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Monitoring of Polychlorinated Biphenyls in the Transboundary Ile River and Characteristics of Its Transformations Along the River's Discharge

Nariman Amirgaliev [1], Akhmetkal Medeu [2], Christian Opp [3,*], Azamat Madibekov [1,4,*], Laura Ismukhanova [1,4] and Askhat Zhadi [1,5]

[1] Laboratory of Hydrochemistry and Environmental Toxicology, JSC "Institute of Geography and Water Security", Almaty 050010, Kazakhstan; namirgaliev.n.a@ingeo.kz (N.A.); ismukhanova@ingeo.kz (L.I.); zhadi@ingeo.kz (A.Z.)
[2] JSC "Institute of Geography and Water Security", Almaty 050010, Kazakhstan; medeuar@gmail.com
[3] Faculty of Geography, Philipps-Universität Marburg, D-35032 Marburg, Germany
[4] Department of Meteorology and Hydrology, Faculty of Geography and Environmental Sciences, Al-Farabi Kazakh National University, Almaty 050040, Kazakhstan
[5] Department Water Resources and Reclamation, Faculty of Water Resources and Information Technology, Kazakh National Agrarian Research University, Almaty 050010, Kazakhstan
* Correspondence: opp@geo.uni-marburg.de (C.O.); madibekov@ingeo.kz (A.M.)

Abstract

This study presents the level of polychlorinated biphenyl (PCB) pollution in the transboundary Ile River in 2015, 2018, 2019, 2023, and 2024. PCB contamination of water, as well as the presence of a large number of individual congeners, including strictly controlled 'marker' and dioxin-like congeners, were detected along the entire length of the river within Kazakhstan. Water samples were analyzed using a Chromos GH-1000 gas chromatograph. Significant interannual variability of river water contamination and a noticeable decrease in 2023 and 2024 compared to the previous periods have been identified. The study examined the PCB concentration transformation in the Ile River, from the transboundary section to the river's confluence with Lake Balkhash, assessing not only fluctuations in total PCB concentration, but also their congener composition. The main natural and anthropogenic PCB sources and factors causing the transformation of the toxicant along the river course were identified. The total amount of transboundary PCB discharge both into Kazakhstan and into Lake Balkhash was calculated. The results can be used by state and local environmental protection agencies for the development of measures to protect rivers from pollution by these highly toxic pollutants, which is in line with the requirements of the Stockholm Convention on POPs.

Keywords: PCB monitoring; Ile River; transboundary inflow; toxicant transformation; Lake Balkhash inflow calculation

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1. Introduction

Polychlorinated biphenyls (PCBs) are synthetic chemical compounds that do not occur naturally in the environment. They remain stable in the environment. That is why PCBs belong to the persistent organic pollutants (POPs) [1]. Exposure to these chemical compounds can have a negative impact on health [1]. That is why POPs were banned by the Stockholm Convention in 2004 [2]. PCBs were widely used during the 20th century. PCBs are non-flammable, chemically stable, and electrically insulated. That is why these

chemical compounds were primarily used for cooling and insulation effects in industrial and consumer products, most commonly in transformers, capacitors, electronic equipment, motor oils, and various insulators [1]. Due to their longevity, PCBs can be found in the environment, although their production has declined in past decades [3]. PCB concentrations can be found in the air, rainwater, snow water and soil. From there they can enter the food chain. As a result of bioaccumulation, PCB levels in species at the top of the food chain can be quite higher than in species at the bottom of the food chain [1]. Due to their low vapor pressure, PCBs can accumulate in the hydrosphere and remain for many years in water organisms [4].

Water security in arid Kazakhstan is an important component of national security. All major rivers in Kazakhstan, including Yertis (Irtysh), Ile (Ili), Syrdarya (Syr Darya), and Zhayik (Ural) and others, are transboundary rivers, which do have a significant quantitative water resource limitation. A total of 48.5% or 44.3 km^3/year of the 91.3 km^3/year total surface water resources comes from neighboring countries, while runoff formed in Kazakhstan amounts to 47.0 km^3/year [5]. Moreover, due to a decrease in the transboundary runoff, a reduction in the discharge volume of transboundary rivers is expected in the long term [6]. In this regard, the resolution of water issues arising from the use of transboundary river resources is becoming an extremely important goal for Kazakhstan [6].

Challenges for Kazakhstan's transboundary rivers are becoming increasingly acute, not only in terms of maintaining an optimal volume of river discharge into the national water basins. Other challenges are the influx of various toxic compounds, the intrusion of alien aquatic organisms, including fish species, and the introduction of new fish diseases through transboundary rivers [7–9]. All of these influences and impacts are exacerbated by the fact that Kazakhstan occupies the downstream sections of all transboundary watercourses [10].

Considering the persistence of PCBs and their ability to accumulate in fish and other aquatic organisms, even low water concentrations can lead to significant burdens in biota, affecting fishery suitability and food safety. In the Kapshagay Reservoir, measured water concentrations in 2013–2014 were 0.077–7.40 (mean 1.626) and 0.144–7.80 (mean 1.601) μg/L. At the same time, substantially higher concentrations were observed in fish in 2014: pikeperch—muscle 411–999 μg/kg, liver 392–838 μg/kg; bream—muscle 1.38–3.23 μg/kg, liver up to 55.0 μg/kg; asp—muscle up to 23.3 μg/kg, liver up to 160 μg/kg [11,12]. For Lake Balkhash in 2013–2015, average PCB levels in muscle were in the order of 1–12 μg/kg (max. up to 24 μg/kg), and in the liver 6–228 μg/kg (max. up to 1094 μg/kg). These results confirm the significance of bioaccumulation in the regional ichthyofauna [13]. Both "marker" and dioxin-like congeners (e.g., PCB-101, PCB-118) were identified in tissues, increasing toxicological concern. Accordingly, the assessment of water suitability for various uses (fishery, recreation, etc.) should be based not only on drinking-water standards, but also on evidence of PCB accumulation in the biota, and on the congener profile of contamination [11–13]. These observations for Lake Balkhash and the Kapshagay reservoir are consistent with current syntheses indicating that even at modest concentrations, PCBs accumulate in fish and other aquatic organisms [14]. PCB concentrations are associated with reproductive and endocrine disruption in animals and humans [15]. In freshwater ecosystems, PCBs cause sublethal effects in aquatic organisms—slowed growth and development, immune and endocrine alterations—with early life stages being particularly sensitive [16]. From a food-safety perspective, PCBs in fish products remain a relevant risk factor, necessitating the regular monitoring of congener profiles and measures to reduce contamination along the "water → fish → consumer" pathway [17]. In this context, analyses of the water phase and congener profiles in the Ili River basin are necessary to evaluate the suitability for fishery, recreational, and other water uses.

The anthropogenic pollution of the Kazakh water basins is also a result of domestic, industrial, and agricultural discharge [18]. In addition, atmospheric emissions from industrial and municipal enterprises are also significant contamination sources, affecting not only terrestrial areas but also water bodies [19]. This issue is particularly relevant for the Ile River.

Among the priority environmental pollutants in Kazakhstan, there are persistent organic pollutants (POPs), which do not occur in nature. They become distributed into the environment only by human activities. They require systematic analytical monitoring, because they are affecting Kazakhstan's water resources. Organochlorine pesticides such as dichlorodiphenyltrichroroethan (DDT), aldrin, hexachlorobenzene, and hexachlorocyclohexane (HCH), as well as polychlorinated biphenyls (PCBs), which are included in the list of POPs, are characterized by high toxicity to living organisms even at extremely low concentrations in natural environments [20].

Such xenobiotics are characterized by high resistance to physical, chemical, and biological factors [21]. They can be distributed through air, water, and migratory species. They have a strong tendency for bioaccumulation in living organisms. And they can actively migrate through food chains [22]. Unlike poisons that target specific organs, these toxicants disrupt internal regulatory systems, impair reproductive function, and negatively affect the endocrine and immune systems of humans. For these reasons, they are classified as endocrine disruptors [23,24].

