems to be a direct consequence of global warming and climate change on the planet [11–17].

East Siberia has unique forest resources; forests cover an area of up to 2.2 million km² and are subjected to a significant number of fires. Wildfires in Siberia have been recorded from 2001 to 2019 in areas from 34,600 to 196,000 km². From 2015 to 2019, fires engulfed forests in areas of 62,500, 79,500, 44,400, 36,100, and 72,400 km², respectively. In 2019, fires in East Siberia were considered a global environmental disaster: forests in an area of up to 72,400 km² were engulfed in fire; the volumes of emissions of carbon dioxide and fine PM_{2.5} aerosol were ≈ 46 and ≈ 0.39 , respectively [18]. During forest burning, not only carbon dioxide is released into the atmosphere but also persistent organic pollutants (POPs) that include polycyclic aromatic hydrocarbons (PAHs) as the main components.

In the atmosphere and soil, the outcome of PAHs generated during fires has been sufficiently studied [19–26], while studies of PAHs in surface and ground waters are limited [8–10,27]. Water bodies located in clean background areas can be the optimal study objects of the effect of fires on the surface waters because trace levels of the PAH concentrations in these sites suggest a sharp response to the pollutants entering their waters in extreme situations. Lake Baikal located in the southeast of Siberia was chosen as a model for studying the impact of wildfires on surface waters. Lake Baikal covers an area of 31,700 km², contains up to 20% of the world reserves of surface freshwaters, ≈23,600 km³, and is the most important water resource on the planet. Water in the lake is clean, has a low mineralization degree [28] as well as the minimum content of suspended organic matter [29], and POPs [30]. In the studies of POPs in Baikal water, much attention was paid to organochlorine pollutants [31–36], because these substances are resistant in the environment and toxic to wildlife and humans. Systematic monitoring of PAHs in Baikal water has not been carried out, despite the presence of anthropogenic and natural sources of the substances of this class in its ecosystem.

In the Baikal aerosol, PAHs are trace components in the aerosol composition, and their content does not exceed 0.05%. Above the Baikal water surface, the ΣPAH concentrations range from 0.10 to 0.61 ng/m³; in the atmosphere of the cities and settlements on the coast of the lake, it is up to 1.7 ng/m³ [37,38]. Regional transport of polluted air masses from the industrial zone of the Baikal region is considered one of the sources of anthropogenic POPs entering the water area of the southern basin of Lake Baikal. Examination of pine needles (*Pinus sylvestris* L.) as a bioindicator of air pollution revealed that the contribution from of the regional transport of the PAHs to the air pollution of the southern part of Lake Baikal is insignificant and comparable with the input local sources along the coast [39].

Anthropogenic sources of PAHs are represented by atmospheric emissions from small heating plants and house stoves on the coast of Lake Baikal [40]. Natural sources of PAHs include wildfires in the adjacent areas and natural oil seepages in the aquatic ecosystem of Lake Baikal. The composition of oil entering Baikal water during the deep-water discharge is characterized by a wide range of hydrocarbons, containing PAHs. We have shown that the influx of oil to Baikal water takes place at the limited sites of the lake, and the water pollution is localized [41–44]. At the same time, wildfires as sources of PAHs are discussed for the first time, and the impact of wildfire smoke plumes on the water area of Lake Baikal is possible over a large area of the water surface. To assess the impact of wildfires on surface waters in background areas, PAHs were monitored in Baikal water from 2015 to 2020. This period included seasons of intense fires as well as time intervals before and after their occurrence. The block of studied samples included: (i) water from the upper layer (5 m); (ii) water from surface microlayer; (iii) water from the lake tributaries; (iv) water from deep layers (400 m), and (v) aerosol from the near-water layer. The detected PAH concentrations in the selected samples allowed us to assess the level of PAHs in surface water during periods of exposure to forest fires, the toxicity of detected PAHs, and the possible ecological risk for biota.

2. Materials and Methods

Water samples from the pelagic zone of Lake Baikal were collected by an SBE-32 cassette sampler (Carousel Water Sampler, Sea-Bird Electronics, Bellevue, WA, USA) at 21 stations from a 5 m water layer and at 3 stations (6, 11, and 16) from a 400 m water layer (Figure 1a) in June 2015, June and September 2016, June 2018, and June and September 2019–2020. The water samples from the lake's tributaries, stations A–E (Figure 1b), were taken from the water surface at the estuaries of the rivers. The two samples at each station were taken in 1 L glass bottles, to which 0.5 mL of a 1 M aqueous solution of sodium azide (Merck, Darmstadt, Germany) was added as a preserving agent. Water bottles were closed with a lid with an aluminium foil gasket and stored at 5 °C until laboratory analysis. Samples of the upper water layer of the Barents Sea and the East Siberian Sea were collected during the “Arctic-2018” marine expedition in August–September 2018. Water was taken

from the upper water layer (10 m) using a Seabird SBE-32 cassette sampler at 26 stations. The two samples at each station were taken in 100 mL glass bottles. Samples of the Baikal surface water microlayer were taken according to the method given in [44] during the intense wildfires on the lake's coast in 2015 and in the northern areas of Siberia in 2019 as well as during the minimum number of fires in the adjacent territories in August 2018. Samples of aerosol from the near-water layer were collected on a glass microfiber filter (Watman EPM 2000, dimensions 17×21 cm) using a volume air sampler (Model PM-10 Andersen Samplers, Inc, Atlanta, GA, USA) on board the research vessel during the expeditions throughout Lake Baikal in July–August 2016, 2019, and 2020. Each filter was wrapped in an aluminum foil envelope and placed in a sealable plastic bag until use. Filter blanks were assessed in the same manner as the sampling procedure. The filters were stored at -20 °C until chemical analysis.

