Chemistry for Sustainable Development **25** (2017) 255–264

UDC 543.63:547.591"13(282.256.341)

Polychlorinated Biphenyls in Lake Baikal Ecosystem

A. G. GORSHKOV[1], O. V. KUSTOVA[1], E. V. DZYUBA[1], YU. R. ZAKHAROVA[1], S. M. SHISHLYANNIKOV[1], and V. A. KHUTORYANSKIY[2]

[1]*Limnological Institute, Siberian Branch, Russian Academy of Sciences,*
Irkutsk, Russia

E-mail: gorchkov_ag@mail.ru

[2]*Irkutsk State University,*
Irkutsk, Russia

(Received June 28, 2016; revised February 16, 2017)

Abstract

The paper gives assessment of the content of polychlorinated biphenyls (PCB) in the upper water layer (5 m) and deep water levels (900–1500 m) of Lake Baikal at the current stage. The total concentrations of PCB congeners (PCB content from 24 to 34 congeners) are varied in a range of 1.4–7.2 ng/dm^3. Domination of tri-, tetra- and pentachlorinated biphenyls in a series of PCB homologs has been observed, which points out at long-range atmospheric transport as a major source of PCB. PCB content in the upper water layer of Lake Baikal is comparable or significantly lower in comparison with that of water in continental world lakes but higher in comparison with Arctic and Antarctic lakes. Commercial fish species omul (*C. migratorius* Georgi, 1775) were proposed as a biomonitor of PCB in the Baikal ecosystem. By the accumulation level of seven indicator PCB congeners (Nos. 28, 52, 101, 118, 138, 153 and 180 by IUPAC) in omul and bulltrout (*Salmo trutta*) from highland lakes of South and Central Europe, the amounts of bioavailable PCB in water of these lakes are comparable between each other. The results of approbation of the method for determination of indicator PCB congeners in water and omul samples using Gas Chromatography-Tandem Mass Spectrometry (GC-MS/MS) and isotopically labelled internal standards may form the basis of the modern system of monitoring of persistent organic pollutants in the Baikal ecosystem.

Key words: PCB, Lake Baikal, monitoring, environmental indicators

INTRODUCTION

Pollution of surface water by persistent organic pollutants (POP) is a major problem for the world community. To address it in recent years, some fundamental studies related to assessment of toxicity of pollutants, their distribution and control methods in the environment have been performed. Much of the research on this problem is devoted to organochlorine compounds that have high stability in water and terrestrial ecosystems are accumulated in living organisms and characterized by high toxicity [1, 2].

Upon monitoring of organochlorine POP in the environment, special attention is paid to sources of drinking water, including those to Lake Baikal. This is the deepest lake in the world, with the unique flora and fauna, 60 % of which are endemics. Lake Baikal is included by UNESCO in the World Heritage Area. The lake consists of three basins with different depths distinguished by temperature conditions, surface and underwater currents and the volume of water masses. Lake Baikal accommodates up to 23 000 km^3 of water, which is approximately 20 % of the surface freshwater of the world. The water exchange in the lake has been happening over a long period that is almost 330 years.

The first data of organochlorine compounds in Lake Baikal were published in [3, 4], the authors of which found organochlorine pesticides (OCP) and polychlorinated biphenyls (PCB) in zooplankton, Baikal omul (*Coregonus migratorius*, Georgi, 1775) and Baikal seal (*Phoca sibirica*, Gmelin, 1788). A broader series of data of organochlorine compounds in Lake Baikal ecosystem was received later resulting from joint international research carried out in the 1990s and generalised in [8]. According to the data received, OCP and PCB contents in the lake were assessed as background.

The level of found organochlorine POP in the Baikal biota reflected an increase in pollutant accumulation with an increase in the trophic status of biological objects. Thus, the maximum amounts of PCB – from 3300 to 64 000 ng/g lipids – were recorded in the fat of seals that occupied the top of the trophic chain of the ecosystem, depending on specimen age and gender. Dioxins in a range of 0.04–0.12 and 0.22–1.16 pg wet mass (WHO-TEQ) for polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), respectively, were detected in the muscles of Baikal omul. A number of organochlorine POP, depending on the level of their accumulation in the fat of the seal, and in the muscles of the Baikal omul, is represented by the following sequence [6, 10, 11]: PCB ~ DDT > chlordanes > HCH > HCB >>> PCDDs, PCDFs, where DDT is the sum of 4,4′-dichlorodiphenyl-trichloro-ethane and its metabolites, HCH is hexachlorocyclohexane, HCB is hexachlorobenzene, PCDD and PCDF are 2,3,7,8-chlorosubstituted dibenzo-*p*-dioxins and dibenzofurans, respectively.

Studies of POPs in Lake Baikal ecosystem performed later were characterized by the absence of the systematic approach, in particular: 1) water and the biota sampling was conducted randomly and in some papers, without the description of environmental and morphological features of selected biological samples; 2) PCB were determined in collected samples by the author's methods, which does not allow using today these results for accurate assessment of trends of their presence in the aquatic ecosystem [12–16]. By findings of the studies of the 1990s, it was required to include PCB among the priorities of POP for control in Lake Baikal ecosystem on the following reasons: 1) they were distinguished by the maximum accumulation in the Baikal biota, and their arrival to the lake water was related to the local sources; 2) despite the ban on production and use of PCB in 1979 after the discovery of dioxin-like toxicity in a series of compounds of this class, PCB were (and are) used in electrical equipment to serve stations of distribution and consumption of electric power. Considering the scales of development of hydroenergetics in Eastern Siberia, this potential source of PCB represented (and is representing) the maximum threat for the environment, as shown by further studies, the contribution of complanar PCB in the total toxicity equivalent of PCDD, PCDF and PCB (NEQ_{1998}) exceeds 70 % in commercial fish [17] and 50 % for surveyed people in the Pribaikalia [18].