Persistent organic pollutants (POPs) have been recognized by the international community as substances that pose a serious threat to human health and to the environment. In response, a global international agreement—the Stockholm Convention on POPs—was adopted in 2001 to protect human health and the environment [25]. The Convention entered into force in 2004, and Kazakhstan ratified it in 2007. Its objectives include the immediate cessation of POP production, the phase-out of their use by 2025, and the elimination of all related waste by no later than 2028 through environmentally sound methods.

Polychlorinated biphenyls (PCBs) are among the most toxic and globally widespread representatives of persistent organic pollutants (POPs). The protection of the natural environment and the population from the impacts of POPs, including PCBs, also remains one of the most pressing environmental challenges for Kazakhstan. In terms of POP waste reserves, Kazakhstan ranks second among the countries of Central and Eastern Europe, followed by Russia. According to preliminary inventory data from 2004, eight PCB-contaminated "hot spots" were identified in Kazakhstan, with a total area of approximately 2500 hectares. Additionally, PCB-containing equipment includes 116 transformers and around 50,000 capacitors, collectively holding an estimated amount of 980 tons of PCBs [26].

Under the framework of the Helsinki Commission (HELCOM) Convention for the protection of the Baltic Sea from pollution, three main criteria are used to assess the hazard of substances: persistence, toxicity, and bioaccumulation potential [27]. Based on these characteristics, priority groups of hazardous substances, which include dangerous organic compounds, such as POPs and other pollutants, were identified. Accordingly, hazardous xenobiotics, namely PCBs, fully meet all three of these criteria.

In Kazakhstan, a targeted monitoring of water bodies for the implementation of national obligations under the Stockholm Convention on POPs is virtually absent. Observations of these xenobiotics are not conducted by state organizations such as Kazhydromet, the Kazakhstan Hydro-Meteorological Survey, or other relevant agencies of the Republic of Kazakhstan. The "Environmental Safety Concept of the Republic of Kazakhstan for 2004–2015" states that there is no objective assessment of environmental pollution by POPs.

PCB contamination in the major transboundary rivers of Kazakhstan, including the Ile River, is influenced by transboundary runoff originating from the territories of neighboring

countries and associated pollution sources. The negative impact of these toxic compounds on the water quality of the Ile River has become chronic, with periodic intensification observed in certain years.

Taking into account all of the above mentioned POP features and the lack of knowledge of its occurrence in Kazakhstan, the main objectives of the present research were as follows: (1) the determination of the level of PCB contamination in the water resources of the Ile River, (2) the quantitative assessment of the volume of transboundary PCB discharge into Kazakhstan via the Ile River, and (3) the identification of the patterns of their transformation along the river course under the influence of natural and anthropogenic factors. The study is based on objective-related hypotheses that PCB concentrations in last year's water samples should be lower than in samples from the years before (1). However, due to the concentration of highly developed industry zones in the Chinese part of the Ile River catchment, higher PCB concentrations entering the Chinese–Kazakh border are expected, compared with concentrations in the Kazakh river section. PCB concentrations below the Kapshagay reservoir are expected to be quite lower than those in the part of the Ile River before entering the reservoir, because of the matter sink function of the reservoir (2, 3).

Such a systematic study of the quantitative and qualitative characteristics of chemical inflow, as well as the patterns of the anthropogenic transformation of the water quality, will provide new insights into the levels and impacts of both transboundary and national pollution on the aquatic environment of the Ile River. The scientific and methodological approaches of this study may serve as a basis for the development of similar research in other transboundary river basins of Kazakhstan.

2. Material and Methods

2.1. Study Area

The Ile River is the main transboundary artery feeding Lake Balkhash, accounting for up to 70% of all river inflow into the lake (Figure 1). It originates from the Muzart glaciers in the Central Tien Shan (Kazakhstan), with the Tekes River as its headstream. The total length of the Ile River is 1439 km, of which 815 km lie within Kazakhstan. The total catchment area of the Ile River basin is 140,000 km^2 (approximately 75% of the Lake Balkhash watershed), of which 7740 km^2 are located within the territory of the Republic of Kazakhstan. A substantial runoff-forming part of the Ile River basin is located in China, where the hydrographic network is well developed (ranging from 0.6 to 3 km/km^2). Approximately 30% of the Ile River's water resources are formed within Kazakhstan [5]. In the left bank part of the basin, in the middle reaches of the Ile River, it receives several mountain rivers—Charyn, Shelek, Turgen, Issyk, Talgar, and Kaskelen, with its tributaries the Malaya and Bolshaya Almatinka, as well as the Kurty—which generate runoff from the northern slopes of the Trans-Ile Alatau. Before discharging into the Kapshagay Reservoir, these rivers pass through the cities of Almaty, Kaskelen, Talgar, and Yesik, as well as other settlements, and are subject to significant pollution by various toxic compounds.

2.2. Timeline of Data Sampling

First data on PCB contamination levels in the Ile River were obtained during a comprehensive environmental survey conducted by our team in the river basin in 2015. A follow-up investigation was carried out in 2018 and 2019 as part of the laboratory's ongoing research projects. More detailed studies involving systematic monthly sampling of river water at all major hydrological monitoring stations—from the Chinese–Kazakh border cross-section to Lake Balkhash—were conducted in 2023 and 2024 (Figure 1). During the course of these studies, not only were the total PCB concentrations analyzed, but also the levels of individual congeners, which determine the overall toxicity of the water samples.

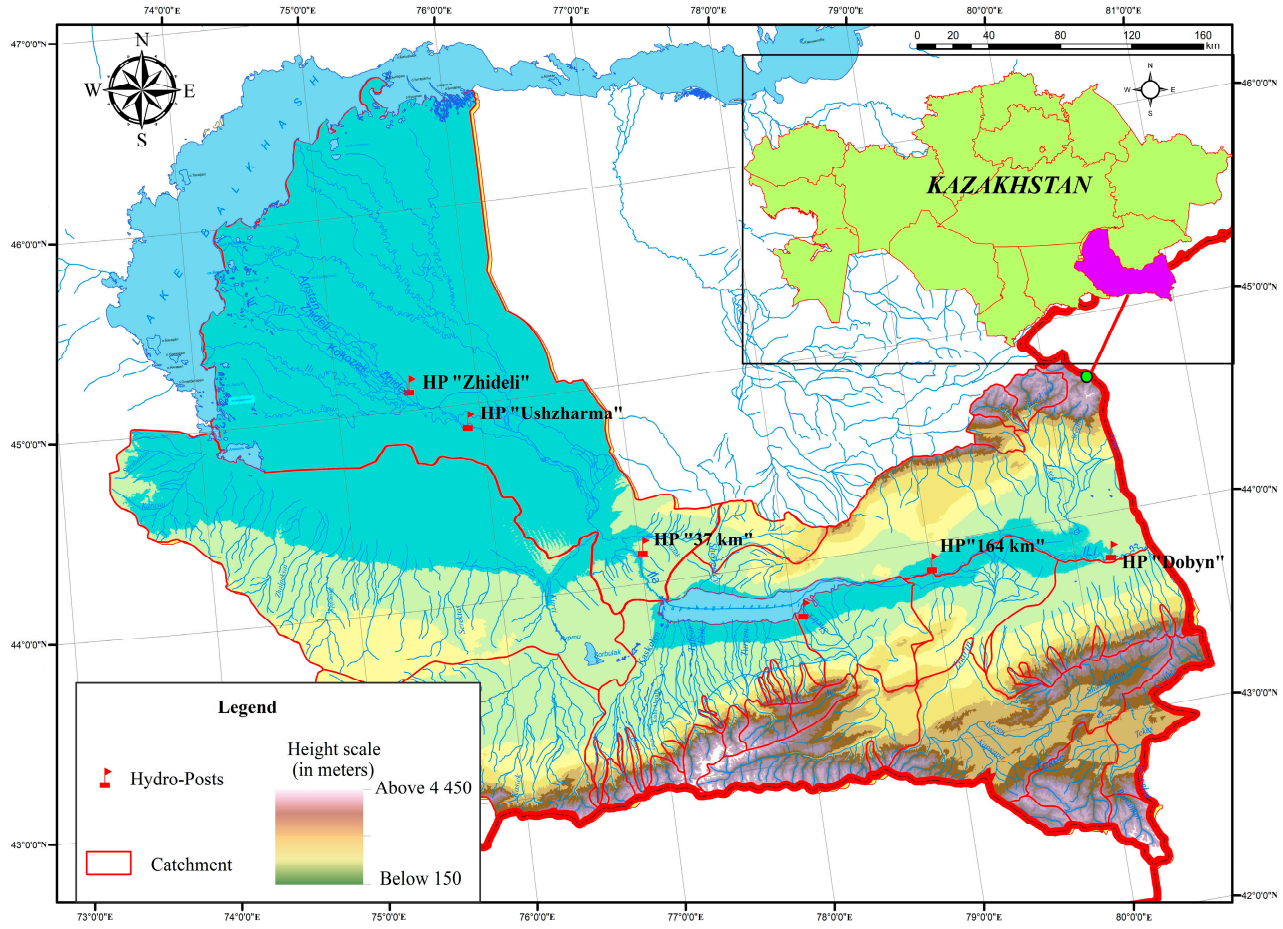


Figure 1. PCB sampling locations (Hydro-Posts HP 1 "Dobyn", HP 2 "164 km", HP 3 "37 km", HP 4 "Ushzharma", HP 5 "Zhideli"/mouth) along the Kazakh part of the Ile River basin.