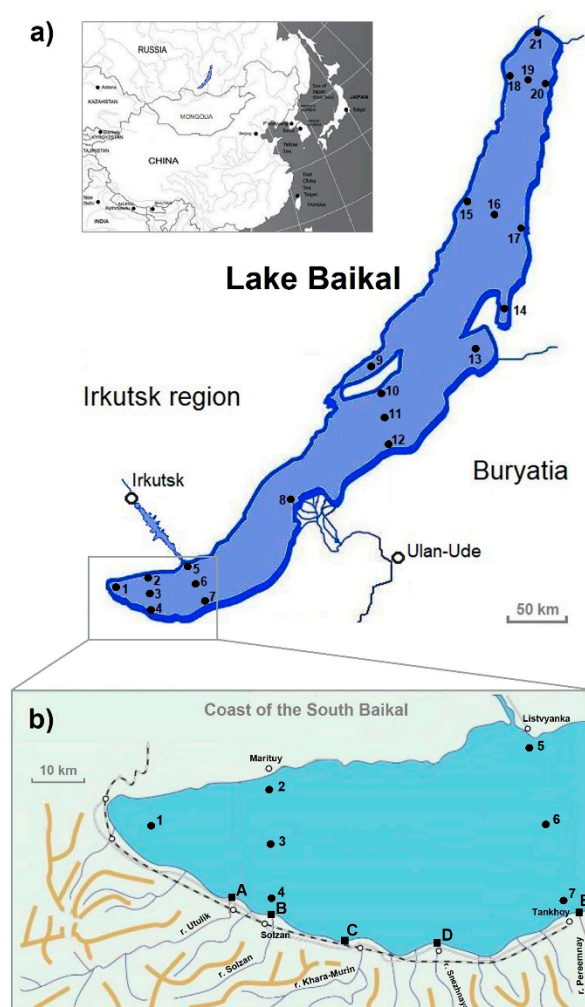


Figure 1. Map of Lake Baikal and sampling sites: (a) Water sampling stations in the pelagic zone of Lake Baikal; (b) Water sampling stations in the tributaries in the southern basin of Lake Baikal.

PAHs were extracted with 25 mL of n-hexane from 1 L of unfiltered water because the concentration of suspended particles does not exceed 0.01 to 0.05% in Baikal water. PAHs on the filters with aerosol were extracted with 30 mL of n-hexane in an ultraviolet bath for 30 min. Before extraction, a mixture of deuterated naphthalene- d_8 , acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12} (Supelco, Bellefonte, PA, USA) was added to water samples and filters (20 μ L mixture, 1 ng/ μ L of each). A 1 mL aliquot was taken from the first extract; then, the extraction of water was repeated, and extracts were combined. The aliquot and the combined extract were dried over sodium sulfate;

the extract was concentrated on a rotary evaporator up to a volume of ≈ 1 mL and then in argon flux up to a volume of ≈ 0.1 mL. Samples of the surface microlayer and water samples collected in the Arctic area were analyzed using the technique given in [45], which differed in the extraction of PAHs from 100 mL of water with 1 mL of n-hexane and GC-MS/MS analysis of the extracts without their concentration [46]. The detection of PAHs in water samples collected in the Arctic area included the extraction of PAHs on board the research vessel followed by the determination of analytes in the extract in the laboratory at Limnological Institute SB RAS. Polychlorinated biphenyls (PCBs) in the water of Lake Baikal were determined as described in [47]. On filters with an aerosol, PCBs were determined according to the method used for the determination of PAHs, and a mixture of PCB indicator congeners Marker-7 PCB Mixture, ^{13}C (Cambridge Isotope Laboratories, Inc., Shirley, NY, USA) was used as internal surrogate standards (10–30 μL , 0, 1 ng/ μL each).

The aliquots and extracts were analyzed using an Agilent Technologies 7890B GC System 7000C GC-MS Triple Quad chromatography-mass spectrometer with an OPTIMA[®] 17 ms Macherey-Nagel capillary column (30 m \times 0.25 mm \times 0.25 μm). PAH and PCB peaks were recorded using the MRM mode [46,47]. The limits of determination (LOD) of PAHs and PCB in the water were estimated at 1.0–0.1 ng/L and 0.01–0.02 ng/L [45,46]; on filters with an aerosol, they were 2.0 and 0.02 pg/ m^3 , respectively. The LOD method was assessed based on the peak-to-peak signal to noise response of each of the PAH and PCB peaks and at the lowest standard concentration. Values for S/N >10 were employed to determine the limit of quantitation (LOQ) for each target compound. The presence of PAH traces in extractant (n-hexane) was considered a systematic error of the determination; it was subtracted from the results of the analysis. Relative standard deviation (RSD_{RI}) for the determination procedure ranged from 15% to 25% for individual PAHs and from 17% to 35% for individual indicator congeners: Nos 28, 52, 101, 118, 138, 153, and 180.

The toxic equivalent (TEQ) for PAHs was calculated using the following equation:

$$\text{TEQ} = C_i \times \text{TEF}_i$$

where C_i (ng/L) and TEF_i are the concentrations and toxic equivalent factors (TEFs) of the individual PAHs with relevance to benzo[a]pyrene [48].

Risk quotient (RQ) was applied to evaluate the eco-toxicity of water contamination after exposure to wildfire. The negligible concentration (NCs) and the maximum permissible concentrations (MPCs) of individual PAHs were used as the quality values (Table S1) [49–51].

$$\text{RQ}_{\text{NCs}} = C_i / \text{NCs}$$

$$\text{RQ}_{\text{MPCs}} = C_i / \text{MPCs}$$

where RQ_{NCs} is the negligible concentrations (NCs) for individual PAHs; RQ_{MPCs} is the maximum permissible concentrations (MPCs) for individual PAHs; C_i is the concentration of PAHs detected in water, ng/L.

