

Article

Long-Term Dynamics of Persistent Organic Pollutants in Water Bodies of the Aral Sea–Syrdarya Basin

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Abstract: The huge decrease in water volume in the Aral Sea, which was caused predominately by enormous water withdrawals from the Aral Sea tributaries, has changed the former world's fourth-biggest inland lake into a new desert called Aralkum. Due to its long-term use in agriculture, persistent organic pollutants (POPs), including organochlorine pesticides (OCPs), and polychlorinated biphenyls (PCBs) play a special role in the pollution of the Aral Sea tributaries and in the Aral Sea itself. For the first time, POPs, OCPs, and PCBs were studied in the Large Aral Sea, Small Aral Sea, and the Syrdarya River. PCBs and OCPs in the collected water samples were analyzed using gas chromatography. The results of long-term and inter-annual analyses of POPs in water resources of the Kazakh part of the Aral Sea–Syrdarya Basin are presented. The analyses covered the Large and Small Aral Seas, the Syrdarya River, reservoirs, lakes of the river delta, and drainage water of the collectors from irrigation areas. The inflow to the Syrdarya River that came from the collector-drainage water was the main cause of water pollution. The pollution levels of toxic compounds, including the trends of temporal and spatial changes in pollutant concentrations, were analyzed and assessed. The latest studies from 2021 and 2022 show a decrease in pesticide concentrations by tens and hundreds of times.

Keywords: environmental crisis; transboundary flow; collector-drainage water; pesticides and polychlorinated biphenyls concentrations



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1. Introduction

The Aral Sea–Syrdarya Basin (ASSB) belongs to four Central Asian states: the Republics of Kyrgyzstan, Tajikistan, Uzbekistan, and Kazakhstan. The Kazakh part of the basin includes two administrative provinces: Turkestan and Kyzylorda, with a population of over 2.6 million people.

The main river in the basin is the Syrdarya River, which originates outside of Kazakhstan in the Fergana Valley at the confluence of the Naryn and Karadarya rivers in Kyrgyzstan. The total length of the Syrdarya River is 2219 km and the total catchment area is 462,000 km²; within the territory of Kazakhstan, these values are 1400 km and 2400 km², respectively [1]. The hydrographic network of the basin within Kazakhstan is shown in Figure 1 [2].

In the last more than 60 years, the global environmental crisis in the Aral Sea basin has deeply affected the population and the socio-economic and natural conditions of the vast Central Asian territory [3–5]. Therefore, for a reliable assessment of the long-term and modern dynamics of natural resources quality in this basin, it is necessary to specify

the main reasons and conditions that have led to a significant degradation of the natural conditions. This is briefly described below.