2.3. Data Analyses

The gas chromatographic analysis of PCBs in water samples was performed in accordance with STB ISO 6468-2003 [28] using a "Chromos GH-1000" gas chromatograph equipped with an electron capture detector (ECD), specialized software (GCMS solution workstation software version 1.3), and a capillary column (30 m × 0.32 mm) (Manufacturer: LLC "Chromos" (JSC STC "Synteko"), Dzerzhinsk, Nizhny Novgorod Region, Russia). Chromatographic conditions were as follows: column temperature—220 °C, injector temperature—240 °C, detector temperature—300 °C, and carrier gas (high-purity nitrogen) flow rate—38 mL/min. As a standard, a certified reference solution of Sovol in hexane was used, representing a mixture of PCB-52, PCB-101, PCB-138, PCB-153, and the total of tetra-, penta-, and hexachlorinated biphenyls.

The method is based on the extraction of PCBs from water samples using an organic solvent (n-hexane), followed by concentration and purification of the extract to remove interfering compounds. Then, the purified extract was analyzed by gas chromatography with an electron capture detector (ECD). The mass concentrations of individual PCB congeners were determined using the external (absolute) calibration method [28].

The volumes of both transboundary discharge of PCBs and their discharge into Lake Balkhash via the Ile River were calculated using the direct method in accordance with the Guideline document (GD) 52.24.508 [29,30], according to the Formula (1)

$$G = \sum_{i=1}^{m} W_1 \cdot \overline{C}_1 \quad (1)$$

where

G—volume of transboundary PCB inflow, thousand tons;
m—number of intervals in the calculation period;
W_1—water discharge volume for the *i*-th interval of the calculation period, km^3;
$\overline{C}_1$—average concentration of PCBs for the *i*-th interval of the calculation period, μg/L.

3. Research Results and Discussion

First data on the dynamics of polychlorinated biphenyls (PCBs) in the water of the Ile River and its tributaries were obtained in 2015. The main results of the research have been discussed in publications [31]. According to the analytical data obtained in 2015, PCBs were detected in water samples from all sampling sites, with the highest concentrations observed in the Chinese–Kazakh transboundary inflow ("Dobyn" HP 1) of the river and at the Ushzharma Hydro-Post (HP 4) (Table 1).

Table 1. PCB concentrations and detected congeners in the Ile River water at five measuring points in 2015.

Parameter	"Dobyn" HP 1	"164 km" HP 2	"37 km" HP 3	"Ushzharma" HP 4	"Mouth" HP 5
Detected congeners	52; 66; 101	52; 66; 153	66; 118	52; 66; 101; 110; 153	52; 66; 70; 86; 101
Total PCBs, μg/L	0.666	0.308	0.170	0.678	0.465

From the border cross-section (HP 1) to the downstream section of the Kapshagay Dam ("37 km" HP 3), the concentration of PCBs in river water decreased to 0.170 μg/L. This is likely due to the continuous deposition of toxicants with suspended particulates, particularly within the Kapshagay Reservoir. This assumption is consistent with the findings of several international studies [32–36], which report that PCBs, owing to their low solubility and high specific gravity, primarily migrate with suspended matter that settles as water flow velocity decreases.

Further downstream, at the "Ushzharma" HP 4, the concentration of PCBs in river water increased nearly fourfold, reaching 0.678 μg/L. The most probable cause of this increase is the inflow of water from the Sorbulaq technical reservoir, which serves as a sewage storage facility for the city of Almaty.

Toward the river mouth, the concentration of PCBs decreased again, likely due to the sedimentation of suspended particles within the Balkash delta lake system, as well as the incorporation of suspended matter by phytoplankton. The important role of phytoplankton in facilitating the entry of PCBs into aquatic food chains has been noted in the literature [37–39].

Calculation results show that, for example, in May 2015, the total PCBs discharge into Lake Balkhash amounted to 0.68 tons and, undergoing no significant transformation, remained close to the transboundary input volume of 0.73 tons [40].

The congener composition of PCBs remained nearly unchanged along the river course from the "Dobyn" monitoring station (HP 1) to the downstream section of the Kapshagay Dam (HP 3). At the "Ushzharma" station (HP 4), located near the apex of the river delta, a slight increase in the number of congeners was observed, likely due to the inflow from the Sorbulaq wastewater reservoir; however, the qualitative composition remained largely unaffected.

A characteristic feature of the PCB congener profile in the river water was the consistent presence of the indicator ("marker") congeners PCB-52 and PCB-101 at nearly all sampling points, while PCB-153 was determined at two sampling points. These PCBs belong to the tetra-, penta-, and hexachlorinated biphenyl groups, respectively. Only at the downstream section of the Kapshagay dam (HP 3) was PCB-118 detected—a congener classified both as a marker and a dioxin-like PCB due to its high toxicity to living organisms.

Thus, the PCBs detected in the river water exhibited a relatively narrow congener profile. However, it was composed primarily of moderately toxic marker congeners, which are subject to strict monitoring in environmental matrices, for instance in Russia, and in many other countries. Kazakhstan should not be an exception.

The analysis of the relative abundance of individual PCB congeners in river water is of particular interest. As shown in Figure 2, the relative concentrations of marker congeners were notably high at nearly all monitoring sites.

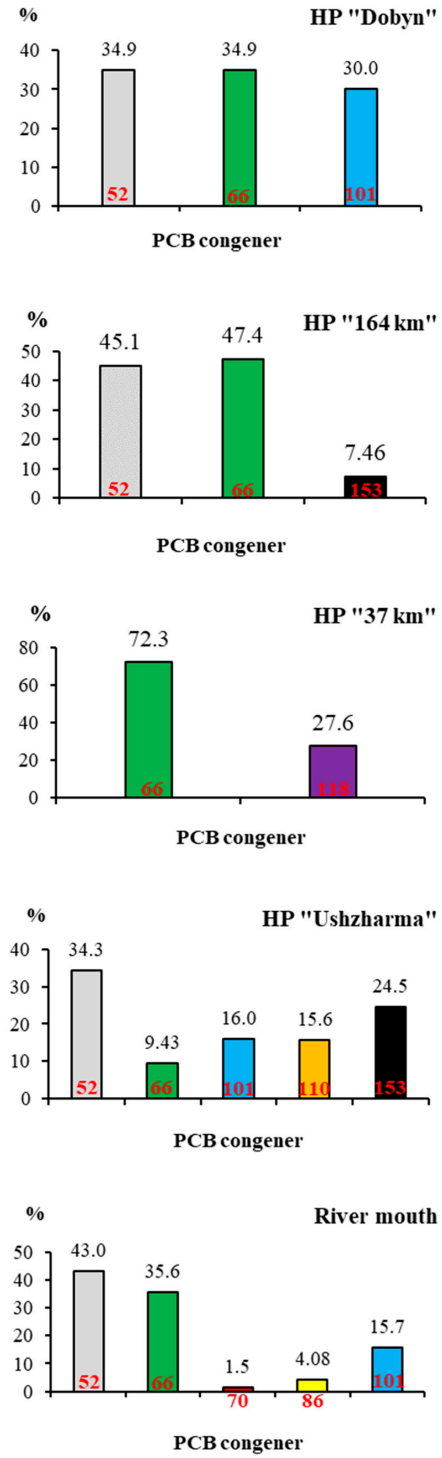


Figure 2. Relative abundance (in percent) of PCB congeners' occurrence in the Ile River water along five Hydro-Posts (HP) from HP 1 upstream to HP 5 downstream in 2015.