The purpose of the present work is obtaining data that may form the basis for the modern system of monitoring of PCB in the unique Baikal ecosystem. A number of issues were studied: 1) assessment of distribution of PCB in the upper and deep aqueous horizons considering the enormous volume of the lake and its dispersal in three basins; 2) an opportunity of using Baikal omul as a biomonitor of PCB in the lake ecosystem; 3) assessment of the modern levels for PCB concentrations found by traditional monitoring and biomonitoring data; 4) introduction to the practice of definition of the indicator congeners of PCB (Nos. 28, 52, 101, 118, 138, 153 and 180 by IUPAC) to assess the presence of PCB in water samples, biota of Lake Baikal and the method of GC-MS/MS using surrogate internal isotopically labelled standards for quantitative determination.

EXPERIMENTAL

Water samples were collected in May–June of 2015 using SBE-32 cassette sampler (Carousel-WaterSampler, Sea-BirdElectronics) in 17 stations from a horizon of 5 m (Fig. 1) and in central points of the cuts Listvyanka–Tankhoy (station *5*), Ukhan–Tonkiy (station *10*), Elokhin–Davsha (station *13*) from horizons 5, 50, 200, 400, 800, 1200 and 1600 m, depending on the depths of the lake basin. Two samples that were closed with a lid of aluminium foil were selected in each station and from each aqueous horizon in glass bottles with a capacity of 1 dm^3, stored at

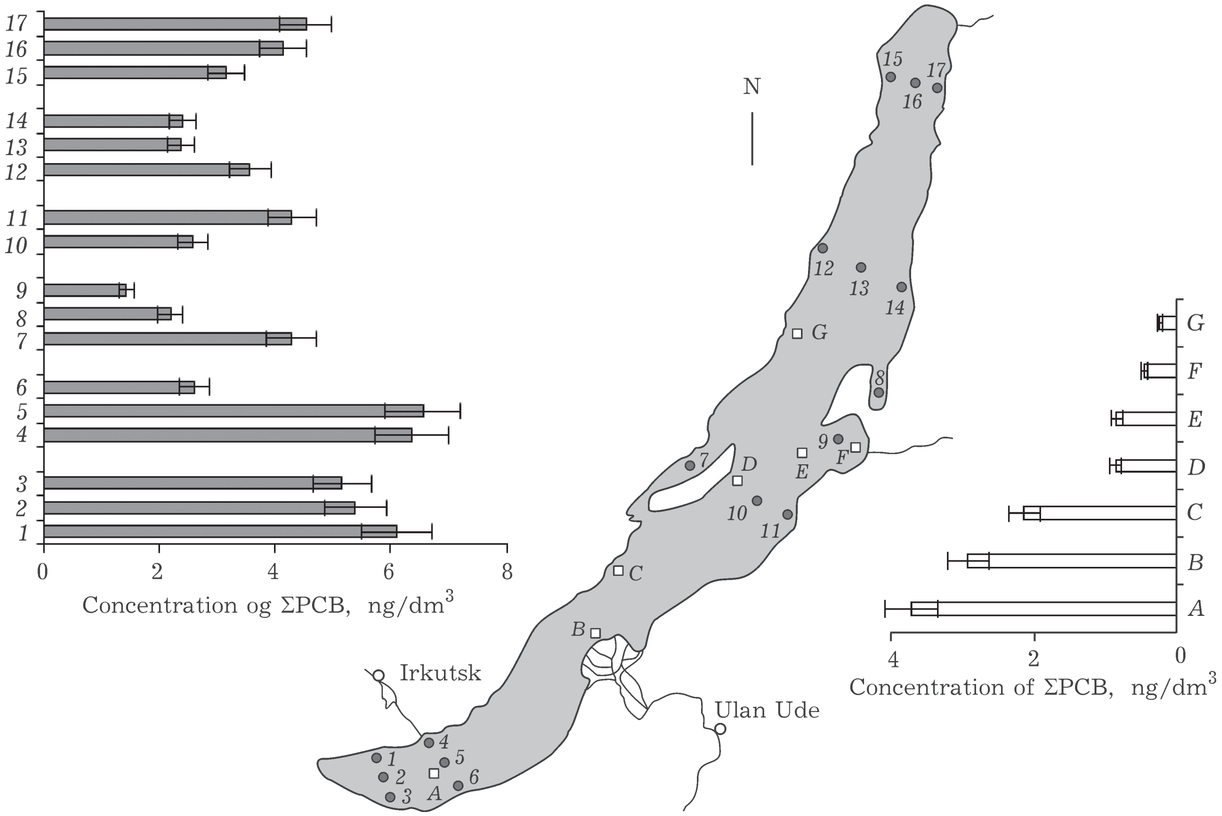

Fig. 1. Location of sampling stations (*1*–*17*) and (*A*–*G*) along the water area of Lake Baikal and concentrations of SPCB in the upper layer of water: *1* – expedition of 2015, LIN SB RAS (*1* – Marituy, *2* – Marituy–Soltan, *3* – Soltan, *4* – Listvyanka, *5* – Listvyanka–Tankhoy, *6* – Tankhoy, *7* – Maloye More strait, *8* – Chivyrkuy Bay, *9* – Barguzin Bay, *10* – Ukhan–Tonkiy, *11* – Tonkiy, *12* – Elokhin, *13* – Elokhin–Davsha, *14* – Davsha, *15* – Baikal'skoye, *16* – Baikal'skoye–Turali, *17* – Turali); *A*–*G* – expedition of 1993 [7].

