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Priority Phthalates in the Lake Baikal Pelagic Zone and Coastal Area

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Abstract

The contents of di-*n*-butyl phthalate (DBP) and di (2-ethylhexyl) phthalate (DEHP) were assessed in the Lake Baikal pelagic zone. The spatial heterogeneity of the distribution of phthalates in the upper and deep water levels for all basins of Lake Baikal was determined from 0.06 to 3.1 μg/dm^3 of DBP and from 0.03 to 1.4 μg/dm^3 of DEHP, seasonal variability of the total concentrations of phthalates in the pelagic zone of the lake being up to 10 times. Background stations of the reference section in three lake basins were proposed as reference areas for monitoring, and the average concentrations of phthalates in the upper aqueous layer (5–200 m) were proposed to assess the present content of phthalates in the water of the lake. The contents of DBP and DEHP in Lake Baikal Water over the period 2015–2016 were 0.35–0.89 and 0.06–0.32 μg/dm^3, respectively, and do not exceed the MPC for water bodies specified in Russia. A simultaneous change in DBP concentration in the upper water layer of the pelagic zone of the southern lake basin and in its coastal area as pollution indicator was noted. Phthalates were determined by liquid-liquid extraction of analytes into *n*-hexane, direct analysis of extracts using chromatography-mass spectrometry in selective detection mode (m/z 149 and 153) and measurements by the internal standard method using di-*n*-octylphthalate-3,4,5,6-d$_4$ as a surrogate standard. Secondary pollution of water and extracts with laboratory phthalates was regarded as the systematic error that was assessed by the value of reagent blanks and subtracted from analysis results. The total error was assessed using the values of 25 and 20 % for DBP and DEHP, respectively.

Key words: di-*n*-butyl phthalate, di(2-ethylhexyl)phthalate, monitoring, Lake Baikal, gas chromatography-mass spectrometry.

INTRODUCTION

Drinking water sources, including Lake Baikal containing to 23 000 км^3 of water, ~20 % of the world's fresh surface water are found under special attention during monitoring of persistent organic pollutants (POPs). Under conditions of environmental degradation of the Lake Baikal coastal zone [1], the issue of possible changes in water of the pelagic zone of the lake, particularly, with the absence of systematic monitoring of organic pollutants, POPs content level wherefrom currently remains open. To answer this question, priority POPs that are diesters of *o*-phthalic acid (phthalates) in water of the pelagic zone of the lake and coastal areas were determined.

Phthalates are the most important commonly used products of the chemical industry in ordinary household goods, cosmetics, detergents, plastics, paints, and medical products. In polymeric materials, phthalates are used as plastifiers that are not chemically bound with a polymer matrix, therefore, they enter the environment directly or indirectly during the production process, the use and disposal of plastics. According to the monitoring of POPs, phthalates in natural objects are present in the atmospheric aerosol, sea, river and drinking water, bottom sediments [2–9].

The risk of pollution of samples with secondary phthalates during selection, transport, and storage or at the time of analysis is a distinctive feature of the ongoing analysis when determining phthalates in water bodies at trace level concentrations. Secondary pollution may lead to false positive or inflated results of phthalates determination and is related to the presence of analytes not only in water but also organic solvents, the ambient air and products made of plastic used for analysis. For this reason, the lower boundary of phthalates measurements is limited not by possibilities of analytical methods but content levels of these substances in laboratory background. To determine these pollutants in water at the MPC levels, specialized techniques were developed, and the risks of sample pollution with secondary phthalates were assessed [10–15].

It should also be noted that producers of aquatic ecosystems are able to produce phthalates, particularly bacteria and some species of seaweeds [16, 17]. For instance, an opportunity for synthesis of de novo biosynthesis of di-*n*-butylphthalate (DBP) and di(2-ethylhexyl)phthalate (DEHP) was demonstrated in the cultivation of freshwater algae and cyanobacteria in media containing isotopically labelled $NaH^{13}CO_3$ or $NaH^{14}CO_3$ [16, 18]. Since the chemical structure of DEHP contains two asymmetric carbon atoms inside acyl substituents, therefore, a mixture of appropriate enantiomers is formed in the synthesis of this phthalate. Only one enantiomer, *e.g.*, optically active bis-2R(-)ethylhexylphthalate isolated from cultured cells *Aconitum baicalense* (Turcz ex Rapaics 1907), is formed resulting from biosynthesis of DEHP [19].