The marker congener PCB-52 accounted for 34% to 45% of the total detected congeners in water samples from four river cross-sections. The highest relative concentrations of this congener were recorded in the transboundary (HP 1) and delta (HP 5) zones of the river. When summing up the relative contents of the identified marker congeners, their combined proportion in the transboundary zone (at the "Dobyn" HP 1 station)—specifically PCB-52 and PCB-101—reached 65%. At the "164 km" (HP 2) station, the combined share of PCB-52 and PCB-153 was 52%, while at "Ushzharma" (HP 4), the sum of the same congeners amounted to 59%. Notably, the most toxic dioxin-like congener, PCB-118, showed a relatively high proportion (28% of the total PCB congeners) in the water sample from the downstream section of the Kapshagay dam (HP 3).

Based on the findings, it can be concluded that, even during the initial observation periods, the transboundary discharge and the water entering Lake Balkhash via the Ile River were already characterized by a relatively high level of PCB contamination. This can be justified by the presence of both marker and dioxin-like congeners. It is known that the maximum permissible concentration (MPC) for PCBs in drinking water is set at 1.0 μg/L [41]; therefore, the PCB levels in the river water did not exceed this threshold. However, the water did not meet the regulatory standards for fisheries water bodies, where the presence of PCBs is strictly prohibited [42].

In 2018 and 2019, water samples for PCB analysis were collected at four Kazhydromet monitoring stations, which represent characteristic sections of the Ile River within Kazakhstan, including the transboundary "Dobyn" cross-section. In 2018, PCBs were detected in the water at all monitoring sites, with concentrations ranging from 0.091 to 0.143 μg/L (Table 2).

Table 2. Changes in PCB concentration and congener composition in the Ile River water along the course of the river.

Hydro-Posts	Concentration of PCB Congeners (μg/L)				ΣPCB, μg/L
	44	49	74	155	
2018					
Dobyn				0.772	0.772
164 km upstream of HPP				0.143	0.143
37 km downstream of HPP	0.0129			0.0784	0.091
Ushzharma			0.0279	0.104	0.132
2019					
Dobyn			n.d.		n.d.
164 km upstream of HPP	0.220				0.220
37 km downstream of HPP	0.210				0.210
Ushzharma	0.057	0.44		0.049	0.546

Note: n.d.—not detected. HPP—hydropower plant.

The highest PCB concentrations were recorded in the transboundary discharge (HP 1), while further downstream PCB levels in river water decreased noticeably—particularly below the Kapshagay Hydropower Plant (HP 3). The decrease in PCB concentrations at this cross-section was attributed to the sedimentation of suspended particulates in the reservoir, where PCB levels were higher than in the water itself. A similar behavior of the toxicant was observed in 2015. Further downstream, at the apex of the river delta (at the "Ushzharma" HP 4 monitoring station), a slight increase in PCB concentration was observed. This can be explained by the discharge of wastewater from the Sorbulaq sewage storage facility of the city of Almaty, as well as by atmospheric deposition from major PCB

emission sources located along the northwestern shore of Lake Balkhash, as reported in other studies.

In 2019, PCBs were detected in water samples from three cross-sections located within the territory of the Republic of Kazakhstan, with concentrations ranging from 0.210 to 0.546 μg/L (Table 2). No PCBs were detected in the water at the transboundary ("Dobyn" HP 1) section. The decrease in PCB concentrations from the maximum levels observed in 2018 to their absence in 2019 was possibly related to the seasonal variability of the river discharge. The lack of stable sources of PCB-input can be another reason, which affects falling concentrations below the detection limit. The highest concentrations, as in 2015, were recorded at "Ushzharma" HP 4. The PCBs identified in river water were characterized by a narrow congener composition, predominantly comprising lighter congeners such as PCB-44, PCB-49, and PCB-74, which belong to the tetrachlorobiphenyl homolog group. The relative proportions of marker and dioxin-like congeners were 8% and 11%, respectively.

Thus, based on observations from the specified years, the accumulation of PCBs in the water of the transboundary Ile River has been a consistent feature, contributing to the contamination of the river water both in the People's Republic of China and in the Republic of Kazakhstan. The transformation of PCB flux within Kazakhstan occurs under the influence of various anthropogenic sources.

In 2023, the concentration of PCBs in the transboundary discharge of the Ile River ranged from 0.006 to 0.033 μg/L. A significant variation in concentrations was observed along the river's course, with the highest value (0.055 μg/L), recorded at HP 4 ("Ushzharma" village) in December 2023. In November, the concentration of the toxicant was somewhat lower (see Table 3).

Table 3. PCP analyses results from November and December 2023.

Sampling Location	Date	Detected PCB Congeners	Total PCBs
Ile River Border Hydrological Station			
Dobyn HP 1	02.11	44; 49; 52; 66/95; 70/76; 74; 82; 85; 86; 87/115; 97; 101; 105; 110; 114; 118; 128; 129; 137; 138; 141	0.006
	09.11		0.022
	01.12		0.030
	02.12		0.033
Ile River downward HP 1			
HP "164 km" HP 2	01.11	44; 48; 49; 52; 66,95; 70,76; 74; 82; 85; 86; 87,115; 97; 101; 105; 110; 114; 118; 119; 121; 128; 129; 137; 138; 141; 146; 151; 153; 155; 171	0.020
HP "37 km" HP 3	02.11		0.035
Ushzharma HP 4	03.11		0.019
Zhideli HP 5	03.11		0.036
HP "164 km" HP 2	03.12		0.038
HP "37 km" HP 3	11.12		0.032
Ushzharma HP 4	13.12		0.055
Zhideli HP 5	16.12		0.020

The water of the Ile River was characterized by a wide congener profile of PCBs. As shown in Table 3, 21 to 29 congeners were identified in the transboundary discharge and further downstream. Among the detected congeners in the river water at "Dobyn" HP 1, PCB-52, 66/95, 86, and 97 dominated, accounting for up to 60% of the total. Further downstream, PCB-44, 97, 118, 146, and 171 showed leading relative proportions of up to 63%, with PCB-52 alone reaching as high as 75%. Among all detected congeners, PCB-52 consistently exhibited the highest relative abundance, and in some cases the highest

absolute concentration. Such elevated levels of PCB-52—both in absolute and relative terms—had not been previously observed in the Balkhash-Ile basin over the course of our long-term monitoring.

One of the key aspects in the study of PCBs is the assessment of concentrations of "marker" and highly toxic dioxin-like PCB congeners in surface waters, because these compounds significantly increase the overall toxicity of aquatic systems. Therefore, they are subject to strict environmental monitoring in many countries [40,42–44].

According to the data presented in Table S1, four marker congeners and three dioxin-like congeners were identified in the river water. The concentration of marker congeners ranged from 0.002 to 0.006 μg/L, with a single exceedance of 0.008 μg/L, observed for PCB-52 in the Ile River, near the village of Ushzharma (HP 4). The relative abundance of marker congeners was generally within the range of 6–16%, except at the transboundary cross-section (HP 1) of the Ile River, where the relative proportion of PCB-52 reached 29% and 31%.

The concentration of dioxin-like PCB congeners in the river waters and the Kapshagay Reservoir varied within a narrow range of 0.002–0.004 μg/L, with their relative abundance ranging from 6% to 12%.

Thus, based on the analysis of data obtained in November and December 2023, it can be concluded that PCB contamination of the Ile River's water resources continued. A broad congener profile of PCBs was observed, including the presence of marker and dioxin-like congeners, which are strictly regulated in environmental legislation. In the Republic of Kazakhstan, a regulatory framework for the management of polychlorinated biphenyls (PCBs) has been established. The Environmental Code of the Republic of Kazakhstan (2021) and the "Rules for Handling Persistent Organic Pollutants and Waste Containing Them" (Order No. 717 from 24 November 2022, as amended on 10 October 2024), set procedures for inventory/record-keeping, storage, transport, disposal/destruction, and reporting on PCBs [45].

