Article

Assessment of PCBs in Surface Waters at Ultratrace Levels: Traditional Approaches and Biomonitoring (Lake Baikal, Russia)

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Abstract: This article presents the results of the assessment of PCB concentrations in surface waters at ultratrace level of concentrations. The assessment of PCB concentrations is based on data from monitoring PCBs in Baikal water within the conventional approach as well as from biomonitoring of PCBs using Baikal omul, *Coregonus migratorius*, Georgi, 1775 (*C. migratorius*), as a bioindicator. The time cycle of the monitoring covered the period from 2014 to 2021. The concentrations of PCBs in the water were estimated from the concentrations of seven indicator congeners: 28, 52, 101, 118, 138, 153, and 180, and from congeners of dioxin-like (dl) PCBs in the tissues of *C. migratorius*. The average value and the statistically significant range of the detected total concentrations (Σ_7 PCBs) in Baikal water were 0.30 and 0.26–0.34 ng/L, respectively. In the tissues of *C. migratorius*, the average value and the range of Σ_7 PCB concentrations were 5.6 and 4.9–6.3 ng/g (ww), respectively, and for dl-PCBs, 1.5 and 1.3–1.7 ng/g (ww), respectively. The total toxicity equivalent of the detected dl-PCBs was in the WHO-TEQ₍₂₀₀₅₎ range from 0.03 to 0.06 pg/g (ww). The concentrations of Σ_7 PCBs in Baikal water and dl-PCBs in the tissues of *C. migratorius* corresponded to the concentration levels in the European alpine lakes and the tissues of *S. trutta* fish inhabiting these lakes.

Keywords: PCBs; monitoring; biomonitoring; statistical analysis; Lake Baikal

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1. Introduction

Accumulation of persistent organic pollutants (POPs) in surface waters is the most important problem of the international community within the framework of its Sustainable Development Goal. The development of reliable methods for monitoring and assessing the concentrations of POPs at the background level of concentrations is one of the tasks, the solution of which requires priority measures [1,2]. Among POPs, polychlorinated biphenyls (PCBs) stand out for their exceptional chemical and biological stability and global distribution: pollutants of this class are found in air, water, soil, and biota. PCBs have many unique physical and chemical properties that have determined their widespread application in various fields of technology. The total world production of PCBs is 1.5 million tons, of which approximately 10% remain in the environment [3–6]. When their toxic effect on living organisms was determined in extremely low doses, together with the ability to accumulate in biological objects, the Stockholm Convention prohibited the production and use of PCBs. They were included in the list of POPs and the OSPAR Convention included them in the list of priority pollutants [7,8].

In the surface water of background areas, PCBs are present at ultratrace concentration levels. For example, in the Arctic water, PCBs were detected in the concentration range from 1.3 to 21 pg/L [9,10]. It should be noted that data on the concentrations of PCBs in the water is scarce. Methodological problems may complicate the detection of PCBs at trace levels of concentrations, in particular, due to hydrophobicity of PCBs, i.e., sorption on the surface of suspended particles in the water column and accumulation in biota

lipids. Increasing the volume of water samples up to 100 L or more [11,12] to reduce the lower limit of the range of detected PCB concentrations increases expended time and resources. A decrease in the number of samples (during the multiple high-volume sampling) increases the likelihood of missing local areas with high concentrations of PCBs. Otherwise, estimation based on the extreme short-term periods of water pollution in individual areas is possible. Passive sampling techniques [13] can estimate the concentrations of dissolved PCBs, but the assessment of the total concentration of PCBs in two phases of water matrix (aqueous solution and solid phase) as a biota habitat is more significant at the background level of pollution. In turn, the detection of PCBs at trace levels of concentration with the required reliability and accuracy is possible using modern gas chromatography–mass spectrometry techniques that provide high sensitivity and specificity [14,15].

Biological monitoring, a determination of pollutants in aquatic bioindicator organisms directly exposed to these substances, is an alternative method to control POPs in surface water. Bioindicators must have certain relevant characteristics, in particular, accumulate PCBs in the amounts sufficient for their detection; their habitat must correspond to the boundaries of the studied water body, and it is possible to collect a sufficient number of specimens of these organisms [16]. Fish is the most widespread bioindicator of PCBs in water bodies; PCBs reflecting water pollution have been detected over a wide range of concentrations for both marine and freshwater species [17–27]. The dependence of the levels of PCB accumulation in fish on the concentrations of these substances in the water was used to assess temporal and spatial variations in surface waters, investigate vertical transport of pollutants from the surface to deep water layers [19,28,29], and estimate the content of pollutants at the background level of concentrations [30–34].

When the industrial production of PCBs was ceased, their concentrations in fish, bottom sediments, and the atmosphere of the Arctic regions decreased [35–37]. At the present stage, the sources of PCBs include dismantling and disposal of equipment containing these substances as a structural material as well as various chemical and thermal processes, during which PCBs are formed as byproducts from landfills, waste disposal sites, or illegal stockpiles [38–41]. As shown in [3,42], the number of PCBs in the environment is currently not decreasing but even increasing in some regions of the world. For instance, as the climate warms, many POPs accumulated in the Arctic environment re-enter the atmosphere as a result of sea ice retreat and temperature rise [43].

We chose Lake Baikal as a model for estimating PCBs in surface water at ultratrace levels of concentration. Lake Baikal covers an area of 31,700 km² and contains up to 20% of the world reserves of surface freshwater, ~23,000 km³. Water in the lake is clean and has a low mineralization degree, and a minimal content of suspended organic matter and POPs [44–47]. The presence of PCBs in the aquatic ecosystem of Lake Baikal was first reported in [48]. At that time, the level of their concentrations in the water corresponded to the world background level [11,49–51]. According to independent studies, there was up to a 4.5-fold increase in the PCB concentrations in 2014 and 2015 [11,52] compared to the levels recorded in 1992 and 1993.