The studies of the biological activity of phthalates indicate their obvious toxicity, impact for human health, particularly its reproductive function, and also cancerogenic properties of compounds of this class [20, 21]. Toxic impact of phthalates has been noted for many types of wildlife – molluscs, crustaceans, fish, and invertebrates [22, 23].

Considering biological properties and production volumes (6 to 8 million tons per year), phthalates have been included among priority pollutants by the United States Environmental Protection Agency, Commission of the European Union, legislative acts of Russia and China. According to the World Health Organization (WHO) recommendations, DEHP concentration in drinking water should be lower than 8 μg/dm^3, the maximum content of DEHP therein is allowed up to a level of 6 μg/dm^3, in the EEC – up to 1.3 μg/dm^3 in fresh and sea water [24]. In Russia, the MPC of phthalates in water bodies with fisheries management, economic-drinking and cultural-domestic value is set at a level of 1 and 8 μg/dm^3 for DBP and DEHP, respectively [25, 26].

The present paper determines phthalates in the upper and deep water levels of the Lake Baikal at different hydrological seasons, and also in the coastal zone of its southern basin during the spring-summer period to assess current levels of phthalates in the water of the lake, the selection of criteria for phthalate monitoring in the aquatic ecosystem of the lake; the possible impact of pollution of the coastal zone on the pelagic zone of the water body.

EXPERIMENTAL

Water sampling was carried out during three expeditions in different hydrological regimes (2015 – spring, 2016 spring, autumn). Samples were selected by SBE-32 sampler (CarouselWaterSampler, Sea-BirdElectronics) in 18 stations from 5 m level (Fig. 1) and in central points of Listvyanka–Tankhoy (station 5), the Wuhan–Thin (station 11), and Elokhin–Davsha sections (station 14) from 5–1600 m horizons depending on the depth of the Lake Basin. Two probes were selected at each station in 1 dm^3 glass sample bottles, to which 0.5 cm^3 of 1 M aqueous solution of

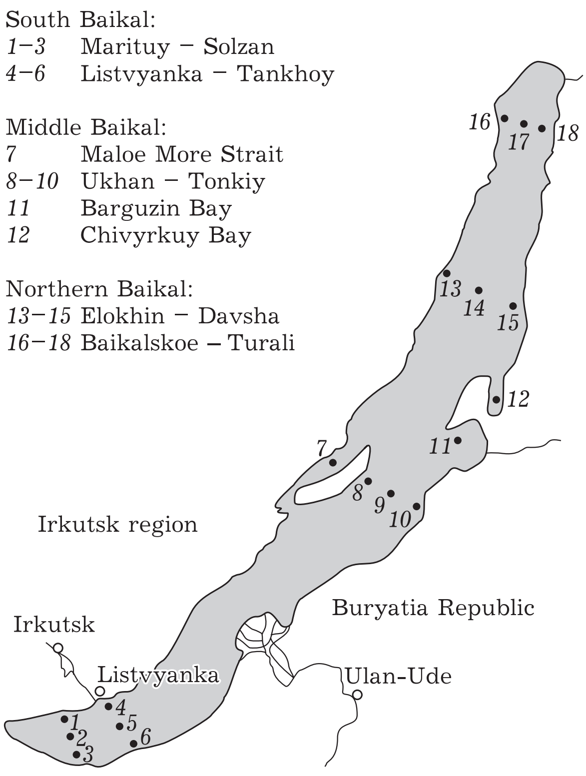

Fig. 1. Map-scheme of sampling of Lake Baikal.

Merck sodium azide (extra pure grade) was added as a preservative. Sample bottles with water were covered with a lid made of an aluminium foil gasket and kept at +5 °C prior to laboratory analysis.