Statistical analysis was performed with the vegan package [52] using the R language (R Core Team). RDA analysis (redundancy analysis) was used to compare the PAH composition in different water samples by sampling site, year, and month.

PAHs influx of PAHs with the waters of the tributaries (M_{PAHs}) was calculated using the following equation:

$$M_{\text{PAHs}} = V_{\text{WR}} \times \Sigma \text{PAHs}$$

where V_{WR} is the volume of water flow during a month, km^3 ; data are from the Russian Hydrometeorological Service [53]; ΣPAHs is the total concentration of PAHs determined in the waters of the tributaries, kg/ km^3 .

Back trajectories of the air transport near Lake Baikal were calculated using the HYSPLIT model [54] and the data from the Russian Hydrometeorological Service [53].

In the analysis of the results of PAH monitoring in Baikal water, the following characteristics were taken into account: (i) water in the southern basin of the lake is more exposed to anthropogenic pollution from local and regional sources than water in the northern basin; (ii) water mixing between the basins is limited [55]; (iii) in the central basin, there is the Gorevoy Utes natural deep-water oil seepage characterized by the influx of crude oil to the lake's water; (iv) the Selenga River, the largest tributary of the lake, flows within the central basin, the water of which is a potential source of POPs in the aquatic ecosystem of Lake Baikal.

3. Results and Discussion

3.1. PAHs in the Upper Layer of the Pelagic Zone of Lake Baikal

Ten compounds represented the qualitative composition of the PAH fraction detected in the upper water layer of the pelagic zone of Lake Baikal, including naphthalenes (naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene), acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, and chrysene. Naphthalenes were the dominant components in the PAH fraction, the total concentrations of which reached 4.8 to 16 ng/L (from 50 to 80% of Σ PAHs). Benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]anthracene, and anthracene were identified in single samples at a concentration level from three to five times exceeding the limit of detection for PAHs (LOD = 0.1 ng/L).

The total concentrations of Σ PAHs were estimated over a wide range of concentrations (Figure 2a, Table S2), which is characterized by seasonal, interseason, and spatial variability. The extreme concentrations of Σ PAHs were recorded in September 2016, in the southern basin of Lake Baikal, and in June 2019, in the northern basin of Lake Baikal (Figure 2b). In the pelagic zone of the southern basin, the mean Σ PAH value was higher than the median of the range of the detected concentrations (210 ng/L—the mean value and 150 ng/L—the median), which indicated the presence of individual areas with high concentrations of pollutants. In particular, at stations 2 and 4 (3 km from the north and south coasts of the southern basin, Figure 1a), the Σ PAH concentrations in the collected samples reached 480 and 610 ng/L. The high level of Σ PAHs was due to an increase in the total fraction of fluorene, phenanthrene, fluoranthene, and pyrene (from 85 to 95% of Σ PAHs). At the same time, at stations 5 and 7, the Σ PAHs concentrations were by an order of magnitude lower and corresponded to the range from 23 to 39 ng/L, with an increase in the share of naphthalenes in the composition (from 21 to 40% of Σ PAHs). In June 2019, the Σ PAH concentrations in the water samples from the northern basin reached 290 ng/L, and the high PAH concentrations, up to 20 times higher than the background (the 2020 season) were recorded at all sampling stations (230 ng/L—the mean value and 260 ng/L—the median). In contrast to the situation in the southern basin of the lake in September 2016, samples with high PAH concentrations had a maximum naphthalene fraction (from 110 to 170 ng/L and from 50 to 62% of Σ PAHs) and the elevated phenanthrene concentrations (from 66 to 92 ng/L and from 28 to 35% of Σ PAHs).

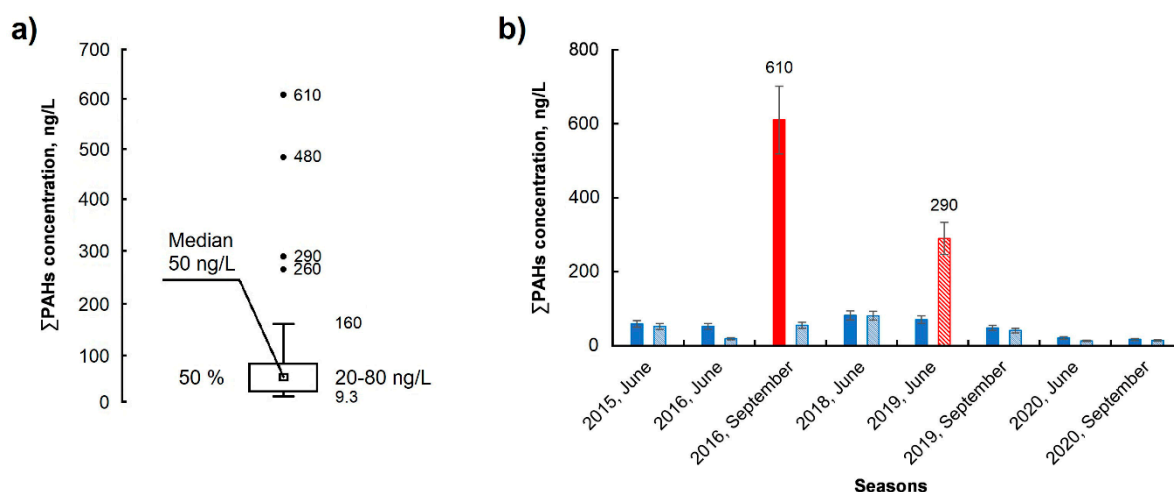


Figure 2. PAH concentrations in water from the pelagic zone of Lake Baikal: (a) Box plot of the Σ PAHs concentrations; (b) Mean concentrations of Σ PAHs in the upper water layer (5 m) of the pelagic zone in Lake Baikal: —southern basin, —northern basin. The extreme concentrations of Σ PAHs recorded in September 2016, and June 2019.