The increase in the PCB concentrations in Baikal water is of special concern because the lake is the most important water resource on the planet. This has highlighted the scientific problem of PCB control in the ecosystem of Lake Baikal, which is associated with the detection of PCBs in the surface water at the ultratrace level of concentrations. This study evaluates the results of PCB monitoring, which were obtained during the observation period from 2014 to 2021 at Lake Baikal. Monitoring of PCBs was carried out within the framework of the conventional approach, including water sampling according to a standardised procedure followed by the determination of the required pollutants in them by the GC–MS/MS method, as well as within the framework of biomonitoring using Baikal omul, *Coregonus migratorius*, Georgi, 1775 (*C. migratorius*), as a bioindicator. To identify the relationship between the concentrations of indicator PCB congeners and their total concentrations in the water and *C. migratorius*, key factors influencing the concentrations of PCBs in the water and bioindicator, we also carried out a comparative statistical analysis.

2. Materials and Methods

2.1. Sampling

Water samples from the pelagic zone of Lake Baikal were collected by using an SBE-32 cassette sampler (Carousel Water Sampler, Sea-Bird Electronics, Bellevue, WA, USA) at 21 stations (Figure 1) in May 2015, May and September 2016, May 2018, May and September 2019, and June and September 2020 and 2021 (Table S1, supplementary materials). At each station, two samples 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 using a lid with an aluminium foil gasket and stored at 5 °C until laboratory analysis.

Figure 1. Map of Lake Baikal and sampling sites. At stations 1, 2, 4, 5, 7, 10, 12, 17, 18, 20, and 21, sampling was carried out from the upper water layer (5 m) at a distance of up to 3 km from the coast; at station 3, 6, 8, 11, 16, and 19 at reference central stations; at station 6—from the water column at depths of 5 to 1200 m; at station 11—from the water column at depths of 5 to 1600 m; at station 16—from the water column at depths of 5 to 800 m; and at station 22, *C. migratorius* was caught.

Baikal omul, *Coregonus migratorius*, Georgi, 1775 (*C. migratorius*), is fish species meeting the criteria for biological objects to be selected as bioindicators [16]: (i) *C. migratorius* migrates throughout the entire water area of Lake Baikal in a depth range up to 350 m, including the zones of river runoff; (ii) it is a commercial fish species, ensuring economic efficiency of the sampling stage during monitoring; (iii) individuals at the age of three to seven years accumulate PCBs in an amount sufficient for their measurement with the

required accuracy [53,54]. *Coregonus migratorius* was caught near station 22 (Figure 1) in March to July 2014, February 2016, March 2018–2020, and September 2017–2018. Collected fish were packed in aluminium foil, frozen, and stored at a temperature of $\leq$ minus 18–20 °C. Identification characteristics of the selected Baikal omul (sex and age, Table S2) were determined according to the methods in [55,56]. The group of fish selected as bioindicators of PCBs included *C. migratorius* aged from three to seven years. The choice of this species of Baikal fish as bioindicators ensured the efficiency of the sampling because Baikal omul belongs to a commercial species.

The following reasons determined the choice of sampling seasons for water and *C. migratorius*. In the spring, after the ice melts, PCBs enter the lake water due to the melting of ice on the water surface of the lake and snow on its coast, in which PCBs have accumulated during the winter. Water samples collected in autumn reflect the accumulation of PCBs in water, which have come from the atmosphere in summer.

2.2. Sample Processing

In water samples and omul specimens, indicator congeners 28, 52, 101, 118, 138, 153, and 180, and dioxin-like congeners (dl-PCBs) 105, 114, 118, 123, and 126 (dl-PCBs 118 is one of the indicator congeners) were determined according to the technique shown in [55,56] (Tables S3–S5). This technique included the following steps: extraction by n-hexane from 1 L of unfiltered water, the concentration of the extract to the volume of ~0.1 mL, and direct analysis of the extracts by GC–MS/MS. Before the determination of PCBs in *C. migratorius*, the fish selected for the analysis were thawed; the head, fins, and entrails of the fish were removed. The fish was then homogenised, discarding the skin, and large bones. PCBs were extracted from the mince via ultrasound extraction with a mixture of organic solvents: n-hexane/acetone (1:1). The extracts were purified with concentrated H₂SO₄.

2.3. Instrumental Analysis

Prepared extracts of the samples were analysed using an Agilent Technologies 7890B GC System 7000C GC–MS Triple Quad chromatography–mass spectrometer with an HT-8, SCE Analytical Science capillary column (30 m × 0.25 mm × 0.25 µm). PCB peaks were recorded using the MRM mode and identified by relative retention times. PCB congeners were quantitated by the method of internal standards using a Marker-7 PCB Mixture ¹³C (Cambridge Isotope Laboratories, Inc., Shirley, NY, USA) as a surrogate internal standard (Tables S3 and S4). The limits of determination (LOD) of PCB congeners in the water and fish were 0.01–0.02 ng/L and 0.10–15 ng/g (ww), respectively. The LOD method was assessed based on the peak-to-peak signal-to-noise response of each of the PCB peaks (N/S) and at the lowest standard concentration. Values for S/N > 10 were employed to determine the limit of quantitation (LOQ) for each target compound. Relative standard deviation (RSD_{RI}) for the determination procedure was 35% for individual indicator congeners in the water: 28, 52, 101, 118, 138, 153, and 180; 25% for individual indicator congeners and dl-PCBs in the fish: 28, 52, 101, 105, 114, 118, 123, 126, 138, and 153; and 45% for congener 180.

2.4. Toxicity Assessment

The dioxin toxicity equivalents (TEQ) for dl-PCBs were assessed as a product of the concentration of dl-PCB congeners (C) and its corresponding toxicity equivalency factor (TEF) established by the International Program on Chemical Safety (IPCS) and World Health Organisation (WHO):

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

where C (pg/L) and TEF_i are the concentrations and toxic equivalent factors (TEFs) of the dl-PCB congeners [57].