Phthalate monitoring in the coastal zone of Lake Baikal (March – September 2016) was carried out in Listvennichny Bay located at Angara river source and spread on 5 km along the lake in northwest direction. Listvyanka village located on the Gulf Coast is a modern tourist centre of southern Baikal (5 million visits a year) with developing infrastructure, which is home to 2000 people (for January 1, 2016). A high level of household waste including plastic products (bottles, containers, packaging) suggests high phthalates levels in the environment including in coastal zone water.

Surface water samples in the coastal zone near Listvyanka village were selected in 1 dm^3 glass sample bottles (four samples for each selection) with 15–30 day periodicity at ~100 m distance from the coast. Water samples were analysed the same day in the laboratory.

Phthalates were determined by traditional liquid-liquid extraction of analytes into n-hexane followed by direct analysis of extracts using chromato-mass-spectrometry in selected ion mode. Prior to extraction, 30 mm^3 of a solution of Fluka 3,4,5,6-d_4-di(n-octyl)phthalate (DOP d) with 100 ng/mm^3 levels was added to water samples (1 dm^3 volume). Phthalates were extracted with 30 cm^3 of n-hexane to improve phase separation (separate samples from the upper levels) 5 g of NaCl was added into water (GOST 4233–77). For purification, Panreac, ITW Companies n-hexane was distilled prior to analysis over potassium hydroxide, sodium chloride (GOST 4233–77) was calcined at 300 °C for 6 h.

Extraction of water samples was carried out without preliminary filtration, since suspended matter content in Baikal water did not exceed 0.01–0.05 %. The number of suspended particles in water samples was determined by the gravimetric method filtering off the solid phase through Millipore Supelco filters with 1.0 μm pore size.

Extract aliquot with 1.0 cm^3 volume was transferred into vial autosampler of the chromatograph and analyzed using Agilent Technologies 7890B GC System 7000C GC-Triple Quad MS gas chromatography-mass spectrometer with OPTIMA®-17 ms capillary column (30 m × 0.25 mm × 0.25 μm) in programming mode of column temperature from 50 to 300 °C at 10 °C/min rate. Injector temperature is 280 °C; source temperature is 230 °C; ionization energy is 70 eV. The volume of the sample introduced into the chromatographer column in the mode without dividing the stream was 2 mm^3. The peaks of phthalates and internal standard were recorded in selected ion mode with m/z 149 and 153 and identified by relative retention times.

Quantitative determination of phthalates was carried out by the internal standard method using DOP-d_4 as a surrogate standard. The chromatograph was calibrated in the range of concentrations of phthalates from 0.03 to 3.0 μg/cm^3. Calibration solutions were prepared by diluting the standard mixture EPA 606-M Phthalate Esters Mix, Supelco. Response factors (k) corresponded to 0.9867 (R^2 = 0.9965) and 1.5046 (R2 = 0.9986) for DBP and DEHP, respectively. Secondary pollution of water and extracts with laboratory phthalates was regarded as the systematic error that was subtracted from analysis results. A systematic error of determination of DBP and DEHP was assessed by the reagent blank value (a term introduced Vasil'yeva and Mikheeva [13]). The reagent blank value was determined prior to extraction (twice) and after extraction (twice) of each ten samples in a series from 68 Baikal water samples using the entire set of glass ware, reagents and chromatography equipment. The contents of DBP and DEHP were represented as the average value of analysis results of two parallel samples from each station and each water horizon. The lower limit of determination was assessed as the standard deviation value of blank reagents ($3S_r$) from the mean (see Table 1). Intralaboratory precision of the measurement technique of phthalates content was assessed by cal-

TABLE 1

Phthalates content in blank reagents and measurement range limits

Phthalates	Blank reagents, μg/dm^3	S_r^1 (n = 28)	Measurement range limits μg/dm^3	±δ, % (P = 0.95)	MPC[2], μg/dm^3
DBP	0.10	0.02	0.06–3.0	25	1.0
DEHP	0.05	0.01	0.03–1.5	20	0.8

Note: [1] Relative standard deviation of the reagent blank value from the mean.
[2] MPC specified for DBP [25] and DEHP [26].

culation of relative dispersions of deviations in parallel results from the mean values (with the number of degrees of freedom (f) of 30) [27].