It should be noted that the ratios of the individual PAHs in the samples with the maximum concentrations Σ PAHs radically differed from the profile of pollutants in Baikal water. In the autumn of 2016, fluorene, phenanthrene, fluoranthene, and pyrene dominated the PAH fraction, and in the spring of 2019, it was naphthalenes (Figure 3a). A statistical analysis of the Σ PAH concentrations in Baikal water exposed to the smoke from fires has revealed that that fluoranthene and naphthalene are the main compounds affecting an increase in the Σ PAHs. The naphthalene concentrations were much higher in June 2019 in the northern basin, and in 2016, the fluoranthene concentrations were much higher in the southern and northern basins. Moreover, stations 2 and 4 (with extreme concentrations) stand out dramatically against the general pattern of the results of RDA analysis (Figure 4b).

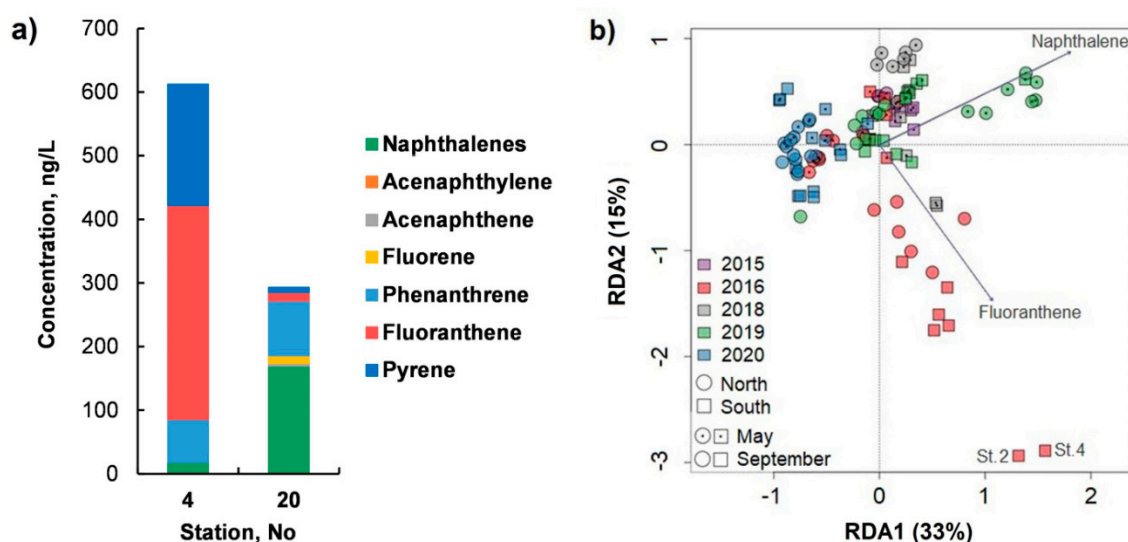


Figure 3. (a) The PAH ratio in the extracts of water samples: St. 4-southern basin, September 2016; St. 20 northern basin, June 2019; (b) RDA analysis of the PAH compositions in different water samples by sampling site, year, and month.

Obviously, the change in the ratio of individual PAHs is associated with the influx of pollutants from different sources. In this context, the 2016 data on the southern basin can be associated with the local transport of the smoke from wildfires that took place in

that season on the coast of the lake, whereas an increase in the PAH concentrations in the water of the northern basin in 2019 due to light naphthalenes—with the long-range atmospheric transport of the wildfire smoke from the northern areas of the Baikal natural territory [18,56].