2.5. Statistical Methods

Confidence intervals for the mean values of the concentrations of PCB congeners and the total concentrations of seven indicator PCB congeners (Σ_7 PCBs) were estimated using the bootstrap method in the «boot» package and the R programming language. Because of technical problems, a small part of the primary data on some PCB congeners for *C. migratorius* was unspecified. For further analysis, these missing data were replaced with averages for these congeners according to the recommendations [58].

PERMANOVA testing in the R package ‘vegan’ [59] was used for analysing an impact of the explanatory parameter: the year, month, the basin of Lake Baikal, and sampling depth for water, along with the year, month, age, and sex for *C. migratorius* (Tables S6 and S7). In the range of concentrations of the studied PCB congeners and Σ_7 PCBs in the samples of Baikal water and *C. migratorius*, *p* values of the PERMANOVA analysis were corrected for false discovery rate in multiple comparisons using the Benjamini–Hochberg equation [60].

To determine the similarity and difference between water samples and separately between the specimens of *C. migratorius* in the concentrations of various PCB congeners and Σ_7 PCBs, principal component analysis (PCA) was applied by using the «factoextra» package [61] for the R programming language. For analysis, data on water and *C. migratorius* were previously converted into ‘integral samples’, which were average values for the concentrations of PCB congeners over a set of explanatory parameters, indicating, according to the results of PERMANOVA analysis, a significant effect on PCB concentrations in the samples. Before PCA, all PCB concentrations were transformed to eliminate the physical dimensions by ranging from 0 to 1.

Pairwise correlations between all concentrations of the studied PCB congeners and the total concentration of PCB in samples of Baikal water and Baikal omul (*C. migratorius*) were estimated with Spearman’s *r* correlation coefficient. Only reliable correlation coefficients (*p* < 0.05) were included in analysis. *p* values for the correlation coefficients were calculated using Spearman’s «W» statistics and corrected for false discovery rate in multiple comparisons using the Benjamini–Hochberg equation [60]. Unreliable values of correlation coefficients were replaced with 0 values. Pairwise correlations were visualized with a heat map generated using «gplots» [62] in R. Lines and columns in the correlation matrix were clustered and grouped in order of similarity (i.e., Euclidean distance metric and the complete-link clustering method).

To determine the relationship between the concentrations of the studied PCB congeners and Σ_7 PCBs for the samples of Baikal water and *C. migratorius* averaged over the year of sampling, the Mantel test [63,64] was used based on the Pearson correlation coefficient; the significance of the correlation was determined by the permutation test (10,000 permutations). Distance matrices for the Mantel test that determine the differences for concentration of PCB congeners between the water samples and between *C. migratorius* samples were calculated using the Euclidean metric. The Mantel test was performed using the R package ‘vegan’ [59].

Relative error statistics for repeated measurements of PCB concentrations for all samples from Lake Baikal were estimated as a relative difference between the maximum and minimum concentration of analytical repetitions of one measurement (relative error = $100 \times (\max - \min) / \max$, %) (Tables S8 and S9).

All primary data are available in tables table_Sup_1.xlsx—water data, table_Sup_2.xlsx—*C. migratorius* data in supplementary material.

3. Results and Discussion

3.1. PCBs in the Upper Water Layer of the Pelagic Zone and Deep Layers of the Water Column of Lake Baikal

The concentrations of PCBs in the water of Lake Baikal were characterised by seasonal and interannual variability (Figure 2). In May 2015, we detected the maximum total concentrations of PCB congeners (Σ PCBs) ranging from 1.4 to 6.6 ng/L. There were 24 to 34 congeners of PCBs dominated by homologues of penta-dichlorobiphenyls as well as 7 indi-

cator congeners 28, 52, 101, 118, 153, 138, and 180. The total concentrations of indicator PCB congeners (Σ_7 PCBs) ranged from 0.43 to 2.0 ng/L, and the contribution from Σ_7 PCBs to the total concentration of all detected congeners ranged from 28 to 35%. In September 2019, the concentration of Σ_7 PCBs also increased at some stations (19 and 21) to 0.24–2.8 ng/L with an increase in the number of the detected congeners to 27. Indicator congeners were detected in the concentration range from 0.17 to 1.3 ng/L with a contribution to Σ PCBs of up to 40–70%. The minimum concentrations of Σ PCBs in Baikal water ranged from 0.11 to 0.82 ng/L, and the number of the detected congeners were recorded in September 2016, May 2018 and 2019, and in the spring and summer of 2020 and 2021. The concentrations of Σ_7 PCBs in these seasons ranged from ≤ 0.11 to 0.47 ng/L. The average concentration and statistically significant range of detected Σ_7 PCB concentrations in Baikal water were 0.30 and 0.26–0.34 ng/L, respectively. Notably, the indicated level of the detected Σ PCB concentrations was comparable with the concentrations of PCBs in Lake Baikal identified previously in 1992 and 1993 (0.08–1.9 ng/L) and estimated as background [49,51].

Figure 2. Average concentrations of Σ_7 PCBs in the pelagic zone (hatched bars) and deep layers (solid blue bars) of Lake Baikal determined during the monitoring of PCBs in Baikal water.

The global atmospheric transport is the dominant source of PCBs in Baikal water [11,49–51]. An increase in the concentrations of Σ PCBs in May 2015 and September 2019 was likely due to the influx of PCBs from additional sources, which a change in the ratio of indicator congeners indicated. In spring 2015, the proportion of indicator congeners with a high degree of chlorination (138, 153, and 180) increased in water samples up to 30–37%. In autumn 2019, the proportion of pentachlorinated congeners 101 and 118 increased, and the proportion of ‘light’ tri- and tetrachlorinated congeners 28 and 52 decreased compared to the monitoring data during spring 2015. During the minimum concentrations of PCBs in the water of the pelagic zone of Lake Baikal, tri-, tetra-, and pentachlorinated homologues (28, 52, 101, and 118) predominated in the composition of indicator congeners, whose total concentrations reached 80–90% in the fraction of indicator PCBs.