RESULTS AND DISCUSSION

Phthalates content in Lake Baikal Water

When determining phthalates in water maximum extraction of six priority compounds is reached upon extraction into dichloromethane or n-hexane with the addition of sodium chloride into a probe, the degree of extraction is minimal for low-molecular weight di-n-methylphthalate and di-n-ethylphthalate in case of extraction into n-hexane without salting out of the analytes [13]. Analysis of Lake Baikal water demonstrated the presence in probes of DBF and DEHP under conditions of maximum extraction of phthalates, and di-n-methylphthalate, di-n-ethylphthalate, benzylbutylphthalate, and di-n-octylphthalate were not detected out of the list of priority POPs above the lower limit of determinable concentrations or were identified in single water samples. On this basis, when monitoring Lake Baikal water DBF and DEHP were determined by a technique that included phthalate extraction with n-hexane and ensured the minimum contribution of secondary phthalates from laboratory background.

The total contents of DBF and DEHP (total phthalates content) in the aqueous layer of in the Lake Baikal pelagic zone changed in a wide range of concentrations from 0.03 to 3.7 μg/dm^3 (Table 2) in the observation period of 2015–2016. Maximum concentrations of total phthalates content were found in samples selected in the spring of 2016 in the South and Middle Lake Baikal (stations 1–10, Fig. 2, B). The total phthalates content in the Listvyanka–Tankhoy section during this period of observation was recorded in the range from 2.1 to 3.4 g/dm^3 (with maximum at the west coast station 4), with the dominant contribution of DBF (over 90 %) into the former. The samples selected at stations 9 and 10 in the medium basin of the lake were an exception. The latter probes contained no less than 30 % of DEHP. Water samples taken in the spring of 2015 (see Fig. 2, A), were characterized by a lower level of the total phthalates content – from two to six times and a higher relative content of DEHP. The samples from station 1 that were characterised by a comparable level of the total phthalates content and a close ratio of DBF and DEHP levels when sampling in 2015 and 2016 should be noted. Apparently, a single source of phthalates is present at this section of Lake Baikal. The concentration of phthalates in the upper water layer at the northern basin of the lake (stations 13–18, sampling in the spring 2015–2016) was assessed by a very narrow range of total phthalates concentrations – from 0.33 to 0.66 μg/dm^3, and in a series of samples of 2016, the content of DEHP corresponded to the level of the lower limit of the determinable concentrations (0.03–0.04 μg/dm^3).

Total concentrations of phthalates in the autumn of 2016 were substantially lower than their levels identified in the spring (see Fig. 2 C). They decreased by an order of magnitude at stations 1 and 4 (to 0.14 and 0.39 μg/dm^3, respectively), and at station 6 – to the lower limit of the determinable concentrations (0.03 μg/dm^3). Moreover, a decrease in total phthalates concentrations was related to a sharp decrease in DBP content (from 10 to 30 times). Phthalates were detected in the northern basin of the lake in the samples from the Baikalskoe–Turali section (stations 16–18).

In Elokhin–Davsha (stations 13–15), DBP was found only in minimum amounts, not more than 0.2 μg/dm^3.

Wide ranges of DBP and DEHP concentrations detected in the upper and lower levels of the lake (Table 3) indicate high heterogeneity of the distribution of phthalates in the water mass of Lake Baikal. It is noteworthy that the upper layer (to 300 m) is characterised by intense water mass redistribution during a year [28, 29]. Resulting

TABLE 2

Ranges and the mean values of concentrations of phthalates during 2015–2016
Upper water layer (5 m) of Lake Baikal, μg/dm^3