According to observations from 2024, PCB concentrations in the transboundary discharge of the Ile River ranged from 0.015 to 0.078 μg/L (Table 4). A significant variability in concentrations was observed throughout the monitoring period, with the maximum value (0.078 μg/L) recorded in February. Overall, PCB concentrations in the transboundary discharge (HP 1) remained within the same order of magnitude during the study period, although higher levels were noted during the winter months. The total PCB concentration dynamic in the transboundary discharge throughout the entire stationary monitoring period is illustrated in Figure 3.

The transboundary discharge of the Ile River was characterized by a broad congener composition of PCBs. A total of 36 PCB congeners: 40; 41,64,71; 42; 44; 48; 49; 52; 66,95; 70,76; 74; 82; 85; 86; 87,115; 97; 101; 105; 110; 114; 118; 119; 121; 128; 129; 137; 138; 141; 146; 151; 153; 171 were detected in water samples (Table 4). Among the identified congeners, PCB-97, 128, 153, and 171 predominated, comprising 52% of the total. The light congener PCB-44 was present in 63% of the analyzed samples. The highest relative abundance (89%) was recorded for the marker congener PCB-52.

According to the data presented in Table S2, four congeners from the group of "marker" PCBs and three congeners from the dioxin-like group were detected in the transboundary discharge of the river. The concentration of "marker" congeners ranged from 0.002 to 0.023 μg/L. Elevated concentrations of PCB congener 52 were observed in water samples during the winter months and in August. The relative content of the "marker" congeners ranged from 3% to 49%, with the highest values recorded for PCB 52.

Table 4. PCB concentrations and their congeners in the transboundary discharge of the Ile River at the border monitoring station (Dobyn village—HP 1) from 9 January 2024 to 20 January 2025.

Date	Total PCBs (μg/L)
9 January 2024	0.049
20 January 2024	0.051
30 January 2024	0.037
20 February 2024	0.078
26 February 2024	0.032
1 March 2024	0.044
9 March 2024	0.041
14 March 2024	0.026
20 March 2024	0.022
1 April 2024	0.021
9 April 2024	0.025
20 April 2024	0.036
1 May 2024	0.043
9 May 2024	0.025
20 May 2024	0.024
4 June 2024	0.025
9 June 2024	0.025
20 June 2024	0.022
1 July 2024	0.033
9 July 2024	0.030
20 July 2024	0.023
1 August 2024	0.037
9 August 2024	0.034
20 August 2024	0.045
1 September 2024	0.059
9 September 2024	0.015
11 September 2024	0.027
1 October 2024	0.045
9 October 2024	0.050
20 October 2024	0.026
1 November 2024	0.056
6 November 2024	0.023
22 December 2024	0.045
20 January 2025	0.033

Thus, based on the analysis presented above, it can be concluded that the pollution of the Ile River's water resources with PCBs, originating from the transboundary discharge entering the territory of the Republic of Kazakhstan, continues to be persistent. The data obtained for 2024 and 2023 reveal similar patterns. Given the wide congener composition of PCBs and the presence of strictly regulated "marker" and dioxin-like congeners in natural environments, it can be assumed that the transboundary discharge of the river exhibits an elevated level of PCB-related toxicity. It should be emphasized that although the absolute

concentrations of PCBs in the Ile River water do not exceed the sanitary threshold for drinking water (1.0 μg/L), the detected marker congeners (PCB-52, PCB-101, PCB-153) together with dioxin-like congeners (e.g., PCB-118) materially influence the toxic profile of the aquatic system.

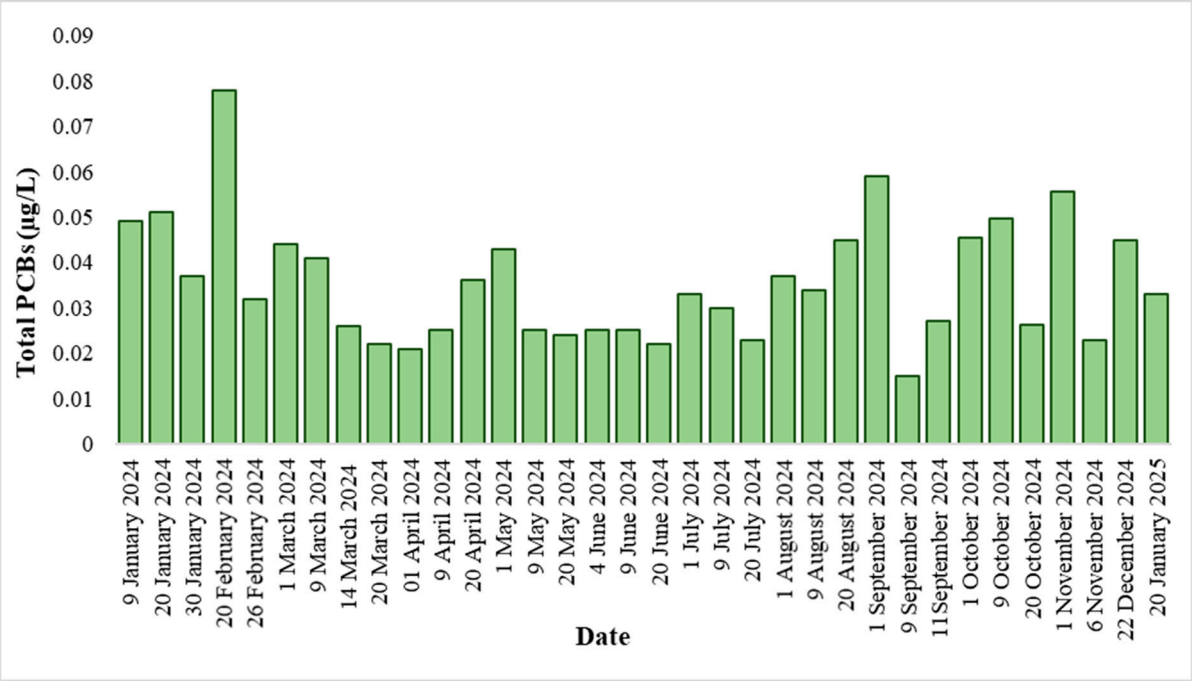


Figure 3. Total PCB concentration dynamic in the transboundary discharge at (Hydro-Post HP 1) of the Ile River in 2024.

According to recent syntheses, low-chlorinated markers (e.g., PCB-28 and PCB-52) prevail in the dissolved phase, exhibit relatively higher mobility and volatility, and therefore they are most sensitive to atmospheric and surface runoff inputs. These congeners respond more rapidly to seasonal variations in hydrological conditions and input sources. That is why they are useful indicators for the assessment of short-term anthropogenic impacts. In contrast, higher-chlorinated markers (PCB-101, PCB-138, PCB-153, and PCB-180) are strongly hydrophobic, less likely to occur in the dissolved phase, and predominantly accumulate in suspended particles and bottom sediments. Their contribution to the overall toxicological profile increases with higher water discharge and during re-suspension processes. Previously deposited congeners are reintroduced into the water column, reflecting their long-term persistence in the ecosystem. Dioxin-like PCBs (e.g., PCB-118) are characterized by high biological activity, although they account for only a small proportion of the total mass. They exert strong toxic effects that can disrupt biochemical processes in organisms, which makes them significantly hazardous even at trace concentrations and explains their role as key factors of ecological risk [15,16].

Therefore, even low aqueous concentrations of PCBs may pose serious ecological threats and impose restrictions on the fisheries' use of water bodies. This is due to their persistence, ability for bioaccumulation and biomagnification through food chains, and long-term retention in bottom sediments, from which they may be remobilized into the biotic cycle. These factors are consistent with strict regulatory requirements for the quality of fisheries waters and ongoing concerns regarding the food safety of fish products. Hence, ecological monitoring and risk assessment should take into account not only the total PCB concentration (ΣPCBs) but also the congener profile, which provides a more comprehensive evaluation of the toxicological potential of aquatic ecosystems [16,17].