Seasonal changes in the PCB concentrations in the upper water layer (5 m) of the pelagic zone in May 2015 and September 2019 were not tracked throughout the water column to depths of 800–1600 m (depending on the depth of the lake’s basin). In May 2015, a high level of Σ_7 PCBs in the upper water layer (5 m) of the southern basin of the lake, up to 3.1 ng/L, was recorded at some stations. However, in deep water layers of the water column (50–1200 m), the Σ_7 PCB concentrations remained in a narrow range from 0.20 to

0.51 ng/L. An increase in the Σ_7 PCB concentrations in the upper water layer at stations 19 and 21 to 1.6–2.2 ng/L in autumn 2019 was also not accompanied by an increase in the Σ_7 PCB concentrations at depths of 50 to 800 m, which remained at a minimum level from 0.31 to 0.69 ng/L.

3.2. PCBs in *Coregonus migratorius*

We studied Baikal omul, *C. migratorius*, as a bioindicator of PCBs in Baikal water. In the course of biomonitoring, we collected and analysed 46 individuals of the *C. migratorius* population of Lake Baikal. The analysis revealed that the concentration of PCBs in fish specimens depends on the season and year of sampling (Figure 3). In the investigated specimens, we detected from 30 to 47 PCB congeners, including seven indicator congeners. The average concentrations and statistically significant range of the detected Σ_7 PCBs in *C. migratorius* were 5.6 and 4.9–6.3 ng/g (ww), respectively.

Figure 3. Average concentrations of Σ_7 PCBs in specimens of *C. migratorius* (per season) collected during the monitoring of PCBs in Baikal water.

Biomonitoring of PCBs in the lake water revealed five dl-congeners: 105, 114, 123, 126, and 156, which were present in the water below the LOQ of the method used to analyze the water. The total concentrations of dl-congeners in *C. migratorius* ranged from 1.3 to 1.7 ng/g (ww). The most toxic congener, 126 (the toxicity equivalence factor, TEF₂₀₀₅ is 0.1), was found in single individuals of the older age group (4 out of the 46 investigated individuals), reaching 0.5 ng/g (ww).

The age of fish is a critical biomonitoring factor, since the concentration of PCBs in individuals of the older age group increases [31]. During the biomonitoring, we chose individuals of *C. migratorius* aged from three to seven years. In this group of fish, the level of concentration of Σ_7 PCBs changes insignificantly: Σ_7 PCBs were 3.9 (3 year), 4.9 (5 year) and 5.4–5.6 (6–7 years) ng/g (ww), and the proportion of congeners with a high degree of chlorination (153, 138, 180) increased. In the muscle tissues of the individuals of the older age group (8 years, 2 specimens), the number of PCBs reached extreme values: Σ_7 PCBs to 32 ng/g (ww) and Σ_{dl} PCBs to 9.0 ng/g (ww).

3.3. Assessment of the PCB Concentration in the Water of Lake Baikal

Global atmospheric transport is the dominant source of PCBs in the aquatic ecosystem of Lake Baikal. Therefore, the assessment of the concentrations of pollutants of this class in Baikal water by the concentrations of indicator congeners is reasonable and provides adequate results [65]. We carried out a comparative statistical analysis to study the influence

of the year and season of sampling, locations of sampling stations in the pelagic zone of the lake and layers of the water column, and the age and sex of omul on the ratio and concentrations of indicator congeners of PCBs detected in the water samples and tissues of *C. migratorius*. To identify relationships between the concentrations of PCBs in Baikal water and *C. migratorius*, selected as a bioindicator of PCBs, a correlation analysis of the results of determining PCBs in water and *C. migratorius* was carried out.

3.3.1. Statistical Analysis of the Results of ‘Conventional’ Monitoring

The results of the PERMANOVA analysis (Table S6) indicated that among all studied factors only year and month of sampling significantly influenced the concentrations of the investigated PCB congeners, including Σ_7 PCBs, in Baikal water (year factor— $R^2 = 0.163$; month factor— $R^2 = 0.074$; p -value < 0.05). At the same time, based on the coefficients of the R^2 covariation, the sampling year factor had the maximum effect on the concentrations of PCBs. Further data analysis by PCA based on the PERMANOVA results was carried out for the values averaged by the factors of the pelagic zone of the lake’s basin and sampling depth.

The analysis of the results of the determination of PCB indicator congeners by PCA revealed that all data were divided into two groups (Figure 4a). The first group in the second quarter of the coordinate plane included the average data obtained in September 2016, May 2018–2019, and June and September 2020–2021. All points of this group were characterised by minimum concentrations of all indicator congeners and Σ_7 PCB concentration ranging from ≤ 0.11 to 0.47 ng/L. The second group (the first quarter of the coordinate plane) includes the data obtained in May 2016 and September 2019. These data referred to extreme concentrations of all indicator congeners and Σ_7 PCBs (1.3 – 2.0 ng/L) relative to the minimum level determined during the monitoring between 2015 and 2021.

On the PCA biplot (Figure 4a), the PCB concentration gradient vectors form a codirectional group that includes all investigated indicator congeners of PCBs and Σ_7 PCBs, except for congener 28 (a congener group with a positive correlation). The vector of congener 28 is directed almost perpendicular to the main group, and the concentration of this pollutant depends (correlates) to a lesser extent on the concentrations of other indicator PCBs. Perhaps, the sources of congener 28, its further fate in the aquatic ecosystem, and (or) congener properties (the minimum hydrophobicity and the maximum water solubility among indicator congeners) affect its concentration in Baikal water.