Sampling sections	DBP	DEHP	Total phthalates content
South Baikal	0.06–3.1 (0.70)	0.03–0.57 (0.26)	0.03–3.7 (0.96)
Middle Baikal	0.06–1.4 (0.49)	0.03–0.97 (0.40)	0.03–2.4 (0.89)
North Baikal	0.06–0.48 (0.25)	0.03–0.38 (0.09)	0.03–0.86 (0.34)
Maloe More Strait	0.24–0.80 (0.46)	0.03–1.1 (0.38)	0.24–1.9 (0.83)
Barguzin Bay	0.13–0.58 (0.38)	0.03–0.76 (0.28)	0.16–1.3 (0.67)
Chivyrkuy Bay	0.57–1.5 (0.99)	0.03–1.3 (0.43)	0.57–2.8 (1.4)

TABLE 3

Average phthalates content in 5–200 and ≥800 m levels at background stations of the reference section (*5*, *9*, *14*, see. Fig. 1) during 2015–2016

Sampling sections	DBP		DEHP	
	Level, m		Level, m	
	5–200	≥ 800	5–200	≥ 800
South Baikal	0.07–3.1 (0.89)	0.20–2.0 (0.95)	0.05–0.79 (0.32)	0.26–1.2 (0.79)
Middle Baikal	0.06–2.2 (0.63)	0.06–1.6 (0.69)	0.03–0.59 (0.26)	0.03–1.4 (0.59)
North Baikal	0.06–0.60 (0.35)	0.06–1.7 (0.72)	0.03–0.09 (0.06)	0.06–0.51 (0.21)

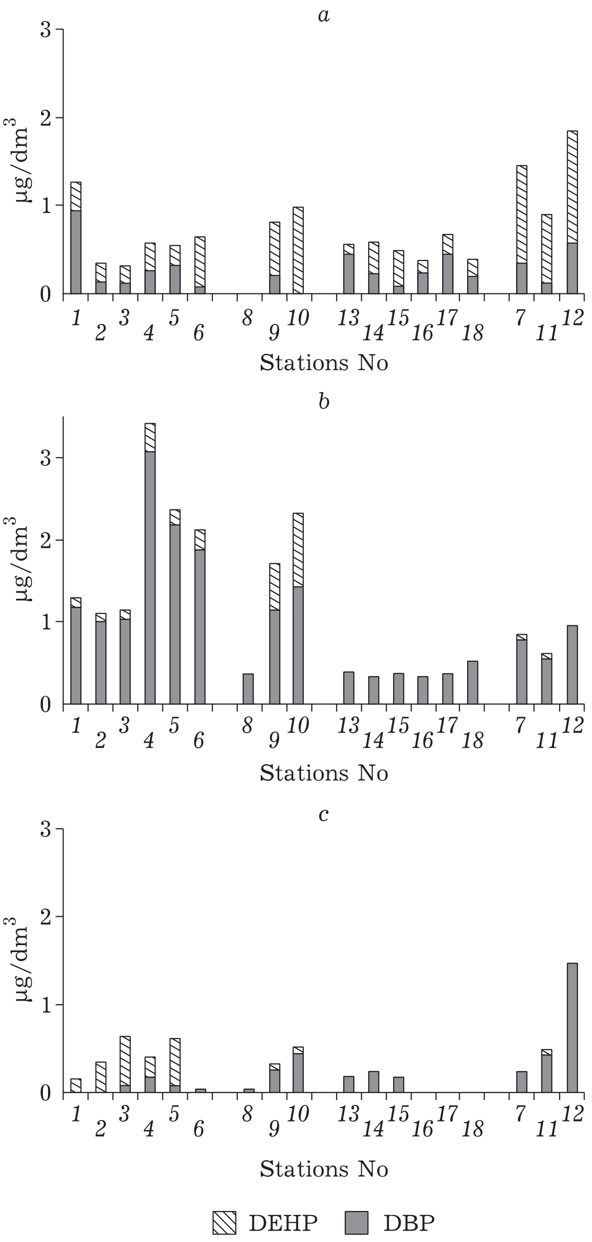

Fig. 2. Total phthalates concentrations (μg/dm^3) in the Lake Baikal pelagic zone, the level is 5 m.
Monitoring: spring of 2015 (*a*), spring (*b*) and autumn (*c*). Phthalates: DBP and DEHP.

