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Contamination of the Lake Baikal Basin with Polyaromatic Hydrocarbons: the Gusinoe Lake

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Abstract

In surface water and bottom sediments of the Gusinoe Lake (the Lake Baikal basin), there were concentration profiles determined for 19 polycyclic aromatic hydrocarbons (PAHs). It has been found that the total PAH content amounts to 7.1–33.7 ng/L for the surface water and 42.6–221.8 ng/g of dry solid matter for bottom sediments. It has been demonstrated that the presence of PAHs in the samples of surface water and bottom sediments of the Gusinoe Lake could mainly be caused by local sources having pyrolytic nature.

Key words: polycyclic aromatic hydrocarbons, Lake Baikal basin

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) represent the most common environmental pollutants. Many of them exhibit toxic, highly carcinogenic and mutagenic activity.

As far as the hundreds of PAHs detected in the environmental objects are concerned, the list for assessing the environmental hazard adopted by the United States Environmental Protection Agency (EPA US) includes 16 priority substances those can form the basic background of PAH contamination. They are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene [1].

The group of priority PAHs for surface waters includes six representatives from the mentioned list: benzo(a)pyrene, benzo(b)fluoranthene (severe carcinogens), benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene (weak carcinogens) as well as non-carcinogenic, but toxic fluoranthene and benzo(k)fluoranthene. According to the recommendations of the World Health Organization (WHO), the total concentration of the priority PAHs in potable water should not exceed 0.2 µg/L at the concentration level of benzo(a)pyrene being lower than 5 ng/L [2, 3].

As it is known, the PAHs come in the environment from pyrolytic and petrogenous sources. The pyrolytic sources include the processes of an incomplete combustion of organic matter (coal, oil, plant residues, wood), as well as the emissions of internal combustion engines. The petrogenous sources represent the processes of

transformation of vegetable matter (fossil oil, gas, the products of processing thereof and the processes of modern diagenesis) [4].

In the atmosphere, the PAHs are mainly sorbed on solid aerosol particles. Falling the PAHs with atmospheric precipitations leads to the accumulation thereof in soil and surface water [5].

The Gusinoye Lake is the second one after the Lake Baikal with respect to water mass among the Transbaikalian water reservoirs; it represents a buffer environmental zone of the Baikal natural territory. The Bain-Gol River flowing out of the southeastern part of the lake flows into the Selenga River, the main tributary of the Lake Baikal. The catchment area of the Gusinoye Lake basin is equal to 924 km² [6].

The Gusinoye Lake is subject to a significant anthropogenic influence. The most significant sources of contamination located directly on the lake shore are presented by the largest in the region Gusinozersk TPP, coal mines,

roads and railways, the Gusinozersk city with the population of about 25 thousand people.

Earlier, there were assessed falling the PAHs onto the snow cover of the Lake Baikal, near the settlements of the southern Baikal region, as well as there was determined a level of contamination of bottom sediments in the Lake Baikal tributaries (Selenga, Turka, Khaim, Barguzin rivers), the Zmeevaya Bay (the Chivyrkuy Bay) and the Gulf of Sor-Cherkalovo [7, 8].

Reliable information concerning the level of contamination of the Gusinoye Lake with hazardous PAHs ecotoxicants, as well as the analysis of the ways how pollutants come in the lake are required in order to take efficient measures to preserve the ecosystem thereof and the ecosystem of the Lake Baikal basin.

The present work consisted in establishing the patterns of the income and distribution of the PAHs in the ecosystem of the Gusinoye Lake with the use of a gas chromatography-mass spectrometry technique.