The PCA data on the concentrations of PCBs in Baikal water allowed us to draw the following conclusions: (i) an increase or a decrease in all indicator congeners, except for congener 28 and the concentration of Σ_6 PCBs, occurred synchronously; (ii) within the framework of conventional monitoring, the assessment of the PCB concentrations in Baikal water based on the total concentration of six indicator congeners (Σ_6 PCBs, excluding congener 28) would meet more stringent criteria.

Figure 4. Results of the concentration distribution analysis of the investigated PCB types and the total PCB concentration based on PCA. (a) Analysis of water samples: point on the plane characterise the average PCB concentrations in Baikal water (entire water area of the lake) by the year and month of sampling (a point is the average PCB concentration in water samples taken in a certain month of one year); (b) analysis of the distribution of PCB concentrations in omul specimens: points on the plane characterise the average PCB concentrations in omul by the year, month, and age of the individuals (a point is the average PCB concentration in individuals of the same age collected in the same year and the same month). Vectors on the planes show the directions of the concentration gradients of the investigated PCB types (blue vectors and green vectors are dioxin-like PCBs), the total PCB concentration (orange vectors), and the age of omul individuals (red vector).

3.3.2. Statistical Analysis of Biomonitoring Results

Based on the PERMANOVA data (Table S7), among all studied factors, the year and month of sampling and the age of individuals (year factor— $R^2 = 0.193$; month factor— $R^2 = 0.107$; age factor— $R^2 = 0.075$; p -value < 0.05) significantly influenced the concentrations of PCBs in the muscle tissue of *C. migratorius*. The R^2 covariation coefficients indicated that the year of sampling was the main factor of influence followed by the less significant month of sampling and the age of fish (Figure 4b). As the sex of the *C. migratorius* individuals was not a critical factor ($R^2 = 0.002$), PCA for *C. migratorius* was based on the sex-averaged data.

PCA of the concentrations of PCB congeners in *C. migratorius* distinguished three groups of averaged data (Figure 4b). The first group is located in the upper part of the coordinate plane at the border of the first and second quarters and included the data on *C. migratorius* caught in February 2016 and March 2018 and 2020. The age of the individuals in this group ranged from five to eight years.

All fish from this group were characterised by high dl-PCB concentrations ranging from 1.0 to 2.2 ng/g (ww), whose proportion in Σ_7 PCBs reached 33%, and by relatively low total concentrations of congeners 28 and 52, ranging from 1.1 to 2.6 ng/g (ww). Notably, this group of the *C. migratorius* fish was caught in the spring during the freezing period on the lake after the winter lifecycle with the corresponding feeding structure [66].

The second group of data located at the border of the first and fourth quarters of the coordinate plane included the results of the determination of PCB concentrations in *C. migratorius* that were caught at the end of the feeding period in August and September of 2016, 2017, 2018, and 2019. In this group of specimens, the concentration of PCBs was in the Σ_7 PCB range from 5.2 to 6.8 ng/g (ww) with the concentrations of Σ_{dl} PCBs ranging from 0.7 to 1.2 ng/g (ww). The age of the individuals was from four to seven years and predominated by five-year-olds. The group of points in the fourth coordinate plane includes the data on the *C. migratorius* specimens that differed in high concentrations of 'light' congeners 28 and 52, with up to 33% of the Σ_7 PCB concentration.

In the third quarter of the coordinate plane, there was the third group of the data on *C. migratorius* caught in March and August 2014 and September 2018. The presence of PCBs in this group was characterised by the maximum concentrations of Σ_7 PCBs ranging from 6.8 to 8.7 ng/g (ww) with the dominance of congeners 28 and 52 in the total proportion, with 50% of Σ_7 PCBs. Individual points in this part of the coordinate plane characterised the *C. migratorius* individuals caught from March to August 2014 and in September 2017. PCBs detected in these fish specimens had high concentrations of Σ_7 PCBs, from 10 to 13 ng/g (ww). Noteworthy was the result of the determination of PCBs in an eight-year-old *C. migratorius* individual. The PCB concentrations in this individual reached extreme values: Σ_7 PCBs 32 ng/g (ww) and Σ_{dl} PCBs 9.0 ng/g (ww), with minimum total concentrations of 'light' congeners 28 and 52 at less than 7.0% of Σ_7 PCBs.

On the PCA biplot (Figure 4b), the gradient vectors of average data on the PCB concentrations in *C. migratorius* formed three codirectional groups. The first group included the vectors of indicator congeners 138, 153, and 101, and dl-congeners 126, 118, and 114, together with the vector of the age of individuals. All these characteristics, including the age of individuals, were positively correlated with each other. The second group included the vectors of congeners 28 and 52, whose concentrations were associated with a strong positive correlation with each other and a weaker positive correlation with the vectors of the first group. The third group of vectors included dl-congeners 156, 105, and 123, whose concentrations were associated with each other by a strong positive correlation and a weaker positive correlation with the vectors of the first group.

The vectors of the third and second groups were almost perpendicular to each other. Therefore, the concentrations of PCBs in the specimens from these groups were not correlated and interconnected with each other.

The evaluation of *C. migratorius* as a bioindicator of PCBs in Baikal water by PCA based on the analysis of the results of the detection of PCBs in its tissues revealed that (i) the

age of the fish determined the concentrations of indicator congeners with a high degree of chlorination (101, 138, and 153) and dioxin-like congeners 114 and 118, including the most toxic congener 126; (ii) the concentrations of 'light' congeners 28 and 52 did not depend on the age of the fish and were not associated with the accumulation of other congeners.