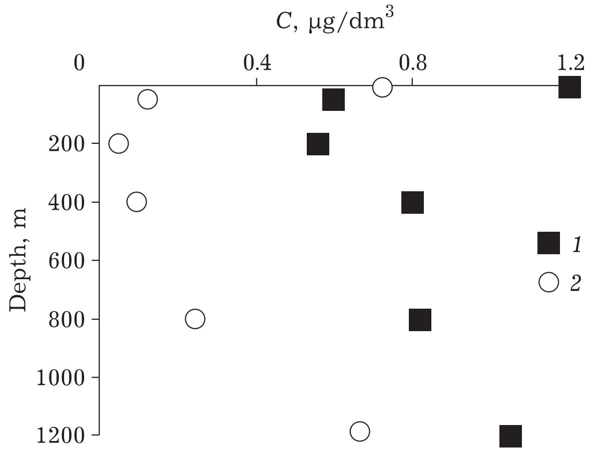

Fig. 3. Vertical profiles of DEHP in the southern basin of Lake Baikal, Listvyanka–Tankhoy station (center): September of 1996, September of 2016, station 5.

from this phenomenon, the upper water layer of Lake Baikal reflects the current level of concentrations of pollutants. On this basis, the average concentrations of phthalates at a level (5–200 m) recorded in background stations of the reference section (stations 5, 9, and 14) can be taken for DBP and DEHP levels in the basins of Lake Baikal at the present stage.

Systematic monitoring of phthalates in the water of Lake Baikal has not been carried earlier, paper [10] on the study of the vertical distribution of DEHP in the southern basin of the lake is an exception. According to the results published in the sited paper and our data, the amount of DEHP in the upper water layer (5–200 m) decreased to six times over the last 20 years, in 1200 m horizon – in 1.5 times (Fig. 3).

Assessment of the content of phthalates detected in Lake Baikal at the modern stage is presented in Table 4. DBP and DEHP levels in Lake Baikal are comparable with the content of phthalates in water of Western Europe rivers and lakes in China but significantly lower than in rivers of Russia. The average concentrations of phthalates

TABLE 4

Phthalates content in water of the world lakes and rivers, μg/dm³

Sampling sections	DBP	DEHP	Total phthalates content	Reference
Chao Hu (China)	0.01–18	$5 \cdot 10^{-4}$–0.58	0.47–18[2]	[33]
Dong Hu (China)	9.0	14	23	[34]
Da Ming Hu (China)	51	8.0	59	[34]
Ensemble of lakes in Beijing	0.01–0.53	0.14–0.52	0.58–1.5	[35]
River Ebro (Spain)	–	0.70	–	[36]
River Seine (France)	0.37–0.42	1.6–3.5	2.8–4.7[2]	[37]
River Marne (France)	0.14–0.22	0.31–0.71	0.62–1.0[2]	[38]
River Somme (France)	0.22–3.9	5.2–21	6.9–1.0[2]	[39]
Novosibirsk Reservoir	7–180	<8–80	–	[40]
Ob river	9.0–85	<8–72	–	[41]
Ufa River	6.4[1]	5.5[1]	–	[41]
Angara River	–	0.1–0.5	–	[42]
Lake Baikal	0.35–0.89[3]	0.06–0.32[3]	0.41–1.2[2]	Current studies

Notes: [1] The maximum concentrations detected in samples of Ufa River;
[2] The sum of six priority phthalates;
[3] Average concentrations of phthalates in the upper aqueous layer (5–200 m) in the background stations of the reference section.

in the upper water layer (5–200 m) do not exceed the MPC specified for DBP and DEHP in water objects with fisheries management, economic-drinking and cultural-domestic value [25, 26], despite the exceedance of established standards in individual seasons and in local areas of the pelagic zone of the lake.