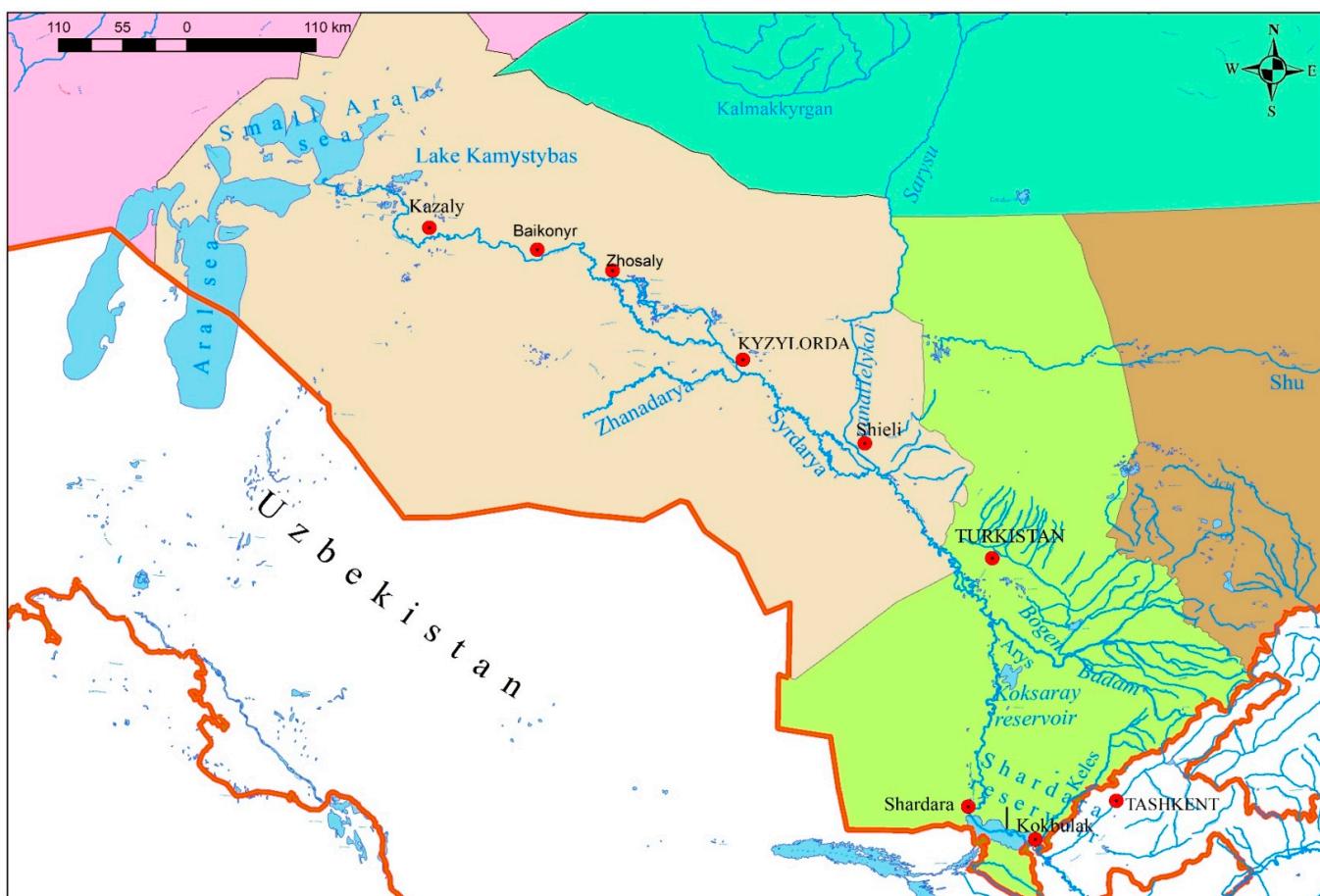


Figure 1. Hydrographic network of the (Small) Aral Sea–Syrdarya Basin on the territory of Kazakhstan (own draft).

1.1. Causes of the Ecological Crisis and Its Consequences

The Aral Sea is one of the largest inland water reservoirs. It is located in the desert zone of Central Asia, within the Turan Depression at the eastern edge of the Ust-Urt Plateau. The average annual lake level from 1911 to 1960 was 53 m above sea level (a.s.l.) of the Baltic System (BS) according to the data of instrumental observations. At this level, the lake area of the Aral Sea was about 68.3 thousand km²; the water volume was 1064 thousand km³ and the average depth was 16.1 m. The lake contained 11,000 islands, which gave the lake its name: “Aral” means “island” in the Kazakh language [6,7]. Another description of the term “Aral” or “island” is a translation from the Turkish language, which, in this case, means “a water island, surrounded by deserts”.

Based on the morphological structure of the Aral Sea basin, after the lake level had dropped dramatically, today, the Aral Sea is separated into two water bodies: a relatively isolated smaller northeastern part, namely, the Small Aral Sea, which has an area of 6000 km² at the level of 53 m a.s.l., with a water volume around 80 km³ (9.1 and 7.5% of the lake's former total area and volume, respectively), and the Large Aral Sea [8,9].

The lake's water and salt balances, hydrological and hydrochemical regime, biological productivity, and the existence of the Aral Sea itself as a geographic entity are determined by the tributaries of the two large Central Asian rivers: Amudarya and Syrdarya, and their catchments. The former total average annual runoff from these river basins was estimated at 112 km³ (75 km³ and 37 km³ for Amudarya and Syrdarya, respectively).