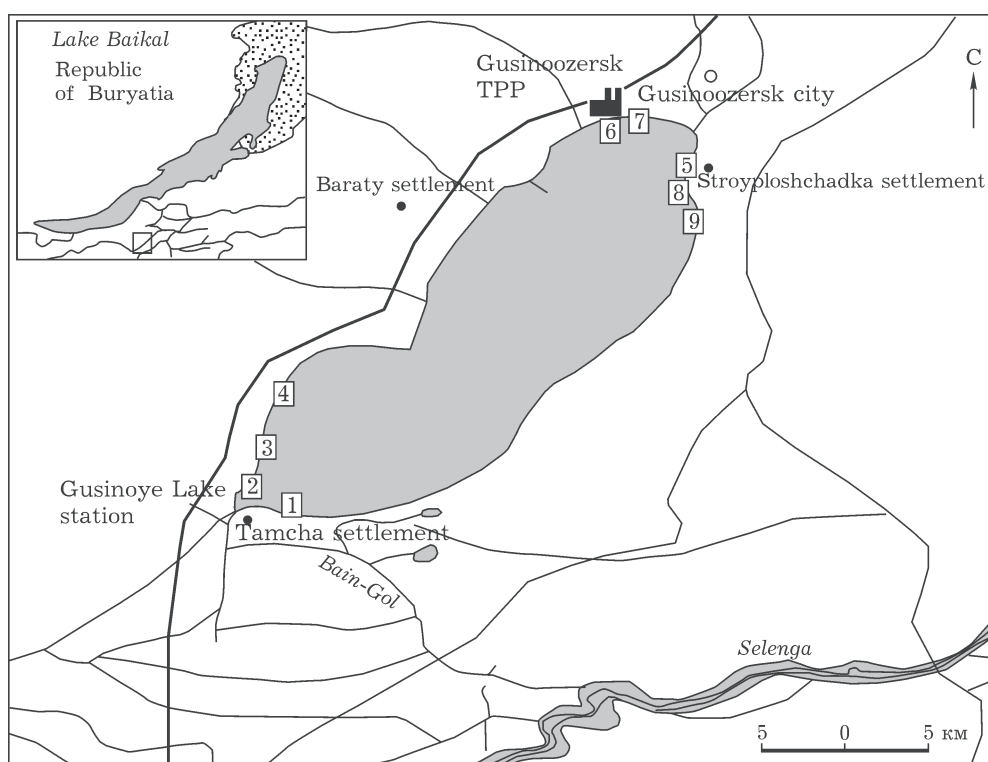


Fig. 1. Schematic map of stations for sampling the experimental material (1-9): 1 - Tamcha settlement; 2-4 - Gusinoye Lake stations; 5, 8, 9 - Stroyploshchadka settlement; 6 - Gusinozersk TPP; 7 - Gusinozersk city.

EXPERIMENTAL

The objects under investigation for determining the levels of PAH contamination in the Gusinoye Lake were presented by the samples of bottom sediments and surface waters, taken in autumn of 2009. The map of the location of stations for sampling bottom sediments and surface waters is shown in Fig. 1.

The samples of surface water were preserved *via* adding a special purity grade concentrated HCl taking 1 mL of the acid per 1 L of solution. The bottom sediment samples were taken from the surface layer up to 10 cm thick using a Wildlife Supply Co. bottom sampler (USA). The samples were dried at a room temperature, sieved through a sieve with a mesh size of 0.4 mm.

The preparation of bottom sediment samples (5 g) and of surface water samples (2 L) consisted in the extraction of PAHs with methylene chloride and purification of the extracts

obtained *via* passing through a column packed with activated alumina. For the analysis of the extracts we used a gas chromatography-mass spectrometry technique (Agilent Technologies 6890N GC with an AT 597 5N mass selective detector and an AT 7683B autosampler) in the mode of detecting the individual characteristic ions of the compounds under determination.

The sample components under analyzing were separated using a HP-5MS quartz capillary column 30 m long with a diameter of 0.25 mm and a coating thickness equal to 0.25 μm . The conditions of gas chromatographic determination were as it follows: the detector temperature 280 °C, ion source temperature 230 °C, the quadrupole unit temperature 150 °C, helium being used as the carrier gas. The column oven temperature increased from 50 (holding time 2 min) up to 280 °C (holding time 20 min) at a rate of 10 °C/min. The delay of