5 °C before analysis in the laboratory at 0.5 cm^3 pressure of a 1 mol/L aqueous solution of extra pure reagent grade sodium azide (Merck KGaA, Darmstadt, Germany). Samples of the omul of the North-Baikalian population were taken in March–June of 2015 using gill nets (cell of 32 mm) from depth of 120–230 m in the in the area of Bolshiye Koty settlement (the southern basin of Lake Baikal). After capture, the fish was wrapped into aluminium foil and stored at –70 °C.

Before analysis, 30 mm^3 of a surrogate internal standard that is a mixture of $^{13}C_{12}$–PCB (Nos. 28, 52, 101, 118, 138, 153, 180; Marker-7 PCB Mixture (W/PCB-118)) with a concentration of each congener of 0.11 ng/mm^3 was added to water samples. Polychlorinated biphenyls were extracted with 30 cm^3 of *n*-hexane (twice), extracts were combined and concentrated in a rotor evaporator up to a volume approximately equal to 0.5 cm^3, the concentrate was transferred to chromatography autosampler vials.

The contents of the digestive tract of fish was removed before chemical analysis, then it was cut into pieces and homogenized using a blender, not separating bones, skin and scales. An internal standard that is 50 mm^3 of $^{13}C_{12}$–PCB (Marker-7 PCB Mixture (W/PCB-118)) was added to 0.5 g (accurate weight) of a sample weight of the homogenized material, then the sample weight was grinded with mortar with approximately 1.5 g of anhydrous Na_2SO_4 calcined at a temperature of 300 °C for 6 h. Polychlorinated biphenyls were extracted twice with a mixture of solvents, such as *n*-hexane/acetone (1 : 1 by volume) in an ultrasonic bath (40 kHz, 20 min). The extracts were combined and centrifugated, supernatant was separated and concentrated using a rotary evaporator to a volume approximately equal to 1 cm^3 (if necessary, dried with an additional portion of anhydrous Na_2SO_4) and in the current of argon to a volume of approximately 0.2 cm^3.

The concentrate was applied to a Discovery® SPE DSC-Si silica gel cartridge, the mass of the sorbent of 0.5 g that was prepared by consecutive washing with 3 cm^3 of carbinol, 2 cm^3 of methylene chloride, then with 2 cm^3 of a mixture of methylene chloride/*n*-hexane (1 : 19 by volume). The PCB fraction was eluted with 4 cm^3 of a mixture of methylene chloride/*n*-hexane (1 : 19 by volume). The eluate was concentrated in the current of argon to a volume approximately equal to 0.5 cм^3.

The prepared samples were analysed using an Agilent Technologies 7890B GC System 7000C GC/MS Triple Quad chromatography-mass spectrometer with an OPTIMAв-17 MS capillary column (30 m × 0.25 mm × 0.25 μm) in the temperature programming mode from 80 to 310 °C with a rate of 7 °C/min. The injector temperature of 280 °C; the source temperature of 230 °C; the energy of ionization of 70 eV; the volume of the sample introduced into the column in the mode without dividing the stream was 2 mm^3.

Peaks of PCB were registered using selected ion monitoring (SIM) mode, identified by relative retention times (t_r), quantitative determination was carried out by the method of internal standards, in which capacity 4,4′-dibromodiphenyl was used. The total content of detected congeners was calculated as a sum of homological groups of PCB [19]. Peaks of indicator congeners were registered in multiple reactions monitoring (MRM) mode, identified by t_r values of ^{13}C labelled internal standards, the concentration of analytes was calculated by the method of internal standards. Mass spectrometric parameters for GS-MC/MC are given in Table 1.

The total content of PCB congeners was measured twice in each sample, the obtained results were averaged. The total measurement error did not exceed 10 %. The correctness of measurements of PCB was assessed by analysis of a standard sample of mackerel fat Certified Reference Material BCR®-350 with the certified content of five ecological congeners and by the method of additions.

Total biological fish analysis was carried out according to [20, 21], the fat content was assessed by the gravimetric method, extracting lipids with a mixture of chloroform/methanol = 1 : 2 (by volume). NPK KRIOKHROM Ltd. (St. Petersburg) 1st grade *n*-hexane for chromatography, acetone, methylene chloride and chemically pure reagent grade chloroform (EKOS-1 JSC, Moscow), chemically pure reagent grade carbinol (Vekton JSC, St. Petersburg), pre-distilled acetone methylene chloride and chloroform were used for extraction. The purity of solvents, glassware and the chromatographic system were assessed by blank experiments.