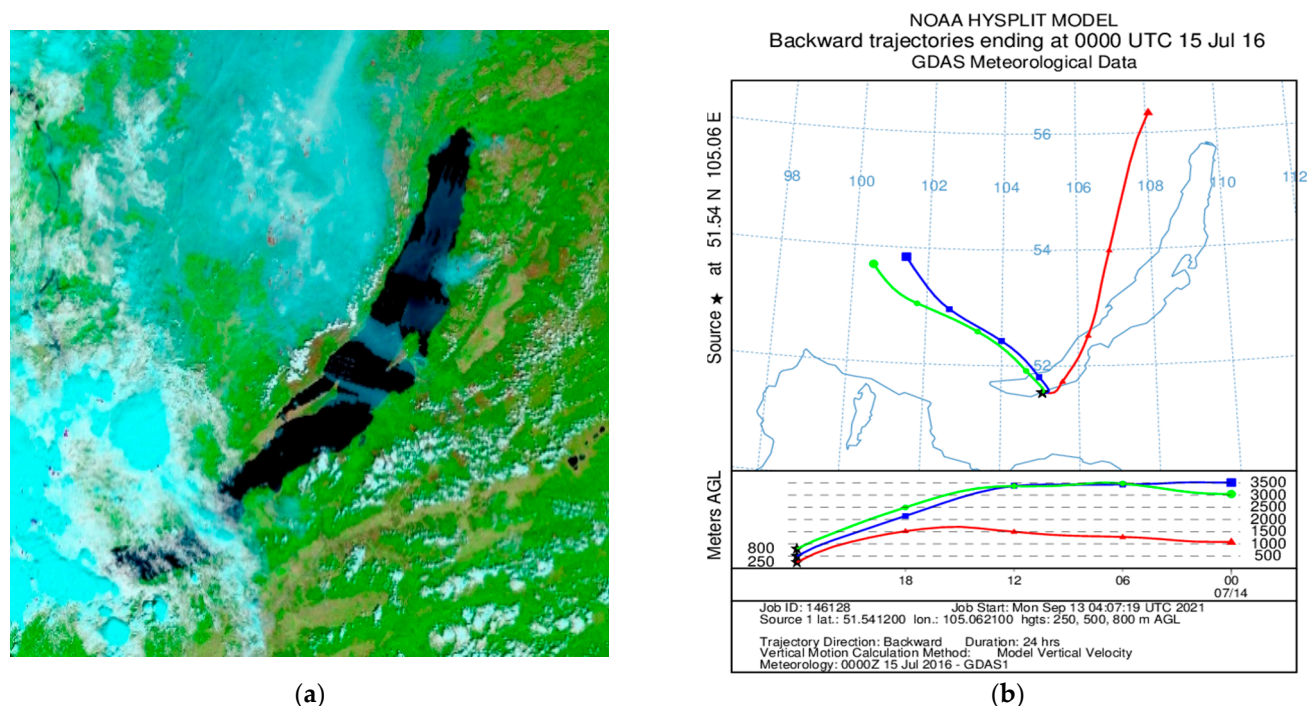


Figure 4. The wildfires in Siberia in July 2016: (a) Satellite image on 28 July 2016 [57]; (b) Back trajectories of air mass transport to the southern basin of Lake Baikal.

3.2. PAHs in the Baikal Aerosol

An increase in the PAH concentrations in the upper water layer of the pelagic zone of the lake in 2016 and 2019 can be explained as a result of the impact of plumes from wildfires in the adjacent areas of the water area of Lake Baikal. These seasons [18] were distinguished by the most severe wildfires. In July 2016, the fires were recorded in an area of 28,100 km², and in September, they were recorded in an area of 14,100 km². In the samples of aerosol from the near-water atmospheric layer taken in July along the west coast of the southern basin of Lake Baikal, the Σ PAHs concentration reached 130 ng/m³; in the samples collected in the northern basin of Lake Baikal, the Σ PAH concentrations were lower by several orders of magnitude and did not exceed 0.84 to 8.9 ng/m³. The calculations of back trajectories of air mass transport using the HYSPLIT model and satellite imagery for this period (Figure 4) confirms the transport of smokes from fires to the water area of the southern part of Lake Baikal and, hence, the source of the extreme Σ PAH concentrations in the aerosol and the upper water layer of the pelagic zone of the southern basin in 2016.

In May 2019, wildfires in the north of the Irkutsk Region were recorded in an area of 8600 km², whereas in July, the areas of fires reached 28,000 km² (Figure 5a), and in September, they decreased to 1700 km² [18]. The calculation of back trajectories of air mass transport (Figure 5b) testified to the possibility of combustion products entering the water area of the northern basin of Lake Baikal. In the samples of aerosol collected at station 21 (Figure 1a) during northerly winds, the Σ PAHs concentrations ranged from 0.17 to 3.9 ng/m³. In the samples of water from the upper water layer collected in the pelagic zone of the northern basin in June before the intense fires in the north of the region, at stations 17, 19, 20, and 21, the PAHs concentrations ranged from 130 to 290 ng/L (the average value is up to three times higher than the average value for Σ PAH concentrations in the southern basin during this period). Notably, in September, the areas of fires reduced to

1700 km², and the Σ PAH concentrations in the upper water layer decreased by a factor of eight, confirming the insignificant contribution from wildfires in the northern areas of Siberia to the concentration of PAHs in Baikal water.

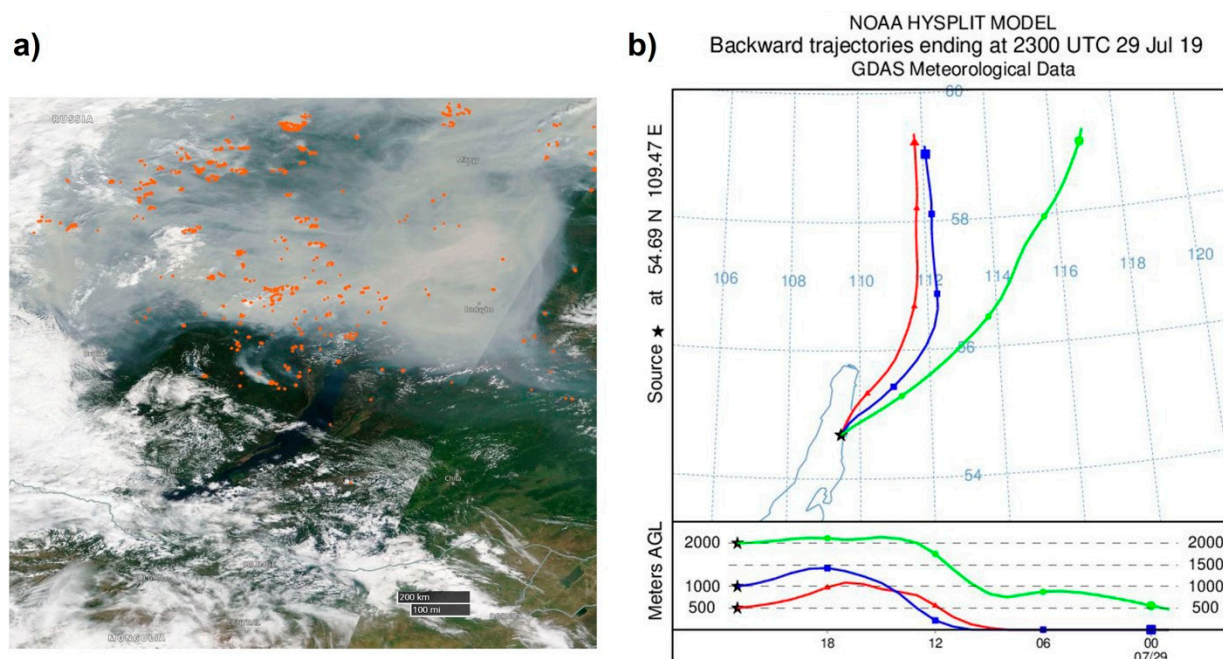


Figure 5. (a) Map of wildfires in Siberia in July 2019 [57]; (b) Back trajectories of air mass transport to the northern basin of Lake Baikal.