TABLE 1

PAH content in the samples of bottom sediments, ng/g for dry solid matter

Compounds	Sampling stations								
	1	2	3	4	5	6	7	8	9
Acenaphthylene	0.1	0.2	0.2	0.4	0.9	0.7	0.8	0.6	0.3
Acenaphthene	0.4	0.7	0.4	0.6	2.8	1.0	1.5	1.8	0.8
Naphthalene	5.3	5.5	12.7	10.3	19.8	19.5	22.9	21.4	16.0
Fluorene	1.1	7.4	2.9	1.8	6.6	3.5	3.2	3.2	1.3
Phenanthrene	9.8	51.4	19.3	13.0	35.9	17.6	22.3	17.6	8.6
Anthracene	1.4	7.7	2.5	1.4	8.0	2.6	4.4	8.0	1.2
Fluoranthene	8.2	6.7	3.4	3.6	31.7	7.1	17.6	15.5	5.5
Pyrene	5.6	5.3	2.2	2.3	20.0	5.9	16.2	12.5	4.2
Benz(a)anthracene	2.6	0.4	0.5	0.8	4.4	n/d	4.5	4.3	1.8
Chrysene	4.7	1.4	1.1	2.2	11.6	1.4	16.6	10.2	3.4
Benzo(b)fluoranthene	3.6	0.4	0.3	1.2	5.0	1.0	12.5	5.3	1.6
Benzo(k)fluoranthene	2.9	0.4	0.2	1.2	6.4	0.7	7.6	5.8	2.1
Benzo(a)pyrene	1.8	0.4	0.1	0.5	5.9	1.0	10.9	5.9	2.1
Indeno(1,2,3-c,d)pyrene	4.8	0.1	0.1	0.6	5.2	0.0	7.4	3.9	1.6
Dibenz(a,h)anthracene	0.3	0.0	0.0	0.1	0.5	0.1	2.8	0.5	0.3
Benzo(g,h,i)perylene	8.6	0.3	0.3	0.8	6.0	0.7	17.2	5.7	2.4
Benzo(j)fluoranthene	0.6	0.1	0.1	0.1	0.8	0.1	0.9	0.8	0.4
Benzo(e)pyrene	4.4	0.4	0.2	1.2	5.6	0.8	18.5	6.5	2.8
Perylene	1.2	0.3	0.1	0.6	6.9	1.1	34.5	2.5	1.3
Σ PAH for 19 compounds	67.4	89.1	46.4	42.6	183.8	64.6	221.8	131.8	58.2
Σ PAH for 6 compounds	29.9	8.2	4.4	8.0	60.1	10.4	73.1	42.1	15.2

Note. n/d – not detected, below the detection limit equal to 0.02 ng/g of dry weight.

TABLE 2

PAH content in surface water samples, ng/L

Compounds	Sampling stations								
	1	2	3	4	5	6	7	8	9
Acenaphthylene	0.8	0.7	0.6	0.5	0.9	0.7	0.9	1.3	1.4
Acenaphthene	0.9	0.7	0.8	0.7	1.1	0.6	0.4	0.7	1.1
Naphthalene	12.0	2.2	7.9	0.7	3.3	5.2	2.4	11.7	7.4
Fluorene	2.1	1.1	0.9	0.7	1.5	0.8	0.8	1.1	1.3
Phenanthrene	7.0	7.0	2.2	1.8	3.8	2.0	1.2	1.8	3.8
Anthracene	0.6	0.4	0.3	0.2	0.8	0.2	0.1	0.2	0.3
Fluoranthene	2.1	1.5	0.6	0.7	2.7	0.7	0.7	0.5	1.9
Pyrene	1.9	0.8	0.4	0.4	1.9	0.6	0.3	0.3	1.5
Benzo(a)anthracene	0.7	0.3	0.3	0.4	1.1	0.4	0.3	0.1	0.5
Chrysene	0.8	0.4	0.3	0.3	1.1	0.3	0.3	0.1	0.6
Benzo(b)fluoranthene	0.9	0.1	0.1	0.1	0.7	0.2	0.1	n/d	0.3
Benzo(k)fluoranthene	0.7	0.1	0.1	0.1	0.6	0.1	0.1	n/d	0.3
Benzo(a)pyrene	0.7	0.1	0.1	0.1	0.8	0.1	0.1	n/d	0.3
Indeno (1,2,3-c,d)pyrene	0.5	0.1	n/d	n/d	0.2	0.1	n/d	n/d	0.3
Dibenz(a,h)anthracene	0.1	n/d	n/d	n/d	0.1	n/d	n/d	n/d	n/d
Benzo(g,h,i)perylene	0.6	0.1	n/d	n/d	0.6	0.1	0.1	n/d	0.3
Benzo(j)fluoranthene	0.1	0.1	n/d	n/d	0.2	n/d	0.1	n/d	0.1
Benzo(e)pyrene	1.1	0.2	0.3	0.3	1.0	0.4	0.2	0.1	0.6
Perylene	0.3	0.1	0.1	0.1	0.3	0.1	0.1	n/d	0.3
ΣPAH for 19 compounds	33.7	15.8	14.9	7.1	22.6	12.5	8.0	17.8	22.0
ΣPAH for 6 compounds	5.50	1.9	0.9	1.2	5.5	1.4	1.0	1.0	3.2