TABLE 1

Mass spectrometric parameters for analysis in the mode of MS/MS

Congeners No.	*R*, min	*m/z*		Dwell time, ms	Collision energy, V
		Primary ion	Secondary ion		
28	21.206	256.0	186.0	10	25
52	22.048	289.9	219.9	10	25
101	24.623	325.9	255.9	10	30
118	26.843	325.9	255.9	10	30
153	27.067	359.9	289.9	10	25
138	28.176	359.9	289.9	10	30
180	29.891	393.8	323.8	10	30
$^{13}28_{12}$	21.196	268.0	198.0	10	25
$^{13}52_{12}$	22.038	301.9	231.9	10	25
$^{13}101_{12}$	24.611	337.9	267.9	10	30
$^{13}118_{12}$	26.832	337.9	267.9	10	30
$^{13}153_{12}$	27.056	371.9	301.9	10	25
$^{13}138_{12}$	28.164	371.9	301.9	10	30
$^{13}180_{12}$	29.881	405.8	335.8	10	30

RESULTS AND DISCUSSION

Distribution of PCB in water levels of Lake Baikal

From 24 to 34 PCB congeners were detected in water samples from the upper (5–200 m) and deep levels of the lake (to 1600 m). The total content of PCB congeners (ΣPCB content) in the upper layer of water varies in a range of 1.4–7.2 ng/dm^3. The maximum PCB concentrations were detected in samples from the southern basin of the lake (see Fig. 1, stations *1–5*), the minimum in water samples from the Chivyrkuy and Barguzin bays (stations *8* and *9*) off the eastern coast. The concentration of ΣPCBs in the samples from stations on the northern tip of the lake (stations *15–17*) are comparable to those in samples from the southern basin of the lake (stations *1–5*), minimal – in water samples from the Chivyrkuy and Barguzin bays (stations *8* and *9*) near the eastern coast. PCB concentrations in samples from stations on the northern tip of the lake (stations *15–17*) are comparable to those in samples from the southern basin.

Earlier [6, 7], the trend of increasing ΣPCB content in the upper layer of water was observed when moving to the southern basin of the lake (see Fig. 1). The tendency was associated with the ingress of PCB into the southern part of Lake Baikal from local sources. It is obvious that this trend representing increased anthropogenic load in the southern part of the lake also currently remains but with deciding contribution of distant atmospheric transfer.

The profile of homological groups of PCB in all samples of pelagial of the lake is similar and characterized by the domination of tri-, tetra-, and pentachlorinated biphenyls, and also by the minimum number of congeners (5.4–8.4 %) having six or seven chlorine atoms in the structure (Fig. 2). This ratio of homologs indicates long-range atmospheric transport as a major source of pollution. Herewith, samples from the southern part of the lake (stations *1–5*) were characterized by the high amounts of congeners with the high degree of chlorination that is 11–19 % of the sum of all detected PCB, what is probably driven by additional anthropogenic pollution of water from local sources.

ΣPCB concentrations in the bottom levels of lake water body are almost three times lower compare to the upper layers. For example, in the south basin, at the 5 m level, they are (6.6±0.7) ng/dm^3, and in deep water (1200 m) – (2.3±0.2) ng/dm^3, in a medium basin – (3.8±0.4) ng/dm^3 (5 m) and (1.7±0.2) ng/dm^3 (1600 m) (Table 2). One should draw attention to samples from the level of 1200–1600 m (station *10*), where the PCB content does not exceed 1.8 ng/dm^3. These data are comparable with the maximum PCB content in the surface water of the lake detected in 1996 [6, 7].

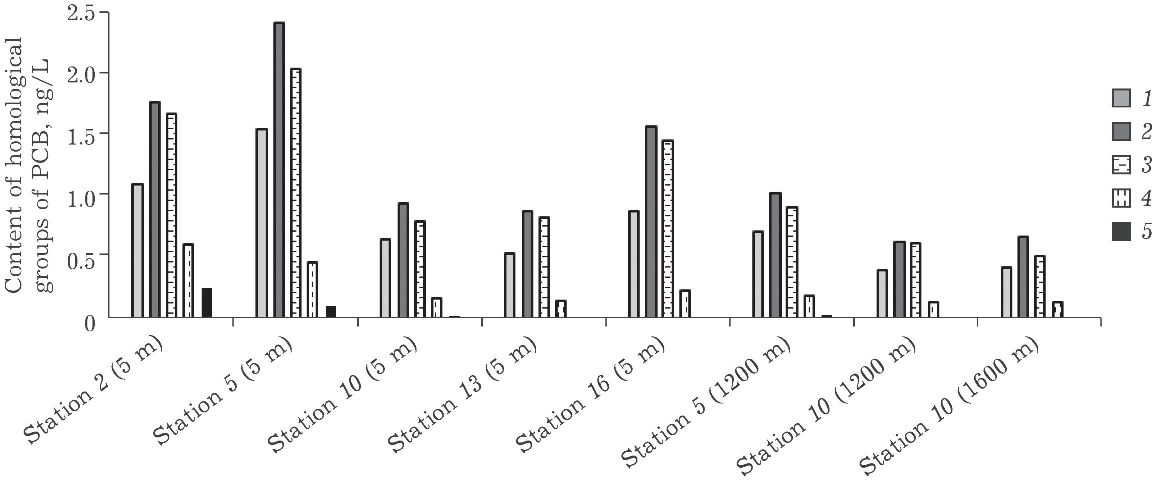

Fig. 2. Ratio of homological groups of PCB in the upper and upper and deep aqueous horizons: tri- (*1*), tetra- (*2*), penta- (*3*), hexa- (*4*), and heptachlorinated (*5*) biphenyls.

TABLE 2

ΣPCB concentrations in the upper and deep levels of Lake Baikal

Water level, m	Basins (maximum depth, m)					
	South (1419), station *5*		Medium (1637), station *10*		North (890), station *13*	
	Concentration, ng/dm^3	Water age*, years	Concentration, ng/dm^3	Water age*, years	Concentration, ng/dm^3	Water age*, years
5	6.6	1	2.6	1	2.4	1
50	5.9	1	3.5	1	3.9	1
200	7.2	1	5.3	1	2.3	1
5–200**	6.6	1	*3,8*	1	*2.9*	1
400	5.8	2	4.3	2	2.5	2
800	2.6	14	2.5	11	2.4	8
1200	2.8	14	1.8	15	–	–
1600	–	–	1.7	16	–	–

Note. The dash indicates not determined.