Phthalates content in the coastal zone of Lake Baikal

The water in recreational areas of Lake Baikal that are the bays of the lake and its coastal belt is characterised by higher total contents of phthalates. For instance, the latter were on a level of 1.8 μg/dm³ in samples from the bays of Barguzin and Chivyrkuy selected in spring of 2015 and 2016. During the summer of 2016, phthalates content in the Barguzin Bay almost did not change, and in the Chivyrkuy Bay, it increased by half. At the same time, a decrease in the concentration of phthalates was noted during this period of the year in the Maloe More Strait (Central part), as in the pelagic zone of the Middle Baikal. It is noteworthy that an increase or decrease in the total phthalate content is due to a change in DBP contribution (from 0.93 to 1.5 μg/dm³ in the Chivyrkuy Bay, from 0.80 to 0.24 μg/dm³ in Maloe More Strait) at constantly low levels of DEHP concentrations that do not exceed 0.04 μg/dm³.

To assess the seasonal variability of the phthalates content in the coastal zone, monitoring of DBP and DEHP was carried out in Listvennichny Bay during the spring-summer season of 2016. It was found that DBP was characterized by two maxima in May and August, a high concentration of DEHP was observed only in March (Fig. 4). Since DBP and DEHP represent plasticizers of plastics and are widely used in chemical products with a wide range of applications, therefore apparently, they must have one relatively constant source of entrance into the lake in the area of monitoring. Nevertheless, the maximum contents of DBF and DEHP was detected in samples selected in different time intervals, which suggests the existence of different sources of their entrance. In this regard, the marked maxima of DBF content and inhomogeneity of its distribution in the pelagic zone during the spring and summer period may be related to technogenic pollution of the lake water – in spring, with the discharge of melted snow water into the lake, and in summer, with their entrance from precipitation. While the maximum content of DEHP in water samples selected in March–April may be related to the period of the under-ice diatomic algae bloom, and a decrease in the level of the concentration of phthalates in the pelagic zone of the lake in September (see Fig. 2, c) may be the result of their biodegradation and photolysis [30–32].

Monitoring of phthalates at Listvennichny Bay station also allowed considering the coastal zone of the lake as an indicator of pollutant content in the pelagic zone of South Baikal. Particularly, high concentrations of phthalates in Listvennichny Bay in spring and their decrease at the end of the summer season were reflected by appropriate contents of phthalates in samples from the Listvyanka–Tankhoy section. Moreover, a fall in con-

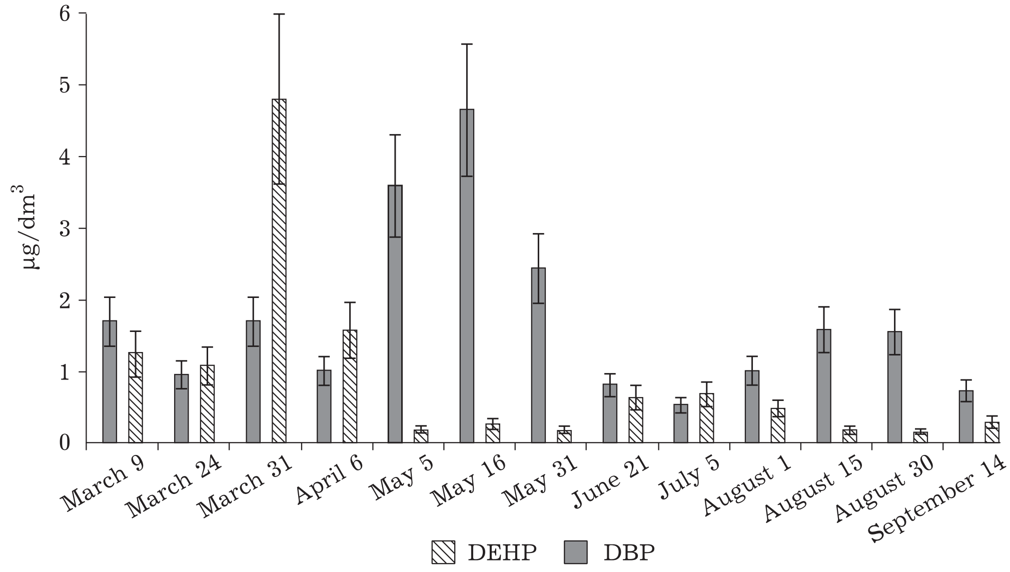

Fig. 4. Change in the concentrations of DBP (< >) and (< >) DEHP during 2016 in the coastal zone. Listvennichny Bay station (0 m horizon).

centration level of phthalates in the centre of the southern basin in 2–2.5 times (Fig. 5) was related to a decrease in a fraction of DBP in the total content of phthalates, while the content of DEHP in samples from the Listvennichny Bay and the Listvyanka–Tankhoy section remained at the same level during this period. Clearly, this phenomenon proves different sources of DBP and DEHP.