Note. n/d – not detected, below the detection limit equal to 0.05 ng/L.

turning cathode ion source on for missing the solvent peak of was equal to 5 min.

The content of 19 individual PAHs those were included in the priority list of pollutants adopted by the European community (EC) (acenaphthylene, acenaphthene, naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene, benzo(j)fluoranthene, benzo(e)pyrene, perylene) was determined. For the quantitative determination we used a standard sample of the mixture of PAHs (NR No. 85006035), as a surrogate standard (witness) we used 9,10-di(trideuteriummethyl)phenanthrene; the accuracy of determination was better than 20 %; the detection limit being of 0.02 ng/g in the case of analyzing 5 g of bottom sediment, and

0.05 ng/L in the case of analyzing 2 L of water, respectively.

RESULTS AND DISCUSSION

Table 1 demonstrates the results of the PAH determination in the bottom sediments of the Gusinoye Lake. From the values of PAH concentrations presented one can see that the level of contamination is relatively low, and the sum of the PAH concentration values with respect to 19 individual compounds ranges from 42.6 to 221.8 ng/g of dry solid matter (for six compounds ranging within 4.4–73.1 ng/g). These values are comparable with the level of PAH concentrations in the surface bottom sediments of the Arctic regions: Ny Ålesund (Norway) according to the total amount for 15 compounds 11–1100 ng/g, the Barents Sea according to

TABLE 3

Literature data for PAH concentrations ratio in bottom sediments used to determine the nature of the contamination sources

Origin of PAHs	Phenanthrene/ Anthracene [16, 17]	Fluoranthene/ Pyrene [16, 17]	Fluoranthene/ (Fluoranthene + Pyrene) [13, 15, 18]	Anthracene/ (Anthracene + phenanthrene) [13, 15, 18]
Pyrolytic	<10	>1	>0.5	>0.1
Petrogenous	>10	<1	<0.4	<0.1

the total amount for 16 compounds 12–353 ng/g) [9, 10]. For the countries with a high anthropogenic load on the environment the concentration of PAHs in the bottom sediments of lakes reaches high values being of serious hazard for aquatic ecosystems and human health because of a high level of PAH bioaccumulation in the tissues of living organisms. For example, for the bottom sediments of the Taihu Lake (East China), the total amount with respect to 16 PAH compounds reaches 1207–4754 ng/g [11].

The average concentration of PAHs was 100.7 ng/g of dry solid matter. The highest concentration values are observed for phenanthrene (21.6 %), naphthalene (14.7 %), fluoranthene (11.0 %) and pyrene (8.2 %), the indicators of anthropogenic sources (industrial emissions, household wastes). The maximum content of these pollutants was detected for samples Nos. 2, 5, 7, 8, taken near the Gusinoye Lake railway station, the Stroyploshchadka settlement, the channel of discharging the purified wastewater of the Gusinozersk TPP.

Table 2 demonstrates the results of the determination of PAHs in the surface water of the Gusinoye Lake. The total concentration of 19 individual PAHs in surface waters, as compared to bottom sediments is significantly lower amounting to 7.1 to 33.7 ng/L due to a low

water solubility of PAH and to absence of suspended particles in significant quantities.