* Data of [21].

** Average concentration for the upper water layer (5–200 m).

The age of Lake Baikal water, *i.e.* the time passed from its residence time, depends on the water level and it is approximately equal to 15 years in the medium basin at a depth of 1200–1600 m [22, 23]. Therefore, one may suggest that deep old water at a level of 1500 m contains PCB accumulated in surface water late in the 20th century. In subsequent years, ΣPCB content in the upper water layer of the lake increased, which is confirmed by research results of two independent expeditions: NPO Tayfun in 2014 [24] and Limnological Institute (LIN SB RAS, Irkutsk) in 2015.

Biomonitoring of PCB

Traditional monitoring methods assume selection and analysis of significant numbers of water samples to receive the overall picture of POP content in a aquatic ecosystems (selection of water samples with a volume to 20–180 dm^3 was performed in case of PCB study in Baikal water) [6, 9]). With this monitoring option, the probability of passage of local sites with a high level of POP or assessment based on extreme short-term pollution periods is probable.

Biological monitoring can be an alternative way of PCB control in aquatic ecosystems. Baikal omul was selected by us as biomonitor due to a relatively high population size of this specie and environmental niche occupied by it in the lake ecosystem (*C. migratorius,* Georgi, 1775) [25]. Its numerical strength reaches 263 thousand exemplars, the specie migrates along the entire Baikal territory in a range of depths to 350 m and refers to commercial fish, therefore, its sampling during monitoring is cost-efficient. From 21 to 43 PCB congeners were detected in specimens of Baikal omul depending on their age (3–7 years). The concentration of ΣPCB in fish tissues varies within 8.5–38 ng/g of dry mass or 100–710 ng/g lipids. With the species age in five to six years, the accumulation level of PCB is sufficient to determine the pollutants with the required accuracy under optimum analysis conditions (material amount, concentration degree).

It is noteworthy that consistent assessment of accumulation levels of POP in fish is often difficult because of using various methods for their determination – the identification and determination of various numbers of PCB congeners, and differences in the age, mass and the content of lipids in individual species selected for analysis [26, 27]. In this regard, it is proposed to determine in soil a limited number of congeners to control PCB in food stock – indicator congeners [28, 29]. This eliminates numerous issues related to chromatography of analytes, the method of their measuring and subsequent monitoring assessments. The use of GS-MS/MS and isotopically labelled internal standards increases determination accuracy and method status up to arbitral.

Indicator PCB congeners

Indicator congeners (Nos. 28, 52, 101, 118, 138, 153, and 180 by IUPAC) are characterized by the maximum content in PCB homologs and identified in all probes of Baikal water and Baikal omul samples except for congener No. 180. The latter has been detected only in water of the south lake basin and fish older than five years. The total concentration of indicator congeners (Σ_7PCB content) in water samples is 0.43–2.2 ng/dm^3, in omul samples – 4.7–15 ng/g of dry mass (56–270 ng/g lipids). It was noted that Σ_7PCB content contribution in the total concentration of all detected congeners was 28–37 % for all water samples and 34–50 % – for omul samples (the age is 5–6 years). Moreover, Σ_7PCB content contribution is characterized by a small scatter from the average value for a series of studied samples (n = 30 (water) and 16 (omul)); relative variance (S_r) = 8.0 and 5 % for samples of water and omul, respectively).

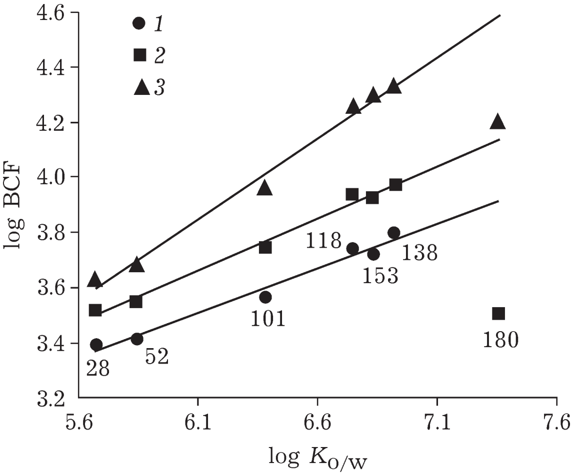

Fig. 3. Accumulation of indicator congeners (log BCF, bioconcentration factor) *vs*. hydrophobic properties of PCB (log $K_{o/w}$, the distribution coefficient). The BCF values were calculated as the ratios of average concentrations of the indicator congeners in tissues of *C. Migratorius* of different ages to their average concentrations in extracts of the upper water level (5–200 m) for three basins of lake water (n = 18); the age of *C. migratorius*, years: *1* – 3–4 (k = 0.3249, R^2 = 0.9789, n = 8), *2* – 5–6 (k = 0.3813, R^2 = 0.9872, n = 15), *3* – 7 (k = 0.5895, R^2 = 0.9899, n = 4); in fish under the age of 5 years, the level of accumulation of congener No. 180 is insufficient for quantitative determination of log $K_{o/w}$.