3.3.3. Analysis of Correlations

The heatmap in Figure 5a shows an analysis of correlations between the concentrations of various PCB congeners and the Σ_7 PCB concentrations in Baikal water. Between all concentrations of PCBs and Σ_7 PCBs, there were significant positive ($p < 0.05$) pairwise correlations with correlation coefficients ranging from 0.6 to 0.9. Among all correlation clusters, a group of indicators stood out, including the concentrations of congeners 52, 101, and 153, dl-congener 118 and Σ_7 PCBs in the water with a high pairwise correlation (correlation coefficient from 0.85 to 0.98). Additionally, there was the correlation group of congeners 138 and 180. The correlation coefficients of the concentrations of these congeners with each other, with the concentrations of other congeners, and with Σ_7 PCBs had lower values (from 0.75 to 0.85). The concentration of congener 28 was distinguished by the minimum correlation coefficient with the concentration of congener 180 (0.6). The results of the correlation analysis of the indicator PCBs in Baikal water indicated a strong agreement in the change in the concentrations of chlorobiphenyls (28, 52, 101, and 118) with each other and with the concentration of Σ_7 PCBs. An increase or a decrease in the concentrations of one of these congeners was accompanied by an increase or a decrease in the concentrations of all congeners from the abovementioned group. The concentrations of congeners 138 and 180 were less correlated with the concentrations of other PCBs. Obviously, various factors determined the qualitative composition of PCB congeners in Baikal water: PCB sources (local and long-range atmospheric transport), water solubility and hydrophobicity, sorption on the particles of the solid phase of the water column, and transition to the bottom sediments.

PCBs identified in the tissues of *C. migratorius* were characterised by more complicated pairwise correlations between the concentrations of different congeners compared to the results of the corresponding analysis of PCBs in Baikal water (Figure 5b). Positive values of the correlation coefficients above 0.5 ($p < 0.05$) were classified as significant. Based on the range of pairwise correlation coefficients and the clusterisation results, all PCB congeners were divided into three groups.

The first group included the concentrations of congeners 153, 180, 101, and 118 together with the concentration of Σ_7 PCBs. In this group, the concentrations of the components were positively correlated with each other and with the rest of the PCB congeners. The second group included congener 138 and dl-congeners 105, 123, and 156. The concentrations of congeners from this group were associated by high correlations with each other ($r > 0.7$) and a small correlation with congeners from the first group ($0.3 < r < 0.6$). There was no significant correlation between the concentrations of congeners from the second group and congeners 28 and 52, and dl-congeners 114 and 126. The third group included congeners 114 and 126 and dl-congeners 114 and 126 that had high correlations with each other ($r > 0.7$) and weak correlations with congeners from the first group ($0.3 < r < 0.6$). There was no significant correlation between the concentrations of congeners from the third and the second groups. The ages of the *C. migratorius* individuals were significantly correlated with the concentrations of congeners 138, 101, and 153 and dl-congeners 123, 105, and 118. At the same time, the correlation coefficients were relatively small, from 0.3 to 0.5.

Figure 5. Heatmaps reflecting the calculations of pairwise correlation coefficients (a) between the concentrations of indicator congeners and Σ_7 PCBs in Baikal water samples and (b) between the concentrations of indicator congeners and Σ_7 PCBs in the tissues of *C. migratorius* and the age of the investigated omul individuals from Lake Baikal. Rows and columns in the heatmaps cluster by the proximity of the spectra of the correlation coefficients. Insignificant values of the correlation coefficients are replaced with zero values; dl-PCBs are marked in green.

The division of the investigated congeners in *C. migratorius* into three groups was likely related to the mechanisms of their accumulation and metabolism in fish bodies. Some indicator congeners of PCBs had a wide range of hydrophobicity properties ($\log K_{ow} = 5.67\text{--}7.36$ [67]), and the level of their accumulation in the tissues of fish corresponded to their hydrophobicity. For this reason, congeners 28 and 52 predominated in the water, having the minimum $\log K_{ow}$ values among indicator congeners. The concentrations of congeners with the maximum numbers of chlorine atoms in the structure increased with the age of individuals. Consequently, the ratio of congeners in fish tissues did not reflect their ratio in water samples. The change in the ratio of congeners in fish tissues was likely owing to not only hydrophobicity of chlorobiphenyls but also to the faster metabolism of congeners with a low degree of chlorination [68]. It was also due to the barriers that occurred during their passage through lipid membranes of cells and (or) to the adsorption caused by the low water solubility [69,70].

Analysis of the relationship between the levels of PCB concentrations in Baikal water and the tissues of *C. migratorius* averaged over years using the Mantel test (Figure 6a) revealed the low and insignificant ($p > 0.05$) Spearman correlation coefficient. This indicated that the change in the concentrations of PCBs in Baikal water did not lead to similar changes in the level of the PCB concentrations in the tissues of *C. migratorius*. The relationship between average annual concentrations of PCBs in the water and their accumulation in the tissues of *C. migratorius* was not statistically confirmed.

Pairwise correlation analysis between average annual concentrations of PCBs in Baikal water and *C. migratorius* (Figure 6b) also did not revealed significant correlations. All pairwise correlation coefficients between the concentration of the investigated PCB congeners in the water and their accumulation in *C. migratorius* did not significantly differ from zero ($p > 0.05$), confirming the conclusions of the Mantel test.

For the Mantel test and correlation analysis between the pairs of dependent and insignificant variables, we took the same-year data on both the water and *C. migratorius*. Perhaps, due to this fact, there was no relationship between the concentrations of PCBs in the water and their accumulation in the tissues of *C. migratorius*. Omul accumulates PCBs gradually during several years, and not only the current concentration of PCBs but also the impact of PCBs in previous years determines the concentrations of the investigated congeners in the tissues of *C. migratorius*. Identification of this relationship requires long series of observations (ten years or more), taking into account other factors that are difficult to consider. These factors affect the processes of PCB accumulation in omul during the observation period, particularly, the change in the qualitative composition of dominant phytoplankton and zooplankton species that are part of *C. migratorius* food web. They also lead to interannual changes in temperature and ice regimes of the lake, which change the speed and direction of migrations and feeding behaviour in fish. Moreover, various factors also affect the qualitative composition of PCB congeners in the water of the lake: PCB sources (local and long-range atmospheric transport), hydrophobicity and water solubility of PCBs, their sorption on particles of the solid phase of the water column, and transition to the bottom sediments.