The observed reduction in PCB concentrations in 2023–2024 is likely attributable to a combination of factors, including hydrological conditions (dilution effects under high-discharge regimes, seasonal snowmelt, and flood dynamics) as well as anthropogenic influences. In particular, environmental protection measures implemented in Kazakhstan and China, such as the gradual phase-out of PCB-containing equipment in accordance with the Stockholm Convention, may have contributed to the PCB concentration decline. The interplay of these factors may explain the observed trends towards reduced contamination levels in the transboundary discharge and within the Ile–Balkhash basin.

Policy and management actions in the basin's two countries provide additional context for the observed decline in PCB levels. In Kazakhstan, a UNDP/GEF initiative financed the replacement, dismantling and environmentally sound processing of approximately 900 t of PCB-containing transformers and capacitors, contributing to the reduction in PCB stocks and potential releases. National rules on the management of persistent organic pollutants (latest revision adopted in 2022) regulate the full life cycle of PCB-containing equipment, including inventory, decommissioning, storage, transport and disposal [46,47]. A recent official documentation from China reports comprehensive POP control measures and indicates that PCB-containing power equipment has been identified. It should be removed and disposed nationwide, according to the Convention's 2025/2028 schedules [48]. These management and regulatory developments, aligned with the Stockholm Convention's obligations, are consistent with the downward trend detected in our multi-year dataset.

The data presented above clearly demonstrate a pronounced interannual variability of PCB concentrations in river water over the ten-year observation period. As illustrated in figures and tables, the concentration of the pollutant along the entire course of the Ile River within the territory of Kazakhstan varied in 2015 from 0.170 to 0.678 μg/L. In 2018 and 2019, concentrations ranged from 0.091 to 0.143 and 0.210–0.546 μg/L, respectively. In 2023 and 2024, the concentration of the pollutant ranged from 0.006 to 0.055 and 0.015–0.078 μg/L, respectively, meaning that both the minimum and maximum PCB concentrations decreased approximately tenfold compared to 2015 levels. The pronounced interannual variability of PCB concentrations in the Ile River can be attributed, at least due to hydrological and climatic conditions. During years with higher discharge, dilution effects generally result in lower average PCB concentrations, whereas under low-discharge conditions, the toxicant tends to accumulate in the water column. Seasonal snowmelt and glacier runoff further enhance the transport of suspended particles, facilitating both the deposition and redistribution of PCBs along the river course. Moreover, climatic anomalies such as unusually warm winters or reduced precipitation in the catchment area may significantly alter the timing and magnitude of PCB fluxes.

Such a reduction in the concentration of toxic substances in river waters is a positive development. It creates favorable conditions for the economic use of water resources and for the life activity of aquatic biota. However, as noted above, the presence of these highly toxic compounds in the waters of fishery water bodies is unacceptable [42]. That is why of particular interest is the quantitative assessment of the transboundary discharge of toxic compounds from the territory of China as the essential input into the Kazakh part of the Ile River. Additionally, the toxic compound volume entering Lake Balkhash (Table 5) via the Ile River is of great importance, because Lake Balkhash is the terminal lake of the river basin. Therefore, it is a matter sink. And it is an important water body for fisheries. This is a crucial issue for the preservation of the ecological integrity of the unique Ile–Balkhash basin. The PCB discharge into the territory of Kazakhstan and its discharge into Lake Balkhash, presented in Table 5, was calculated based on data obtained in 2024, using a standard methodology [44]. The annual PCB discharge through the Dobyn HP 1 amounted to 0.40 tons/year, while the discharge into Lake Balkhash (HP 5) was 0.47 tons/year, i.e.,

these values are relatively close. These figures are significantly lower than those reported for 2015. This reduction reflects a substantial decrease in PCB concentrations in the river water in 2023 and 2024 compared to the earlier period.

Table 5. Volumes of transboundary discharge ("Dobyn" HP 1) of PCBs and their discharge into Lake Balkhash ("Zhideli" HP 5) for 2024.

Indicators	January	February	March	April	May	June	July	August	September	October	November	Average
Dobyn												
PCB concentration, μg/L	0.046	0.055	0.033	0.027	0.03	0.024	0.029	0.039	0.033	0.04	0.039	0.036
Water discharge, m^3/s	0.57	0.59	0.96	1.23	1.69	1.01	0.71	1.22	1.39	1.26	1.01	1.06
PCB load, t	0.026	0.032	0.032	0.033	0.051	0.024	0.021	0.047	0.046	0.05	0.039	0.036
Zhideli												
PCB concentration, μg/L	0.032	0.035	0.033	0.025	0.025	0.027	0.024	0.027	0.026	0.032	0.031	0.029
Water discharge, m^3/s	1.05	1.03	1.00	1.37	1.80	2.02	1.80	1.79	1.67	1.63	1.47	1.51
PCB load, t	0.034	0.036	0.033	0.034	0.045	0.055	0.043	0.048	0.043	0.052	0.046	0.043

As shown in Figures 4 and 5, the intra-annual dynamics of PCB discharge at both hydrological monitoring stations (HP 1 and HP 5) generally follow the variations in river water discharge. At the transboundary site, both water and PCB discharges fluctuate sharply throughout the year, with peak values observed in May and during the autumn period, while the lowest levels occur in winter and in July. At the Zhideli hydrological station (HP 5), the intra-annual pattern of PCB discharge also corresponds to the river water discharge, which exhibits more gradual changes over the year.

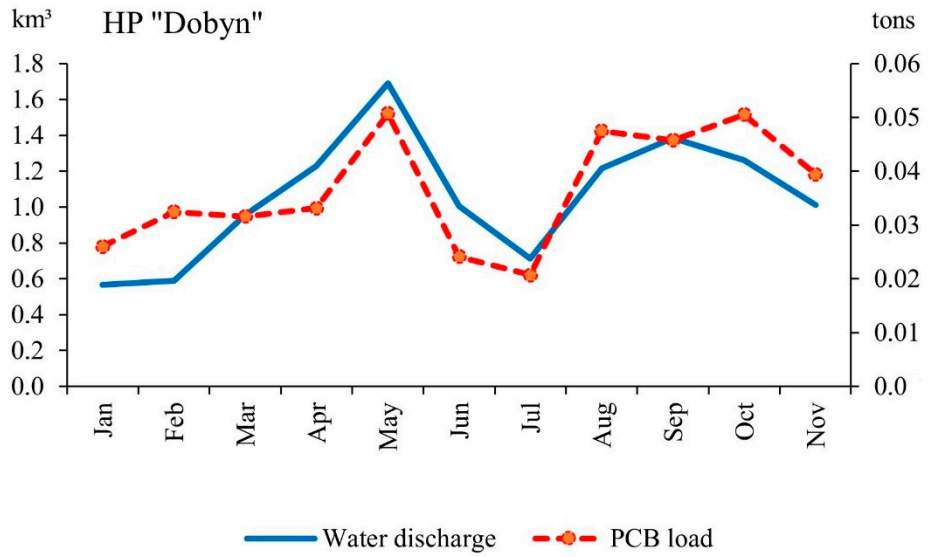


Figure 4. Intra-annual dynamics of water discharge and PCB load in 2024 at HP 1 "Dobyn".

The transformation pattern of PCBs in the water of the Ile River along its course within the territory of Kazakhstan is examined based on the analysis of chromatographic results of water samples collected in 2024 at the main hydrological monitoring stations along the river. As shown in Table 6, the total concentration of PCBs in river water ranged from 0.017 to 0.065 μg/L. Overall, the PCB levels at individual hydrological posts remained within the same order of magnitude. According to Table 6, a total of 31 PCB congeners: 40; 42; 44; 48; 49; 52; 66/95; 70/76; 74; 82; 85; 86; 87/115; 97; 101; 105; 110; 114; 118; 119; 121; 128; 129; 137; 138; 141; 146; 151; 153; 155; 171 were identified in the river water. Among the detected

congeners, a relatively high occurrence was observed for the "marker" congener PCB 52 (up to 79%), as well as for PCBs 138 and 153—33% and 38%, respectively. Additionally, congeners PCB 85 and PCB 171 were also frequently detected, with occurrence rates of 58% and 63%, respectively.