A series of indicator congeners are characterized by a wide range of hydrophobic properties (log $K_{o/w}$ = 5.67–7.36 [30]) and the level of their accumulation in fish tissues corresponds to their hydrophobicity (Fig. 3). For this reason, congeners Nos. 118, 153, and 138 are isolated by the maximum concentration in fish, while congeners Nos. 28 and 52 dominate in water samples and as a consequence profiles of congeners in these fish do not reflect their ratio in water samples. An increase in the proportion of congeners Nos. 101, 118, 153, and 138 fish tissues with a rise in species age may be associated not only with hydrophobic properties of xenobiotics but also a faster metabolism of congeners with the low chlorination degree [31] considering this nutrition ration of omul during the first seven years of life [32]. The minimum accumulation level of congener No. 180 in omul distinguished by the maximum value of log $K_{o/w}$ is associated with barriers that arise upon its passing *via* lipid cellular membranes due to xenobiotic structural features and/or with adsorption problems due to its low water solubility [33, 34].

Assessment of the current levels of PCB concentrations in Lake Baikal

By the data of monitoring performed in 2015 the maximum ΣPCB concentrations in the upper water layer of Lake Baikal have increased in 3.5 times since 1991, minimum – almost in 70 times due to an increase in ΣPCB concentrations in water of the northern end of Lake Baikal (stations *16* and *17*, see Fig. 1). Currently, there is no single criterion to assess water pollution with PCB. According to temporary environmental quality standards (EQS), PCB concentration in surface water in the territory of EES should not exceed 1 ng/dm^3 [35]. By the standards established in Russia, PCB content in water bodies of household-drinking and cultural-domestic water use should not be exceed 1000 ng/dm^3; however, the presence of PCB in reservoirs of fisheries value is not allowed [36]. In accordance with the rules of the U.S. Environmental Protection Agency [37], PCB in water at a concentration of less than 14 ng/dm^3 do not pose a risk to aquatic organisms and human health. Nevertheless, it is noteworthy that PCB levels in Lake Baikal water are high-

TABLE 3

Congener content in water of the world's lakes, ng/dm^3

Lake location	Years	PCB	Ref.
Antarctica, Victoria land	2011–2012	Σ_{127}: 0.046–0.143	[38]
Norwegian Arctic	1999	Σ_{12}: 0.023–0.129	[39]
European alpine lakes	2000–2001	Σ_7: 0.048–0.123	[40]
Himalayas	2007	Σ_5: 0.02–0.45	[41]
Lake Baikal, Russia	2015	Σ_{24-34}: 1.4–7.2	This work
		Σ_7: 0.43–2.2	
Como, Italy	2007	Σ_7: 0.30	[42]
Caspian Sea, Russia	2002	Σ_6: 0.10–7.3	[43]
Baiyangdian, China	2008	Σ_{39}: 19–132	[44]

er in the modern period than in Antarctic and Arctic lakes but comparable or much lower than PCB concentration in water of Continental Lakes – Como (Italy), the Caspian Sea (northern part, Russia), the Baiyangdian Lake (China) (Table 3).

Assessment of levels of PCB accumulation in Baikal omul was performed by Σ_7PCB concentrations. Bulltrout (*Salmo trutta*) that is species close by the taxonomic position to Baikal omul was taken for comparison, moreover, selected specimen are comparable by age and content in lipid tissues. Close concentrations of Σ_7PCB in Baikal omul and bulltrout (Fig. 4) could point to comparable contents of bioavailable Σ_7PCB in water of Baikal and highland lakes of Southern and Central Europe, where bulltrout inhabits [45–47]. Σ_7PCB content value is three to seven times higher than that of Baikal omul (2.600, 1.100, and 330 ng/g lipids, respectively) in the tissues of bulltrout of Lake Iseo and Lake Endine located in the industrial regions of Northern Italy [48].

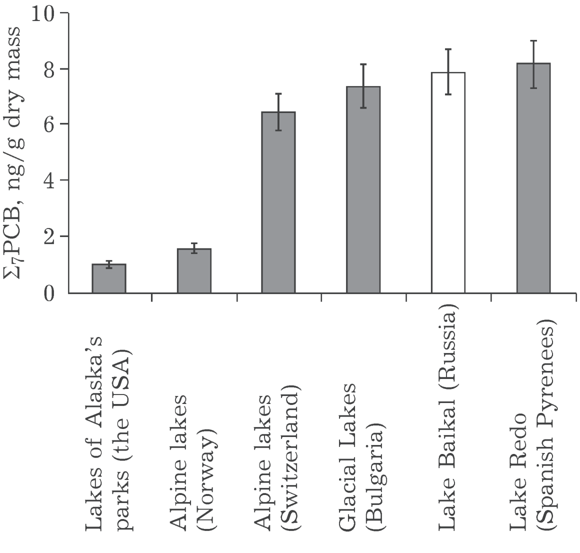

Fig. 4. Σ_7PCB concentrations in bulltrout from lakes of Alaska's national parks, Alpine lakes in Norway [44], South and Central Europe [45–47], in omul from Lake Baikal.

Constant monitoring of PCB concentrations in the tissues of Baikal omul is required not only for the purity of Lake Baikal water but also for control of the quality of this type of fish, since this is one of the major nutrition products for the population residing on the shores of the Lake. A range of ΣPCB concentrations (0.01–0.04 mg/kg dry mass) in omul of 2015 is more than an order of magnitude lower than the maximum allowable level of ΣPCB content in fish used as nutrition products (2.0 mg/kg dry mass [27]). Σ_7PCB content in Baikal omul (4.7–17 ng/g dry mass) in the same period did not exceed the limit of Σ_7PCB concentrations (75 ng/g dry mass) established in EES for fish caught in fresh water reservoirs [49].