The mean value for the concentration of PAHs amounts to 17.2 ng/L, at that the highest content thereof is exhibited by samples Nos. 1, 5, 9, taken near the centers of population (the Tamcha settlement, the Stroyploshchadka settlement). The maximum concentration values are observed for naphthalene (34.0 %), phenanthrene (19.7 %), fluoranthene (7.3 %), and fluorene (6.5 %), which indicates that there are local sources thereof. The content of benzo(a)pyrene in the surface waters of the Gusinoye Lake is equal to 0.1–0.8 ng/L, which does not exceed the MPC level acceptable for water reservoirs aimed at drinking and community water use (the MPC being of 0.001 µg/L) [12].

To determine the origin of PAHs we used ratio values for the concentrations characteristic of individual PAHs those allow to identifying the sources of entering thereof to the environment [13]. The analysis of these relationships is based on the differences in the stability of “kinetic” and “thermodynamic” PAH isomers. In the course of high temperature combustion processes and/or of anthropogenic supplying the PAHs to the environment, these ratio values increase due to increasing the proportion of “kinetic” isomers [14, 15].

TABLE 4

Ratio values for PAHs concentrations in the samples of bottom sediments of the Gusinoye Lake

PAH ratio	Sampling stations								
	1	2	3	4	5	6	7	8	9
Phenanthrene/anthracene	7.0	6.7	7.9	9.4	4.5	6.7	5.1	2.2	7.3
Fluoranthene/pyrene	1.5	1.3	1.6	1.6	1.6	1.2	1.1	1.2	1.3
Fluoranthene/(fluoranthene + pyrene)	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.6	0.6
Anthracene/(anthracene + phenanthrene)	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.3	0.1