In the composition of the aerosol PAH fraction, 19 compounds were detected (Table S3), which were distinguished by significant characteristics confirming the atmospheric transport of PAHs with smoke from wildfires. Indicator ratios of the detected PAHs (anthracene—phenanthrene, fluoranthene—pyrene and benzo[a]anthracene—chrysene) indicated the wood combustion processes and wood soot as sources of the detected polyarenes (Table S4). The ratio of benzopyrenes, benzo[e]pyrene to benzo[a]pyrene, taking into account the rapid degradation of the latter in the atmosphere, confirms the atmospheric transport of the detected PAHs. In the aerosol fraction, we detected perylene, the presence of which in the atmosphere is associated with soil dust, because the soil contains significant amounts of perylene due to the biodegradation of vegetation [58]. The perylene concentration less than 0.002 ng/m³ indicates the minimum contribution of terrigenous material to the aerosol composition. Notably, retene in the composition of the PAH fraction was at a high concentration level, up to 0.33 ng/m³. Retene results from a high-temperature degradation of resinous wood substances [59], and its significant amounts in the aerosol reflect the inclusion of combustion products of forests in East Siberia where coniferous species (*Pinus sylvestris* L and *Larix sibirica*) are dominant (up to 80%).

3.3. Wildfire Effects on the Surface and Watershed Basin of Lake Baikal

A high level of the Σ PAH concentrations in aerosol above the water surface and a 3.5-fold increase in transport rates of airborne particulate matter onto the surface of Lake Baikal are of key importance for explaining the phenomenon of the appearance of the extreme concentrations of pollutants in the upper water layer. During the period of cleaning the atmosphere, the transport of airborne solid particles to the surface of Lake Baikal within 24 h was estimated at 41 $\mu\text{g}/\text{m}^2$; during large fires, it was 150 $\mu\text{g}/\text{m}^2$ [56]. Increased flux of aerosol particles from the atmosphere was recorded with the appearance of the spots of soot and ash on the water surface and the growth in the PAH concentrations in the microlayer of the water surface, up to 960 ng/L. In seasons with the minimum

impact of wildfires on the water area of Lake Baikal, the Σ PAH concentration in the surface microlayer did not exceed 50 to 60 ng/L but were by an order of magnitude higher than in the Antarctic areas (Gerlache Inlet Sea, from 6.0 to 9.1 ng/L [60]). In the surface water microlayer near seaports and harbors characterized by high anthropogenic pressure, the PAH concentrations can reach from 6000 to 17000 ng/L (Chesapeake Bay USA [61], the harbor of Los Angeles [62], Leghorn Italy [63]).

The minimum PAH concentrations recorded during the 2020 season in the pelagic zone of Lake Baikal were grouped separately (Figure 2b) and assessed as corresponding to the global background level and the global atmospheric transport—as a dominant source that determines the PAH concentrations in the Baikal aerosol and the surface waters of Lake Baikal at the trace level. In the upper water layer of the lake's pelagic zone, the Σ_8 PAH (hereinafter the total PAH concentrations among the 16 priority substances are presented) concentrations ranged from 6.0 to 21 ng/L (Table 1); in the upper water layers of the Barents Sea and East-Siberian Sea, Σ_8 PAHs ranged from 16 to 60 ng/L, and in the Antarctic region, Σ_{13} PAHs ranged from 5.3 to 9.4 ng/L (Gerlache Inlet Sea) [60]. In the Arctic aerosol, the Σ_{16} PAH concentrations ranged from 0.57 to 0.86 ng/m³ [64], and the Σ_{16} PAH concentrations in the aerosol above the water surface of Lake Baikal ranged from 0.09 to 0.58 ng/m³.

Polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins, and dibenzofurans detected in wildfire smoke [8,65] indicate wildfires as a potential source of organochlorine pollutants. In the summer seasons of 2019 and 2020 (seasons of intense fires and after their occurrence), the total concentrations of the seven indicator PCB congeners (Σ_7 PCB) in the Baikal aerosol above the water surface were comparable and ranged from 0.09 to 1.9 pg/m³ (with equal mean values and medians, Table S7). At the same time, the Σ_{19} PAH concentrations in the aerosol of the 2019 summer season reached values that were 2.5 times higher than during the 2020 season (Table S3). In the upper water layer of Lake Baikal, PCBs were detected in the Σ_7 PCB concentration range from 0.07 to 0.34 ng/L [47], which corresponds to the previous one determined in 1992–1993 (from 0.08 to 1.9 ng/L) and is estimated as background [31–33]. Apparently, PCBs detected in Baikal waters are not associated with wildfires in the adjacent areas.

Table 1. PAH concentration in the surface waters of the world.

Area	Σ PAHs, ng/L	Reference
Timor Sea, Australia	Σ_{15} 54,000–213,000, mean 100,000	[66]
Jiulong River Estuary and west Xianmen Sea, China	Σ_{16} 7000–27,000, mean 1700	[67]
Poyng Lake, China	Σ_{16} 5.6–270	[68]
Hooghly and Brahmaputra Rivers, India	Σ_{16} 4000–4800, mean	[69]
Sarno River, Italy	Σ_{16} 23–2700, mean 740	[70]
Rivers in the north of France, Belgium	Σ_{16} 1500–7800	[71]
Daya Bay, China	Σ_{16} 4200–29,000	[72]
Langkawi Island, Malaysia	Σ_{18} 6100–46,000, mean 25,600	[73]
Coastal streams, American Samoa	Σ_9 30–380	[74]
Ikpa River Basin, Niger	Σ_{16} 580–900	[75]
Almendares River, Cuba	Σ_{14} 800–16,000	[76]
Angara River, Russia	Σ_{10} 36–95	[46]
Baltic Sea, Europe	Σ_{15} 2.6–7.7	[77]
Gerlache Inlet Sea, Antarctica	Σ_{13} 5.3–9.4, mean 7.1	[60]
Lake Baikal, Russia	Σ_8 6.0–21, mean 12	This study
Arctic (Barents Sea, East Siberian Sea), 2018	Σ_8 16–60, mean 32	This study