CONCLUSION

High inhomogeneity of PCB distribution in water levels in Lake Baikal was found. Total concentrations of PCB congeners (from 24 to 34) are varied within 1.4–7.2 ng/dm^3. Since the upper water layer (to 300 m) reflects PCB content in current time period, monitoring of this water level will meet the challenges of control of this class pollutants in the Baikal ecosystem. It was determined that ΣPCB concentrations in the upper layer of Baikal water was comparable or much lower compare to that in water of continental world lakes but higher than in Arctic and Antarctic lakes. It was demonstrated that the ratio of PCB homologs and indicator congeners in Baikal pelagial was similar and characterized by domination of tri-, tetra- and pentachlorinated biphenyls, and this points out at long-range atmospheric transport as the major source of PCB. Baikal omul meeting the major criteria for a biomonitor was proposed for biomonitoring of PCB in water from Lake Baikal. Close accumulation levels of Σ_7PCB in Baikal omul and bulltrout from highland lakes of Southern and Central Europe indicate comparable amounts of bioavailable PCB in water of these lakes. The results from this study obtained in the present work may form the basis of the modern system of monitoring of PCB in the Baikal ecosystem.

Acknowledgments

The work was performed at the Baikal Analytical Center for Collective Use SB RAS in the framework of the basic budget funding (project: No. 0345-2014-0007, state registration No. 01201353446).

REFERENCES

1 URL: http://www.un.org/ru/documents/decl_conv/conventions/pdf/pollutants.pdf (accessed June 18, 2016).

2 Maystrenko V. N., Klyuev N. A., Ekologo-Analiticheskiy Monitoring Stoykikh Organicheskikh Zagryazniteley, BINOM. Laboratoriya Znaniy, Moscow, 2004.

3 Bobovnikova Ts. I., Virchenko E. P., Dibtseva A. V., Yablokov A. V., Solntseva G. N., Pastukhov D. V., *Gidrobiol. Zh.*, 22, 2 (1986) 63.

4 Malakhov S. G., Bobovnikova Ts. I., Siverina A. V., Dibtseva A. V., III Mezhdunar. Simp. "Kompleksny Global'ny Monitoring Sostoyaniya Biosfery" (Theses), Gidrometeoizdat, Leningrad, 1986, vol. 2, pp. 113?122.

5 Kucklik J. R., Bidleman T. F., McConnell L. L., Walla M. D., Ivanov G. P., *Environ. Sci. Technol.*, 28 (1994) 31.

6 Iwata H., Tanabe S., Ueda K.. Tatsukawa R., *Environ. Sci. Technol.*, 29 (1995) 792.

7 Kucklick J. R., Harvey H. R., Ostrom P. H., Ostrom N. E., Baker J. E., *Toxicol. Chem.*, 15 (1996) 1388.

8 Grachev M. A., O Sovremennom Sostoyanii Ekologicheskoy Sistemy Ozera Baikal, Izd-vo SO RAN, Novosibirsk, 2002.

9 McConnell L. L., Kucklick J. R., Bidleman T. F., Ivanov G. P., Chernyak S. M., *Environ. Sci. Technol.*, 29 (1996) 792.

10 Nakata H., Tanabe S., Tatsukawa R., Amano M., Miyazaki N., Petrov E. A., *Environ. Sci. Technol.,* 29 (1995) 2877.

11 Tanabe S., Niimi S., Minh T. B., Miyazaki N., Petrov E. A., *Arch. Environ. Contam. Toxicol.,* 44 (2003) 533.

12 Otchet o Nauchno-Issledovatel'skoy Rabote "Rol' Regional'nykh Protsessov v Zagryaznenii Ozera Baikal i Yego Regionov", Tema 1.4.2.25, Plan NIR i OKR, Rosgidromet, Moscow, 2003.

13 Otchet o Nauchno-Issledovatel'skoy Rabote "Dat' Utochnennuyu Kharakteristiku Sostoyaniya Ozera Baikal i Yego Basseyna v Usloviyakh Prodolzhayushchegosya Zagryazneniya Okruzhayushchey Sredy i Deystviya Global'nykh Faktorov", Tema 4.2.28, Plan NIR i OKR, Rosgidromet, Moscow, 2006.

14 Otchet "Obzor Sostoyaniya i Zagryazneniya Okruzhayushchey Sredy v Rossiyskoy Federatsii za 2009 g.", Rosgidromet, Moscow, 2010.

15 Otchet "Obzor Sostoyaniya i Zagryazneniya Okruzhayushchey Sredy v Rossiyskoy Federatsii za 2010 g.", Rosgidromet, Moscow, 2011.

16 Poliakova O. V., Lebedev A. T., Petrosyan V. S., Hanninen O., Rensoni A., Savva D., Walker C., *Toxicol. Environ. Chem.*, 75 (2000) 235.

17 Mamontov A. A., Mamontov E. A., Tarasova E. N., McLachlan M. S., *Environ. Sci. Technol.*, 34 (2000) 741.

18 Shelepchikov A. A., Chernyak Yu. I., Brodskiy E. S., Feshin D. B., Grassman J. A., *Sib. Med. Zh.*, 3 (2012) 53.

19 Nikonova A. A., Gorshkov A. G., *ZhAKh*, 67, 1 (2012) 74.

20 Pravdin I. F., Rukovodstvo po Izucheniyu Ryb (Preimushchestvenno Presnovodnykh), Pishchevaya Prom-st', Moscow, 1966.

21 Chugunova N. I., Rukovodstvo po Izucheniyu Vozrasta i Rosta Ryb, Izd-vo AN SSSR, Moscow, 1959.

22 Weiss R. F., Carmack E. C., Koropalov M. V., *Nature*, 349 (1991) 665.

23 Peeters F., Kipfer R., Hohmann R., Hofer M., Imboden D. M., Kodenev G. G., Khodzher T. V., *Environ. Sci. Technol.*, 31 (1997) 2973.