In the early 1960s, the Soviet Union decided to expand irrigation on a new scale in Central Asia and Kazakhstan in order to increase the production of cotton, food, employment, etc. According to Glazovsky N.F. [10], the area of irrigated land in the Aral Sea region was 9,354,000 hectares in 1987, i.e., it increased by 1.7 times compared with 1950 (5,421,000 hectares). Since the beginning of 1960, the area of irrigated land in the Syrdarya River basin has increased from 1,200,000 to 3,260,000 hectares, including the lower reaches of the river from 88,000 to 350,000 hectares [11].

The expansion of irrigated land area was accompanied by an increase in water use. In 1980, the total water consumption in the Aral Sea basin reached 120,690 million m^3 , and water withdrawal for irrigation purposes reached 106,790 million m^3 compared with 60,160 and 56,152 million m^3 in 1960, respectively. In particular, the volume of total water consumption from the Syrdarya River increased by 1.8 times during this period, and water withdrawals for irrigation purposes by 1.7 times, i.e., it reached 46,445 million m^3 versus 27,602 million m^3 in 1960 [12]. The water withdrawal from the Syrdarya River increased during the years of huge irrigation project development from 32 to 55 km^3 per year and in the lower reaches from 3.3 to 6.0 km^3 . This meant the water withdrawal exceeded 1.4 times the available water resources in this region due to the reuse of returned water [11]. More than 1500 irrigation canals, about 40 large- and medium-sized reservoirs, and more than 300 collectors with a total length of 83,000 km were built in the Syrdarya River basin. The length of the irrigation network in the basin exceeded 120,000 km [11,12].

Since 1961, as a result of the abovementioned circumstances, the river runoff to the Aral Sea has declined intensively, accompanied by a rapid drop in the lake level. During 1961–1970, the intensity of the lake level decline was about 0.21 m/year. In 1981–1986, there was no river discharge in some years, and the lake level decline was 0.89–1.09 m/year during some years [13].

At the end of 1987, the Aral Sea level had dropped by 13 m and reached a critical level of 40 m a.s.l., at which point, the Berg Strait connecting the Small and the Large Aral Sea basins dried up, resulting in the division of the Aral Sea into two water bodies [14–16]. At the end of 1989, the level of the Large Aral Sea had dropped to 38.6 m a.s.l. The long-term dynamics of the main characteristics of the Aral Sea are shown in Figure 2.