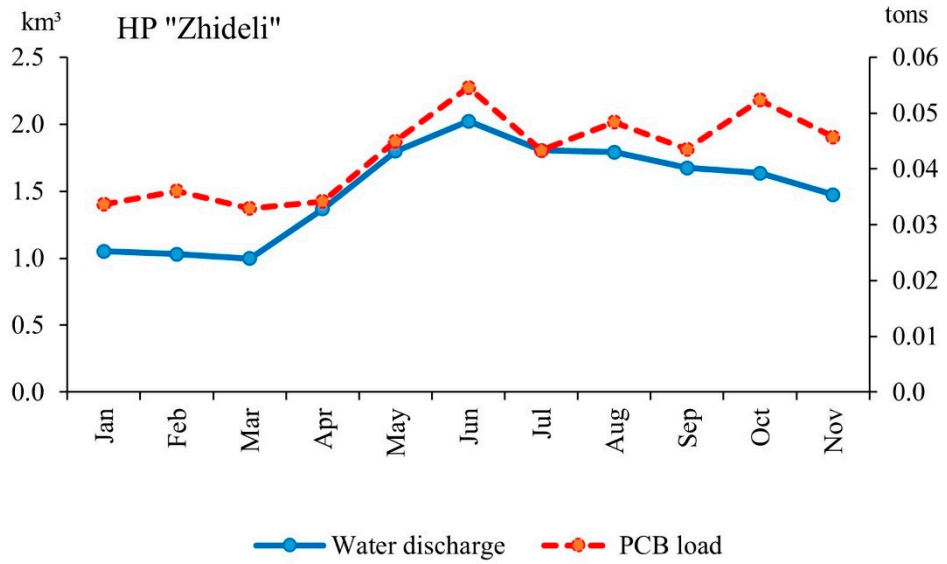


Figure 5. Intra-annual dynamics of water discharge and PCB load in 2024 at Hydro-Post HP 5 "Zhideli".

Table 6. General characteristics of PCB transformation at Hydro-Posts (HP) in the Ile River water along its course (see Figure 1) from January 2024 to January 2025.

Sampling Point	Date	Total PCBs (μg/L)
HP 3 "37 km"	31 January 2024	0.065
HP 4 Ushzharma	31 January 2024	0.040
HP 5 Zhideli	31 January 2024	0.032
HP 2 "164 km"	27 February 2024	0.040
HP 3 "37 km"	28 February 2024	0.024
HP 4 Ushzharma	28 February 2024	0.017
HP 5 Zhideli	28 February 2024	0.035
HP 2 "164 km"	14 March 2024	0.032
HP 3 "37 km"	15 March 2024	0.051
HP 4 Ushzharma	15 March 2024	0.021
HP 5 Zhideli	15 March 2024	0.033
HP 5 Zhideli	13 April 2024	0.025
HP 5 Zhideli	5 May 2024	0.025
HP 2 "164 km"	4 June 2024	0.032
HP 3 "37 km"	5 June 2024	0.023
HP 4Ushzharma	5 June 2024	0.021
HP 5 Zhideli	5 June 2024	0.027
HP 5 Zhideli	17 July 2024	0.024
HP 5 Zhideli	8 August 2024	0.027
HP 4 Ushzharma	11 September 2024	0.033

Table 6. *Cont.*

Sampling Point	Date	Total PCBs (μg/L)
HP 5 Zhideli	12 September 2024	0.026
HP 4 Ushzharma	12 September 2024	0.027
HP 5 Zhideli	14 September 2024	0.026
HP 5 Zhideli	13 October 2024	0.032
HP 3 "37 km"	7 November 2024	0.038
HP 2 "164 km"	7 November 2024	0.043
HP 4 Ushzharma	8 November 2024	0.032
HP 5 Zhideli	8 November 2024	0.032
HP 2 "164 km"	22 December 2024	0.032
HP 3 "37 km"	23 December 2024	0.034
HP 4 Ushzharma	23 December 2024	0.034
HP 2 "164 km"	21 January 2025	0.039
HP 3 "37 km"	22 January 2025	0.030
HP 4 Ushzharma	27 January 2025	0.045

More noticeable fluctuations in the total concentration of PCBs along the river were observed in the winter–spring period, while in summer and autumn the values of this indicator were fairly uniform. This result is in accordance with results from other transboundary rivers in Central Asia [49].

Based on more detailed observations conducted in 2024 regarding the transformation of the toxicant along the river, a slight increase in the total concentration of PCBs (up to 0.051 and 0.065 μg/L) can be noted in the water at HP 3 "37 km" below the Kapshagay dam. Similar dynamics of the toxicant were recorded in our studies in previous years. The main reason for these frequently observed phenomena is the pollution of the Kapshagay reservoir by the effluents of a number of small rivers flowing into it, which pass through cities and large settlements. Table S3 shows that the concentrations of dioxin-like and 'marker' congeners found are similar and characterized by values of the same order. The absolute content of 'marker' congeners ranged from 0.002 to 0.010 and 0.017 μg/L, and that of dioxin-like congeners ranged from 0.002 to 0.005 μg/L. Marker congeners were found more frequently in the analyzed water samples—from 4 to 39%, while the occurrence of dioxin-like congeners ranged from 5 to 16%.

The analysis of monthly data for 2024 at two stations (Dobyn—upstream, Zhideli—downstream) revealed both seasonal and spatial differences in PCB dynamics (Figure 6). At Dobyn HP 1, ΣPCB concentrations were higher, particularly in winter (up to 0.055 μg/L), which is explained by low discharge and limited dilution, while the loads remained relatively low (0.021–0.051 t). In contrast, at Zhideli HP 5 concentrations were lower, but due to substantially higher water discharge, this site accounted for higher PCB loads indicating its key role in the overall export of pollutants from the basin.

Seasonal boxplots demonstrate that Dobyn HP 1 is characterized by stronger variability, with maximum concentrations in winter and minimum values in summer, whereas Zhideli HP 5 shows smoother seasonal fluctuations with lower absolute levels. Thus, the graphical comparison highlights that the upstream station reflects local concentration peaks, while the downstream station represents the integral PCB export determined by the hydrological regime.