24 Otchet "Stoykiye Organicheskiye Zagryazniteli (SOZ) na Baikal'skoy Prirodnoy Territorii", NPO Tayfun, Obninsk, 2015.
URL: (http://www.rpatyphoon.ru/upload/medialibrary/dbc/Baykal_otchet_2015.pdf (accessed June 18, 2016).

25 Gorshkov A. G., Dzyuba E. V., Kustova O. V., Nikonova A. A., Mamontov A. M., Khutoryanskiy V. A., *Voda: Khim. i Ekol.*, 8 (2015)48.

26 Szlinder-Richert J., Barska I., Mazerski J., Usydus Z., *Marine Pollut. Bull.*, 58 (2009) 85.

27 Blocksom K. A., Walters D. M., Jicha T. M., Lazorchak J. M., Angradi T. R., Bolgrien D. W., *Sci. Total Environ.,* 408 (2010) 1180.

28 GOST 31983–2012. Produkty Pishchevye, Korma, Prodovolstvennoye Syr'ye. Metody Opredeleniya Soderzhaniya PKhB.

29 ISO 13876:2013(en). Soil quality – Determination of polychlorinated biphenyls (PCB) by gas chromatography with mass selective detection (GC-MS) and gas chromatography with electron-capture detection (GC-ECD). URL: https://www.iso.org/obp/ui/#iso:std:iso:13876:ed-1:v1:en (accessed June 18, 2016).

30 IARC. Polychlorinated biphenyls and polybrominated biphenyls, vol. 107, 2015. Monographs on the evaluation of carcinogenic risks to humans, Lyon, France.

31 Fox K., Zauke G. P., Butte W., *Ecotoxicol. Environ. Saf.*, 28 (1994) 99.

32 Nikonova A. A., Dzyuba E. V., Gorshkov A. G., Tyagun M. D., in: Sostoyaniye i Problemy Iskusstvennogo

Vosproizvodstva Rybnykh Zapasov Baika'lskogo Regiona (A Collection of Articles), Ulan Ude, 2008, pp.78–80.

33 Gobas F. A. P. C., Opperhuizen A., Hutzinger O., *Environ. Toxicol. Chem.*, 5 (1986) 637.

34 Gobas F. A. P. C., Zhang X., Wells R., *Environ. Sci. Technol.*, 27 (1993) 2855.

35 INERIS. Données technico-économiques sur les substances chimiques en France : Les polyChloroBiphenyles (PCB). DRC-11-118962-11081A, 2011, p. 89. URL: http://www.ineris.fr/substances/fr (accessed June 18, 2016).

36 Gos. Komitet RF po Okhrane Okruzhayushchey Sredy. Prikaz ot 13 Aprelya 1999 g. No. 165. O Rekomendatsiyakh dlya Tseley Inventarizatsii na Territorii Rossiyskoy Federatsii Proizvodstv, Oborudovaniya, Materialov, Ispolzuyushchikh ili Soderzhashchikh PKhB, a takzhe PKhB-soderzhashchikh Otkhodov. URL: http://www.dioxin.ru/doc/prikaz165.htm (accessed June 18, 2016).

37 US EPA 440.5-88.006, 1998. Water quality standards criteria summaries: A compilation of State/Federation criteria. URL: http://www.epa.gov/waterscience/criteria/wqcriteria.html (accessed June 18, 2016).

38 Vecchiato M., Zambon S., Argiriadis E., Barbante C., Gambaro A., Piazza R., *Microchem. J.*, 120 (2015) 26.

39 Fernandez P., Carrera G., Grimalt J. O., *Aquatic Sci.*, 67 (2005) 263.

40 Guzzella L., Poma G., De Paolis A., Roscioli C., Viviano G., *Environ. Pollut.*, 159 (2011) 2552.

41 Villa S., Bizzotto E. C., Vighi M., *Environ. Pollut.*, 159 (2011) 932.

42 ESIM "Edinaya Gosudarstvennaya Sistema Informatsii ob Obstanovke v Mirovom Okeane", 2004. URL: http://esimo.oceanography.ru/esp2/index/index/esp_id/2/section_id/8/menu_id/4218 (accessed June 18, 2016).

43 Dai G., Liu X., Liang G., Han X., Shi L., Cheng D., Gong W., *J. Environ. Sci.*, 23, 10 (2011) 1640.

44 Ackerman L. K., Schwindt A. R., Massey Simonich S. L., Koch D. C., Lett T. F., Schreck C. B., Kent M. L., Landers D. H., *Environ. Sci. Technol.*, 42 (2008) 2334.

45 Schmid P., Kohler M., Gujer E., Zennegg M., Lanfranchi M., *Chemosphere*, 67 (2007) 16.

46 Vives I., Grimalt J. O., Catalan J., Rosseland B. O., Battarbee R. W., *Environ. Sci. Technol.*, 38 (2004) 690.

47 Vives I., Grimalt J. O., Venture M., Catalan J., Rosseland B. O., *Environ. Pollut.*, 133 (2005) 343.

48 Consoli C., Gavazzeni G., Vitali A., Fedrizzi G., Menotta S., *L'Osservatorio*, 4 (2001) 6.

49 Commission Regulation (EU), 2011, No. 1259/2011. URL: http://eurex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:320:0018:0023:EN:PDF (accessed June 18, 2016).