CONCLUSION

Lake Baikal is characterised by high spatial heterogeneity of phthalates distribution in the upper and deep water layers, seasonal variability of the phthalates content in the upper water layer. Considering processes of horizontal and vertical water exchange in Lake Baikal, background

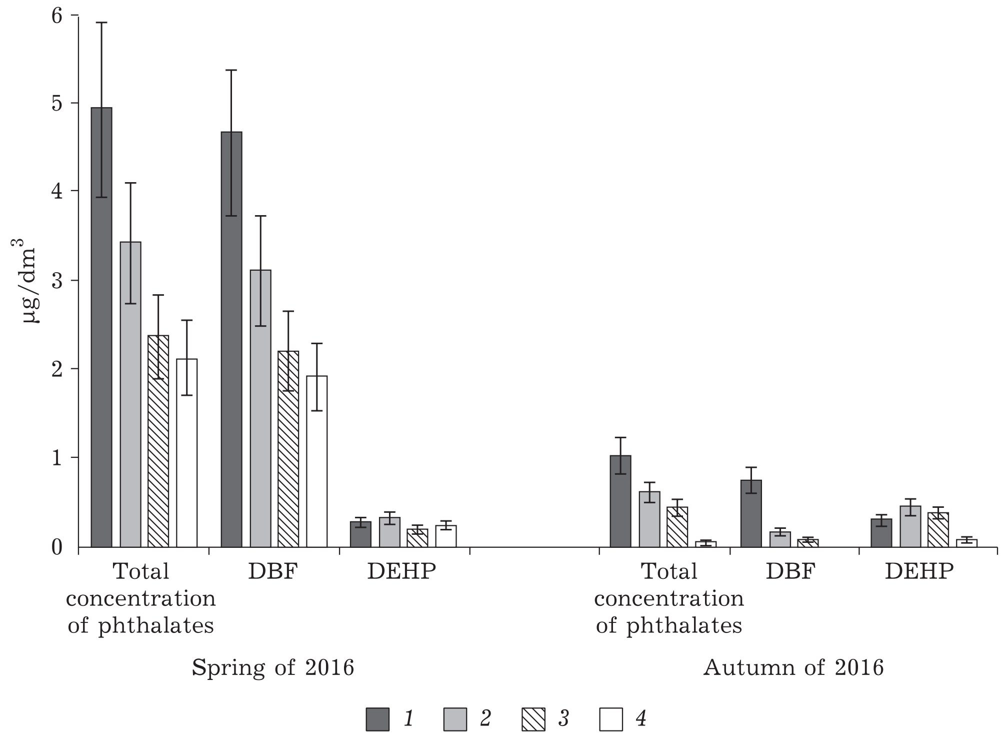

Fig. 5. Concentration of phthalates in water of the coastal zone and in the pelagic zone of Baikal Lake: < > – 100 m from the coast, Listvyanka village; < > – 3 km from Listvyanka village; < > – section of Listvyanka village– Tankhoy, centre; < > – 3 km from Tankhoy village; monitoring data for 2016.

stations of the reference section in three basins of the lake are offered as reference areas for monitoring, and the average concentrations of phthalates in the upper water layer (5–200 m) in selected points – to assess contemporary phthalates content in water of the lake. The contents of DBP and DEHP during 2015–2016 in selected points for monitoring of water in Lake Baikal did not exceed the MPC in water objects specified in Russia for this class of pollutants. The minimum values of DBF and DEHP concentrations in Lake Baikal are comparable, and the maximum ones are lower than the concentrations of these pollutants in water of China lakes and Western European rivers. Higher total phthalate contents in recreational areas of Lake Baikal that are the bays of the lake and its coastal belt were noted.

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