Figure 6. (a) Results of the analysis of the relationship between the concentrations of the investigated congeners and Σ_7 PCBs in the water and *C. migratorius* using the Mantel test (the analysis was carried out for values averaged by years). (b) Heatmaps reflect the calculations of pairwise correlation coefficients between the concentrations of indicator congeners and Σ_7 PCBs in the water and *C. migratorius* (the analysis was carried out for values averaged over years). Rows and lines on the heatmap are clustered based on the proximity of spectra of correlation coefficients; insignificant values of the correlation coefficients were replaced with zero values; dl-PCBs are marked in green.

3.3.4. Toxicity Equivalence for Dioxin-like PCBs

In Baikal water, we did not identify congeners of polychlorinated dibenzo-p-dioxins and dibenzofurans exceeding the detection limit of 0.01 pg/L [11]. Only one dl-PCB congener, 118, was identified during the monitoring of PCBs between 2015 and 2021. Its concentrations ranged from ≤ 10 to 110 pg/L. In seasons with the extreme concentrations of PCBs, its concentration in the water increased to 350 pg/L. The toxicity of this congener was assessed by the dioxin toxicity equivalents (TEQs) for dl-PCB within the WHO-TEQ₍₂₀₀₅₎ pg/L range from 3×10^{-4} to 3.3×10^{-3} . In seasons with the extreme concentrations, the WHO-TEQ₍₂₀₀₅₎ pg/L value reached 0.01 in May 2015 in the southern basin and 7×10^{-3} in September 2019 in the northern basin of Lake Baikal. In the muscle tissues of *C. migratorius*, the total toxicity equivalent of the detected dl-congeners (except for congener 126) was within the WHO-TEQ₍₂₀₀₅₎ pg/g (ww) range from 0.03 to 0.06, and for congener 126, the value was two orders of magnitude higher, up to 4.7.

3.3.5. Comparative Analysis of the PCB Concentrations in the Surface Water of the Background Sites and in Bioindicator Fish

Currently, there is no common criterion for assessing the pollution of water by PCBs. According to the interim environmental quality standard (EQS), the PCB concentration in the surface waters of the European Union should not exceed 1 ng/L [71]. According to the standards established in Russia, the PCB concentration in water bodies for drinking and domestic water use should not exceed 1000 ng/L, but the PCB concentrations are not allowed in the water bodies for fishery purposes [72]. According to the standards of the US Environmental Protection Agency [73], the PCB concentration in water less than 14 ng/L does not pose a danger to aquatic organisms and human health.

The level of PCBs in Baikal water was higher than in the water from the Antarctic and Arctic regions but comparable with or much lower than the concentrations of PCBs in waters of the continental lakes such as Como (Italy), the Caspian Sea (northern part, Russia), and Lake Baiyangdian (China) (Table 1). The use of fish to assess the pollution of different water bodies by PCB pollutants based on the level of their accumulation in fish was a rather difficult task due to the discrepancy between the characteristics of fish (age and the number of lipids) as well as to the methods used for the detection of PCBs (number of congeners).

We compared the accumulation level of Σ_7 PCBs in the muscle tissue of *C. migratorius* with the accumulation of Σ_7 PCBs in *S. trutta fario* inhabiting alpine lakes of Southern and Central Europe. The species *S. trutta fario* was the closest to *C. migratorius* in terms of taxonomic characters. Individuals corresponding in age and lipid content were taken for comparison. Comparable levels of Σ_7 PCBs in *C. migratorius* and *Salmo trutta* indicated the same concentration level of bioavailable PCBs in Baikal water and alpine lakes [30–33]. In the tissues of *Salmo trutta* from Lake Iseo and Lake Endine situated in the industrial regions of Northern Italy [22], the Σ_7 PCB value was three to seven times higher than in *C. migratorius*: 2600, 1100, and 330 ng/g (lw), respectively.

Table 1. The concentrations of PCB congeners in the water from background sites and in the tissues of fish chosen as PCB bioindicators (ng/g, ww).

Area	Year	PCBs in the Water, ng/L	References
Arctic	2011	Σ_{13} PCBs 0.0013–0.021	[9]
Arctic Norway	1999	Σ_{12} PCBs 0.023–0.129	[74]
Canadian Archipelago	2018	Σ PCBs 0.65–46	[42]
Tropical Atlantic Ocean	2021	Σ PCBs 0.0041 ng/L	[12]
Antarctic, Victoria Land	2011–2012	Σ_{127} PCBs 0.046–0.143	[74]
European alpine lakes	2000–2001	Σ_7 PCBs 0.048–0.123	[75]
Himalayas	2007	Σ_5 PCBs 0.02–0.45	[76]
Lake Baikal, Russia	2015–2021	Σ_{24-34} PCBs 1.4–9.7 Σ_7 PCBs 0.30; 0.26–0.34	This study
Lake Como, Italy	2007	Σ_7 PCBs 0.30	[77]
Caspian Sea, Russia	2002	Σ_6 PCBs: 0.10–7.3	[78]
Lake Baiyangdian, China	2008	Σ_{39} PCBs 19–132	[79]

Table 1. Cont.