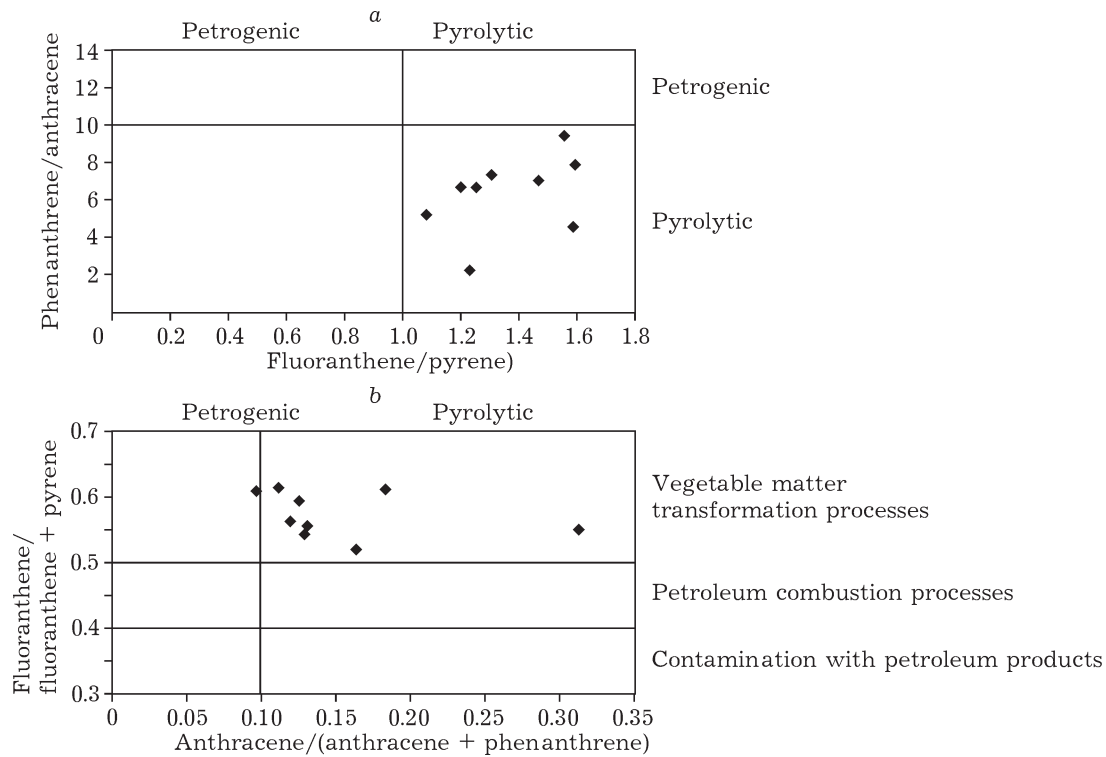


Fig. 2. Correlation between concentration ratio values anthracene/(anthracene + phenanthrene) and fluoranthene/(fluoranthene + pyrene) (a), phenanthrene/anthracene and fluoranthene/pyrene (b) in the bottom sediments of the Gusinoye Lake. For designation, see Table 3.

TABLE 5

Total concentration for PAH groups with different numbers of aromatic rings in the bottom sediments of the Gusinoye Lake, ng/g

Number of aromatic rings	Sampling stations								
	1	2	3	4	5	6	7	8	9
2-3	18.1	72.9	37.9	27.4	73.9	44.9	54.9	52.6	28.1
4	21.0	13.8	7.2	9.0	67.7	14.3	54.8	42.5	15.0
5	14.9	2.0	1.0	5.0	31.0	4.7	87.5	27.2	10.6
6	13.4	0.4	0.3	1.3	11.2	0.7	24.6	9.6	4.0

TABLE 6

Total concentration for PAH groups with different numbers of aromatic rings in the surface water of the Gusinoye Lake, ng/L

Number of aromatic rings	Sampling stations								
	1	2	3	4	5	6	7	8	9
2-3	23.3	12.1	12.6	4.5	11.3	9.4	5.8	16.6	15.3
4	5.6	2.9	1.6	1.8	6.9	1.9	1.6	1.0	4.4
5	3.9	0.7	0.7	0.1	3.7	0.9	0.6	0.1	1.8
6	1.1	0.1	0	0.1	0.8	0.3	0.1	-	0.5

Table 3 demonstrates the literature data concerning the ratio between the concentration values of different PAHs for determining the sources of their origin.

According to data from Table 4, the ratio values of phenanthrene/anthracene and fluoranthene/pyrene range between 2.2–9.4 and 1.1–1.6, respectively. The average values indicate the fact that the PAHs of pyrolytic nature prevail in the bottom sediments of the Gusinoye Lake (Fig. 2, a) [16, 17].

The ratio values anthracene/(anthracene + phenanthrene,) and fluoranthene/(fluoranthene + pyrene) for the bottom sediments amount to 0.1–0.3 and 0.5–0.6, respectively, which also indicates the origin of the PAHs to be of pyrolytic nature (see Fig. 2, b). These sources could be presented by boilers of the Gusinozersk HEPP and TPPs, where coal is used as the main fuel [15, 18].

Tables 5 and 6 present data concerning the total concentration of PAH groups with different numbers of aromatic rings revealed in the samples of bottom sediments and surface waters of the Gusinoye Lake.

The total concentration values for the PAH group with two or three or four aromatic rings in the samples under investigation is much higher than the concentration of the PAHs belonging to other groups, which also indicates PAH entering due to low-temperature pyrolysis processes [19].

CONCLUSION

The data obtained concerning the content and profiles of PAHs, the analysis of relationships characteristic of individual PAHs for identifying the sources of supplying thereof to the Gusinoye Lake allow one to draw the following conclusions:

- The contamination of bottom sediments and surface water by PAH compounds in the Gusinoye Lake is relatively low, it is comparable with the level of contamination of the Arctic seas being mainly caused by the nature of local sources having pyrolytic nature (coal combustion in industry and wood combustion for residential heating).

- The content of benzo(a)pyrene in the surface waters of the Gusinoye Lake does not ex-

ceed the MPC level acceptable for water reservoirs for drinking and community water use (MPC 0.001 µg/L).

The bottom sediments and water surface exhibit prevailing the PAHs containing 2–4 aromatic rings, therewith the content of naphthalene in the surface water is greater than that in the bottom sediments, which could be caused by a relatively high solubility thereof in water.

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