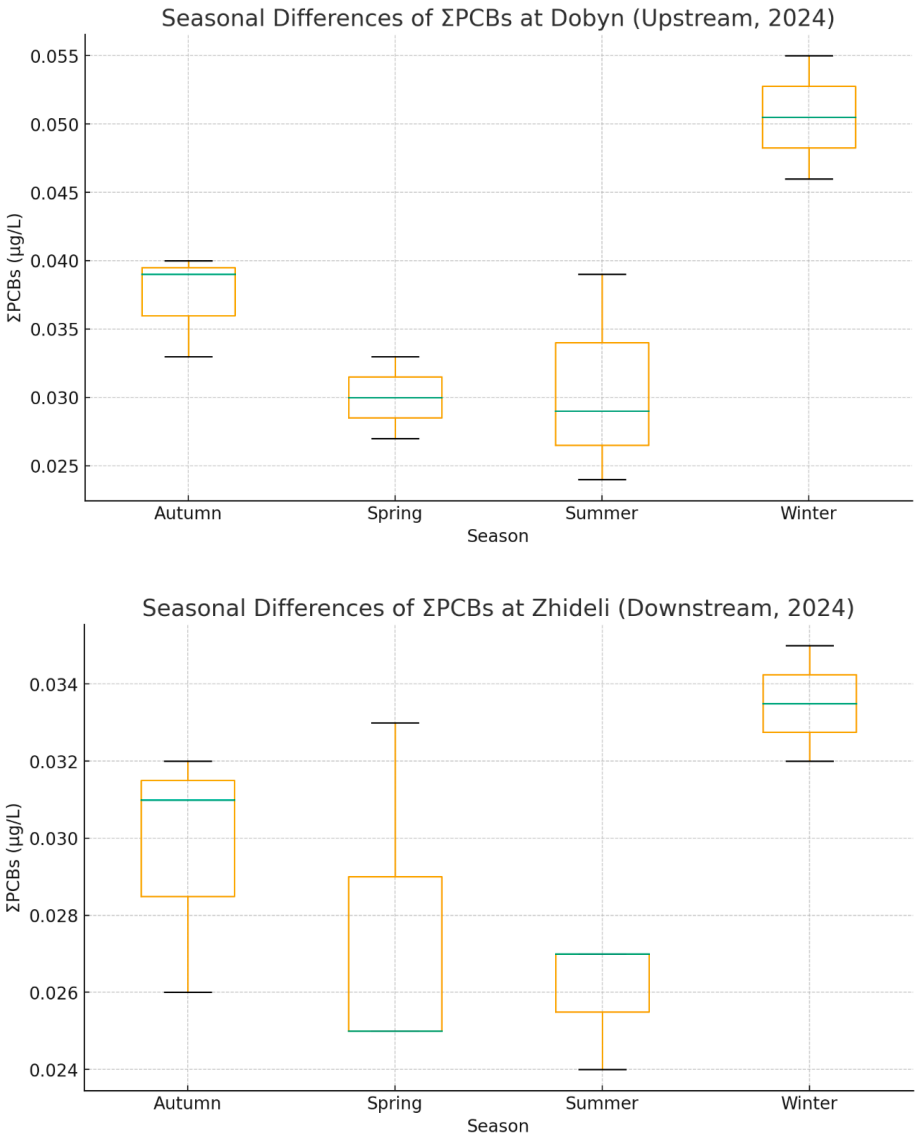


Figure 6. Seasonal variability of ΣPCB concentrations (n 45) in the Ili River at Dobyn HP 1 (upstream) and Zhideli HP 5 (downstream) in 2024.

A comparative data analysis for 2019–2025 shows that total PCBs (ΣPCBs) in surface waters of large rivers vary widely. For example, in the Syr Darya River, concentrations of 130–479 ng/L (2021) and 355–1080 ng/L (2022) were reported [50]. In the Yertysh (Kazakhstan part), levels were only up to 0.411 ng/L during 2020–2022 [51], reflecting a pronounced inter-basin contrast under broadly similar regional climatic conditions. Outside Central Asia, reported ranges are generally lower: for the Yangtze River (China) 0.04–11.0 ng/L in the water and 0.33–69.43 ng/g in the bottom sediments [52,53]; for the Volturno River 4.1–48 ng/L in the water and 4.3–64.3 ng/g in the sediments and for the Sele River 2.94–54.4 ng/L in the seawater and 5.01 to 79.3 ng/g sediment samples (both in Italy) [54,55]; and for the Indus River (Pakistan) 0.003–0.23 ng/L [56]. Against this background, the 2024 values for the Ile River (15–78 ng/L) occupy an intermediate position. They are several times lower than in the Syr Darya, but yet higher than in the Yertys and Indus. The value differences can be attributed to differences in the hydrologic regime (discharge, seasonality, snow melt). The burden of historically accumulated PCBs and the organic–carbon content of sediments could also be different. Value differences can also be an effect of the phase partitioning of congeners between dissolved and suspended fractions. The extent of environmental controls and the specifics of applied monitoring methodologies

can be different in different countries. In terms of congener composition, lower-chlorinated tri-/tetrachlorinated congeners dominate the dissolved phase and are sensitive to atmospheric and surface runoff inputs. Penta-/hexachlorinated congeners (including PCB-101, -118, -138, -153, -180) are predominantly associated with suspended matter. They undergo sorption–desorption dynamics. During high-discharge and resuspension events the particle-bound fraction increases, while during low discharge the contribution of dissolved, lower-chlorinated congeners becomes more pronounced [53,55,57].

The analysis of the long-term dynamics of PCBs in the water of the Ile River indicates that primary natural and anthropogenic factors driving the transformation of these toxic compounds along the river are as follows: the highest concentrations of PCBs are recorded in the transboundary discharge at the border control post HP 1. These values decrease significantly in the waters of the Kapshagay reservoir. This reduction is likely due to the continuous sedimentation of PCBs with suspended particulates. An important contributor to the increased PCB levels in the Kapshagay reservoir is the discharge of contaminated waters from a number of the Ile River's tributaries. In particular, the tributaries in the upper delta, such as the area near the Ushzharma HP 4, are affected by municipal wastewater discharges originating from the Sorbulak technical reservoir. The most significant source of pollution in the lower reaches of the Ile River is the atmospheric transport of PCBs [58], from former and active military installations, including the "Daryal-U" base and other Russian military testing sites. They remained from the Soviet period, as well as the still operating training grounds of the Russian Federation. They are located across a vast area of the northwestern Lake Balkhash region.

Although it was a big success to obtain PCB data for the Ile River from different years and different months, the results are limited to the concrete number and date of water sampling. The results are constrained by the specific number and time of water-sample collections: in the observations during several years, they were episodic, and in 2023 sampling occurred predominantly during late autumn and winter. Because of this uneven temporal coverage, it is not possible to sufficiently draw reliable conclusions about subsequent seasonal and multi-year trends in PCB concentrations. Another limitation is that analyses were conducted only for the water phase, without concurrent measurements of suspended particulate matter, bottom sediments, and biota, and without partitioning into dissolved versus particulate fractions or accounting for organic carbon. This limitation narrows the assessment of PCB phase distribution and precludes a full comparison of ecological risks. In addition, sampling and analysis did not include systematic recording of accompanying hydrological parameters (discharge, turbidity/suspended-sediment concentration, temperature, water level), and mass-load calculations were not performed; therefore, the effects of low-discharge, flood, and snowmelt conditions on PCB transport are evaluated qualitatively. A further important limitation is the absence of primary PCB data from the Chinese part of the Ile River catchment, which hampers a full transboundary interpretation of sources and pathways.

4. Conclusions

The material presented in this article provides more comprehensive information on the current level of PCB contamination in the water resources of the transboundary Ile River. Over the nearly decade-long study period, PCB pollution in the river continued. Given the wide range of detected PCB congeners, including both "marker" and dioxin-like congeners that are strictly monitored in natural environments, it can be assumed that the river waters exhibit an elevated level of toxicity associated with PCBs.

The data presented above clearly demonstrate a high degree of interannual variability in PCB concentrations in river water over the analyzed decade. These interannual changes

are closely linked to hydrological and climatic variability, which controls dilution during high-discharge years and concentration peaks under low-discharge conditions. As shown in the figures and tables, the concentration of the contaminant along the entire course of the Ile River within Kazakhstan ranged from 0.170 to 0.678 μg/L in 2015, from 0.091 to 0.143 μg/L in 2018, and from 0.210 to 0.546 μg/L in 2019. Comparable values were recorded in both 2019 and 2015. In contrast, during 2023 and 2024, the concentration of the pollutant ranged from 0.006 to 0.055 μg/L and 0.015–0.078 μg/L, respectively. This indicates that both the minimum and maximum PCB concentrations have decreased approximately tenfold compared to the levels observed in 2015.

In line with the decrease in PCB concentrations in river water observed in 2024, the volume of transboundary inflow of this pollutant into Lake Balkhash has also significantly declined compared to the values recorded in 2015. The transport of PCBs largely depends on the volume of river discharge and exhibits seasonal fluctuations.

The main natural and anthropogenic factors influencing the transformation of these toxic compounds along the river course include the sedimentation of PCB-containing suspended particles in the main water body of the Kapchagay reservoir, the discharge of polluted water from small tributaries into the dam-adjacent zone of the reservoir, the contamination of the upper delta channels of the Ile River by municipal wastewater, especially from the Sorbulak technical reservoir, and, importantly, the atmospheric transport of PCBs from former and active Russian military sites, located across a vast area of the northwestern Balkhash region.

The ongoing contamination of the Ile River basin also highlights the need for the Kazakh State Hydrometeorological Survey "Kazhydromet" to expand the list of toxic substances monitored in river waters, including polychlorinated biphenyls (PCBs).

Political agreements with the PR of China and scientific cooperation between Kazakhstan and China should be developed in a way that direct detections and comparisons of pollutants analyzed in transboundary river waters become possible.

A further scientific study should focus on the detection and identification of PCBs' and other pollutants' entranceways into the river, to extend the knowledge about the PCB entranceways along the river. This would be a prerequisite for prevention measures.

But already, the findings of this study may be used by governmental environmental protection agencies in developing practical measures aimed at preventing river pollution. They should also be used by specialists in the field of natural water quality assessment in advancing scientific research related to persistent organic pollutants (POPs), taking into account the Republic of Kazakhstan's obligations under the Stockholm Convention.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app152010872/s1.

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