Area	Year	PCBs in the tissues of fish, ng/g ww	
Lake Baikal, Russia	2014–2020	<i>C. migratorius</i> , Σ_7 PCBs 5.6; 4.9–6.3	This study
Alpine lakes of Western Europe	2003–2004	<i>Salmo trutta</i> , Σ_7 PCBs 6.3–13	[30–33]
Southern Moravia, Czech Republic	2013	Carp, Σ_7 PCBs 2.4–14, Bream, Σ_7 PCBs 8.0–210 Pike perch, Σ_7 PCBs 2.4–4	[27]
Baltic Sea, Polish fishing area	2012	<i>Salmo salar</i> , Σ_6 PCBs 7.7–61 <i>Salmo trutta</i> , Σ_6 PCBs: 31–56 <i>Gadus morhua callaris</i> , Σ_6 PCBs: 0.07–2.8	[80]
Legally binding documents, EU	2019	Food products, muscle meat of fish, Σ_6 PCBs 75	[81]
Area	Year	PCBs in the tissues of fish, pg WHO-TEQ/g lw	
Lake Baikal, Russia	2014–2020	<i>C. migratorius</i> 0.03–0.06 <i>Salmo salar</i> , 1.0–7.4	This study
Baltic Sea, Polish fishing area	2003	<i>Salmo trutta</i> , 4.2–9.0 <i>Gadus morhua callaris</i> , 0.62–0.67	[80]
Legally binding documents, EU	2019	Food products, muscle meat of fish, 3.0	[81]

In the muscle tissues of *C. migratorius*, the total toxicity of four dl-congeners 118, 105, 123, and 156 did not exceed the WHO-TEQ₍₂₀₀₅₎ pg/g (ww) value of 0.06. The higher toxicity level of the detected dl-congeners, up to the WHO-TEQ₍₂₀₀₅₎ pg/g (ww) value of 4.7, was observed in the individuals of the older age group (eight years and older) due to the accumulation of congener 126. In the fish from the Baltic Sea, the total toxicity equivalent of dl-congeners was by two orders of magnitude higher than in *C. migratorius* (WHO-TEQ₍₁₉₉₇₎ pg/g (ww) from 0.64 to 6.0) [80].

3.4. Opportunities for Monitoring

The conventional monitoring of PCBs in surface waters with pollutant concentrations close to the background level suggests two stages. The first stage includes water sampling in different seasons, from different depths, and at different stations, taking into account the presence of potential pollution sources, and determining the PCB concentrations in the samples. The second stage includes analysis of the relationship between the detected concentrations of PCBs and sampling factors (year, season, station location, and depth of water layer). Based on the correlation analysis of the data, the congener(s) is (are) selected as indicators (indices) of the group with high positive correlations between the concentrations of congeners in the group. After that, during systematic monitoring, the concentrations of PCBs in a water body are estimated from the concentration of a congener selected as an indicator.

Biomonitoring provides detection of congeners in a water body, whose concentrations are below the LOQ level of the method used, in particular, dl-PCBs. A biological object chosen as a bioindicator must meet all the criteria that bioindicator objects should have [16]. Based on the correlation analysis of the data, a congener is also selected in the groups with high positive correlations between the concentrations of dl-PCBs characterised by higher concentrations and, hence, higher reliability and accuracy of detection. Thereafter, the current monitoring of dl-PCBs is possible for one (several) selected congener(s), a sharp increase in the concentration of which may trigger a more detailed analysis of the monitoring results.

4. Conclusions

The results of assessing concentrations of PCBs in the water of Lake Baikal obtained within the framework of conventional monitoring and biomonitoring confirmed the background level of PCB concentrations. The average concentration and statistically significant

range of the detected Σ_7 PCB concentrations in Baikal water were 0.30 and 0.26–0.34 ng/L, respectively. This concentration level was higher than in the waters from the Arctic and Antarctic areas but is comparable with or much lower than the PCB concentrations in the waters of continental lakes. Biomonitoring of PCBs using *C. migratorius* as a bioindicator in the lake water revealed five dl-congeners that were present in the water below LOQ of the method used. The most toxic congener 126 (the toxicity equivalence factor, TEF₂₀₀₅ is 0.1) was found in single individuals of the older age group. The total concentrations of dl-congeners in *C. migratorius* ranged from 1.3 to 1.7 ng/g (ww). The total toxicity equivalent of the detected dl-congeners (except for congener 126) was within the WHO-TEQ₍₂₀₀₅₎ pg/g (ww) range from 0.03 to 0.06. This level of dl-PCBs corresponded to their concentrations in fish inhabiting European alpine lakes but was much lower than in fish from the Baltic Sea.

In the course of choosing a system for monitoring PCBs in Baikal water, the preliminary stage of the study included water sampling at 21 stations (water surface area 31,700 km²). Based on the analysis of the monitoring results, five reference stations were selected for water sampling: 3, 6, 11, 16, and 19. The reduction in the number of stations did not distort the characteristics for the assessment of the PCB concentrations in the lake water. The control of PCBs in the surface water was possible by determining the concentrations of two of the seven indicator congeners, 52 and 101, because the concentrations of these congeners were highly correlated with each other, all indicator congeners, and Σ_7 PCBs. They also have the maximum level of concentrations in water samples, and homogenous peaks of PCBs were recorded in chromatograms. According to the data on the correlation analysis, the congeners identified in *C. migratorius* were divided into three groups, and we proposed indicator congeners for these groups: congener 101 (correlation group from congeners 118-dl, 153, and 180), 138 (correlation group of congeners 105-dl, 123-dl, and 156-dl) and 52 (correlation group of congeners 28, 114-dl, and 126-dl).

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app12042145/s1>, Table S1: Sampling stations, Table S2: Characteristics of the *C. migratorius* individuals caught in the course of biomonitoring, Table S3: Concentrations of indicator congeners in the water, ng/L, Table S4: Concentrations of indicator congeners in *C. migratorius*, ng/g (ww), Table S5: Concentrations of dl-congeners in *C. migratorius*, ng/g (ww), Table S6: Results of the analysis of the data from conventional monitoring by the PERMANOVA method, Table S7: Results of the analysis of the data from biomonitoring by the PERMANOVA method, Table S8: Relative error statistics for repeated measurements of PCB concentrations in water and *C. migratorius*, Table S9: Statistical parameters of the average values of PCB concentrations in water and *C. migratorius*.

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