The plume of wildfire smoke above the Baikal natural territory affects not only the upper water layer of the lake but also its watershed basin. The tributaries of Lake Baikal,

which have extensive watershed areas on the slopes of the Hamar–Daban mountain range, from 60 to 3000 km² in the southern part and from 600 to 21,000 km² in the northern part of the Baikal natural territory [55], in this case, are the potential sources of PAHs in the aquatic ecosystem of the lake. During the monitoring of PAHs in estuarine waters of the Utulik, Solzan, Khara-Murin, Snezhnaya, and Pereemnaya rivers (Figure 1b), Σ PAH concentrations ranged from 15 to 45 ng/L (43 ng/L—the mean value and 30 ng/L—the median). The composition of PAHs in the waters of the tributaries (Table S5) is similar to the composition of PAHs in Baikal water and demonstrates a high concentration of naphthalenes (from 45 to 80% of Σ PAHs). High molecular weight PAHs such as benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[e]pyrene were detected at a level less than 1.0 ng/L (2.5% of Σ PAHs) in individual samples.

The exception was the 2019 season, during which there was an increase, up to the four-fold mean value, in the Σ PAH concentrations in the waters of the tributaries for the observation period (from 2016 to 2021). In May, the Σ PAH concentrations in the tributaries of the southern basin increased to 110 ng/L; in September, they increased to 140 ng/L at the estuaries of the rivers in the northern basin, the Kichera and the Tompuda. An increase in the PAH concentrations was associated with an increase of naphthalenes in the total concentration (up to 94% of Σ PAHs). During the impact of the wildfire smoke plume on the watershed basins, the Σ PAH concentrations in waters of the tributaries could be higher than or comparable to the pelagic zone of the lake (Figure 6a,b). The calculation of the amount of the PAH release into Lake Baikal has revealed that PAH entering the lake with the elevated concentrations of pollutants in waters of the tributaries up to 18 kg for 30 days (Table S6) are extremely minor compared to the volume of the lake water masses and can increase the concentration of pollutants in the upper water layer (from 0 to 200 m) by less than $\approx 0.001\%$ to 0.05% .

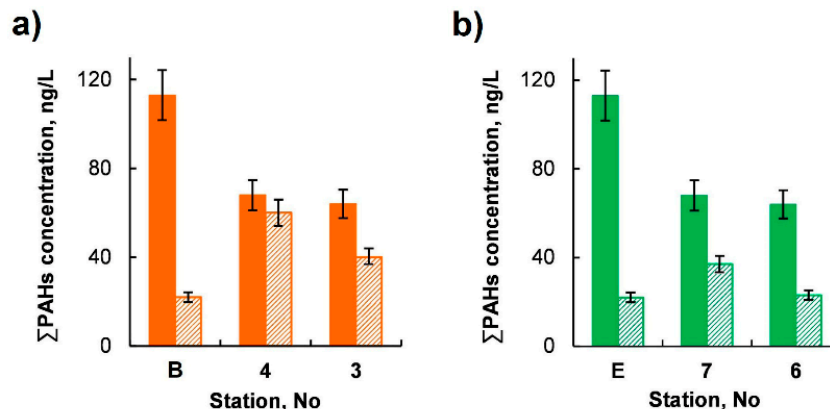


Figure 6. Σ PAH concentrations in the waters of the tributaries in the southern basin of Lake Baikal (a) in May and September 2016; (b) in May and September 2019.

3.4. Toxicity and Risk Assessment

At the elevated PAH concentrations in Baikal water, no pollutants with carcinogenic properties such as benzo[a]pyrene and dibenzo[a,h]anthracene (above LOD of 0.1 ng/L) were detected in the polyarene fraction. In particular, the LOD value of benzo[a]pyrene corresponds to 0.01 of the maximum permissible concentrations (MPC, 10 ng/L) established for this pollutant in drinking water in the European Union and Russia [78,79]. The toxicity of PAHs in the water of the lake and possible ecological risks under conditions of an increase in their concentrations were assessed by the total toxic equivalent (Σ TEQ) and the values of risk quotient (RQ) proposed in [49–51]. The mean values of Σ TEQ for PAHs in the southern basin in 2016 and in the northern basin in 2019 were up to 15 times higher than the background but were down to 50 times lower than MPC. Acenaphthylene, acenaphthene, fluorene, and fluoranthene (80% of Σ TEQ) were dominant in the Σ TEQ value for PAHs in

the water of the southern basin in 2016, whereas in the northern basin in 2019, naphthalene and phenanthrene made the maximum contribution to ΣTEQ (Table S8).

Risk quotient (RQ) was applied to evaluate the eco-toxicity of water pollution. The negligible concentrations (NCs) and the maximum permissible concentrations (MPCs) of individual PAHs and the total PAHs are shown in Table S9. During the 2020 season, the mean RQ_{NCs} values were <1 for the total PAHs in the upper layer of the pelagic zone (Figure 7). The concentrations of acenaphthene and fluorene were an exception, for which the RQ_{NCs} value was >1 . Evaluation by the RQ_{MPCs} criterion, taking into account MPCs of individual PAHs, confirmed a negligible eco-risk effect for biota with the background PAH concentration. With an increase in the PAH concentrations in 2016 and 2019, the RQ_{NCs} values for the individual and total concentrations of the detected PAHs were >1 , except for naphthalene and chrysene (September 2016) as well as acenaphthylene and chrysene (June 2019), for which the RQ_{NCs} values were <1 . We estimate the ecological risk for biota under the impact of the plume of wildfire smoke on the surface Baikal water as moderate ($\text{RQ}_{\text{MPCs}} < 1$).

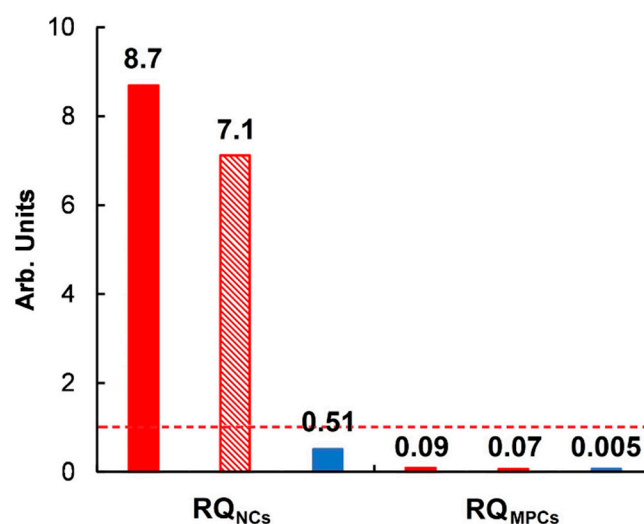


Figure 7. Assessment of the eco-toxicity of water pollution by ΣPAHs . Mean values of RQ_{NCs} and RQ_{MPCs} for the $\Sigma_8\text{PAH}$ concentrations (the total amount of the detected priority PAHs) in the water samples from the upper water layer collected in the southern basin of Lake Baikal in June 2016—■, in the northern basin of Lake Baikal in September 2019—▨, and in the pelagic zone of Lake Baikal during the 2020 season—■.

Importantly, the seasonal increases in the PAH concentrations in the surface water resulting from the impact of wildfires do not lead to significant changes in the concentrations of pollutants in deep layers. During the monitoring of PAHs from 2015 to 2020 in the water column of the lake (400 m), the ΣPAH concentrations corresponded to a narrow range of the $\Sigma_{10}\text{PAH}$ values, from 12 to 51 ng/L, and they were comparable with the background concentration of pollutants of this class in the upper water layer (Table S10).

The preservation of the purity of Baikal water after the impact of wildfire smoke on its surface water is one of the lake's phenomena, which is associated with the presence of appropriate mechanisms in its ecosystem. PAHs entering the neuston of the water surface undergo biodegradation. Model experiments have indicated that communities of Baikal microorganisms effectively biodegrade naphthalenes (up to 95–97%) within five days [45]. Moreover, the *Synedra acus* subsp. *Radians* diatoms, the dominant species of Baikal phytoplankton, accumulated PAHs in their lipid bodies [80].

4. Conclusions

Ten compounds represent polycyclic aromatic hydrocarbons in the upper water layer of the pelagic zone Lake Baikal: naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, and chrysene. The total concentration of the detected PAHs varies in the wide range from 9.3 to 160 ng/L, characterizing by seasonal, inter-seasonal, and spatial variability. The concentration level of priority PAHs (Σ_8 PAHs: 6.0–21 ng/L) recorded during the 2020 season is comparable with the concentration of pollutants of this class in the Arctic and Antarctic waters and is estimated as background. The results of the analysis of aerosol samples from the near-water layer and samples of surface water of the microlayer, as well as the calculation of back trajectories of air transport near Lake Baikal and satellite images, indicate the impact of wildfires in adjacent areas on Lake Baikal and, consequently, wildfires appear to be a natural source of PAHs in Baikal water, with which a seasonal increase in Σ PAH concentrations was associated in 2016 and 2019. The ratio of individual PAHs in water samples distinguished by extreme Σ PAH concentrations indicate the influx of pollutants from various sources. In particular, in 2016, the transport of PAHs to the lake's water in the southern basin was from local sources (wildfires on the lake's coast), and in 2019, the influx of PAHs to the northern part of the lake was due to the long-range atmospheric transport from the northern areas of Siberia. The influx of PAHs from the atmosphere is the main channel of the impact of wildfires on the cleanness of water in the lake. The Baikal tributaries, whose water areas are under the influence of plumes from wildfire smoke, do not significantly affect the PAH concentrations in Baikal water. Notably, the increase in the PAH concentrations is of seasonal nature and detected in the upper water layers of the lake. The toxicity of PAHs detected in extreme situations is up to 50 times lower than the MPC level, and the ecological risk for biota during these periods is moderate.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w13192636/s1>. Table S1: Toxicity equivalency factors (TEF), risk quotient for negligible concentrations (RQNSs), and risk quotient for the maximum permissible concentrations (RQMPCs) of the individual and total PAHs in water; Table S2: Concentration range (mean/median) for the detected PAHs in the upper water layer of the pelagic zone of Lake Baikal (the monitoring from 2015 to 2020); Table S3: Concentration range for the detected PAHs in the aerosol above the water surface; Table S4: PAH ratios in Baikal aerosol during wildfires in adjacent areas; Table S5: Σ PAH concentrations in waters of the tributaries of Lake Baikal; Table S6: Estimation of the influx of PAHs to Lake Baikal with the Baikal tributaries; Table S7: The concentration range for detected PCB indicator congeners in aerosol above the water surface; Table S8: The benzo[a]pyrene equivalent concentrations of PAHs in the upper water layer of the pelagic zone of Lake Baikal; Table S9: Risk quotient for negligible concentrations (RQNSs) and the maximum permissible concentrations (RQMPCs); Table S10. Concentration Σ PAHs in the water column of Lake Baikal (400 m), ng/L.

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