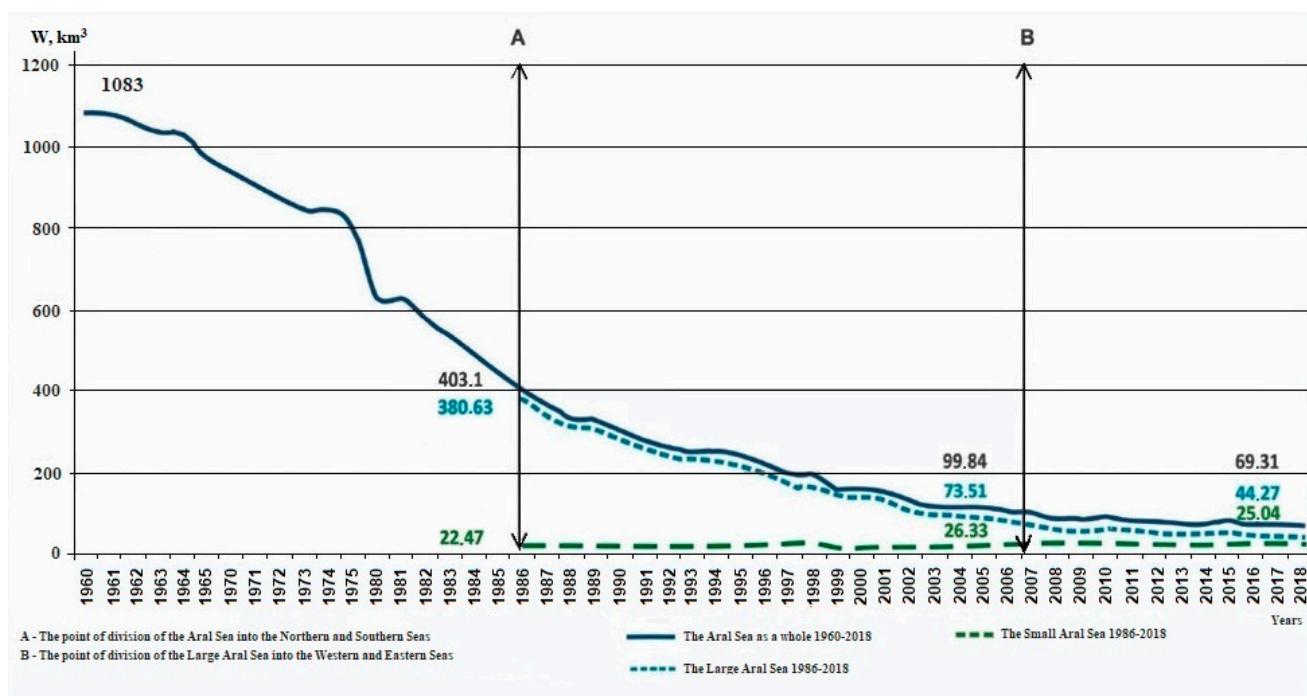


Figure 2. Water volume dynamics of the Aral Sea [17].

Thus, the unprecedented build-up of irrigated areas in the Aral Sea basin, the diversion of large volumes (one-third) of the water outside the basin through the Karakum Canal, and the almost complete regulation of river flow were the leading factors for the destabilization of the ecological conditions of the vast Aral Sea region [10,18–20].

Irrigated agriculture was the main consumer of river water destined for the Aral Sea, accounting for 95% of the water consumption in Central Asia. Over thirty years (1960–1990), about 750–800 km³ of water did not reach the Aral Sea, of which about 600 km³ was lost as a result of extensive irrigation [21].

The Aral Sea ecological crisis holds a special place among global disasters and is a consequence of the largest anthropogenic intervention in the natural environment. According to UN experts, the Aral Sea ecological crisis is one of the greatest disasters of the 20th century. That is why it is called Aral Sea syndrome [5,22].

Among the scale of degradation of all components of the natural environment of the Aral Sea region, deep changes in the aquatic environment of water bodies stand out as an independent problem. There is no analog in the world where these deep processes and changes took place in the aquatic ecosystem of such a huge lake.

The catastrophic drop in the water level of the Aral Sea and the intensive pollution of the entire Aral Sea region caused deep degradation of the natural environment and created environmental, social, and economic problems that are unprecedented in their acuteness and urgency. First of all, they include the death of commercial ichthyofauna and, therefore, the loss of fishery significance of the Aral Sea and other water bodies within the Aral Sea region. Other consequences were fundamental changes in economic activities, employment problems, and migration of the population [23].

It is known that annual catches in the Aral Sea in the late 1950s reached 43,000 tons, on average. During the period from 1930 to 1960, the annual fish catches reached 34,000 tons, and more than 80% of the catches were of valuable fish species: carp, barbel, zander, asp, roach, cherry salmon, and others. The deterioration of the water quality in reservoirs for household and drinking purposes caused a tense sanitary–epidemiological situation in the Aral Sea region, including the deterioration of public health, especially that of children. The decrease in irrigation water quality aggravated the processes of salinization of irrigated lands and reduced crop yields. In total, more than 4 million hectares of land have been degraded in the Aral Sea basin.

The level of the Large Aral Sea after its separation (in 1989) from the Small (Northern) Aral Sea is constantly decreasing. The process of its intensive salinization has been continuing; even this lake part is in a state of ecological disaster. The continuing lake level drop has led to the formation of residual reservoirs, i.e., to the partitioning of the lake water area into separate deep-water areas. The dynamics of changes in the Large Aral Sea in recent decades are shown in Figure 3 [24]. The presented images clearly show a dramatic picture of the Aral Sea water mirror area shrinking from the beginning of the crisis to the present day. This reduction has important consequences, both for the ecosystem and for the people living in the region. Overall, the shrinking of the Aral Sea remains a serious environmental problem and its solution requires concerted and long-term efforts at the global level. It also serves as a reminder of the importance of sustainable water management and environmental stewardship for future generations.

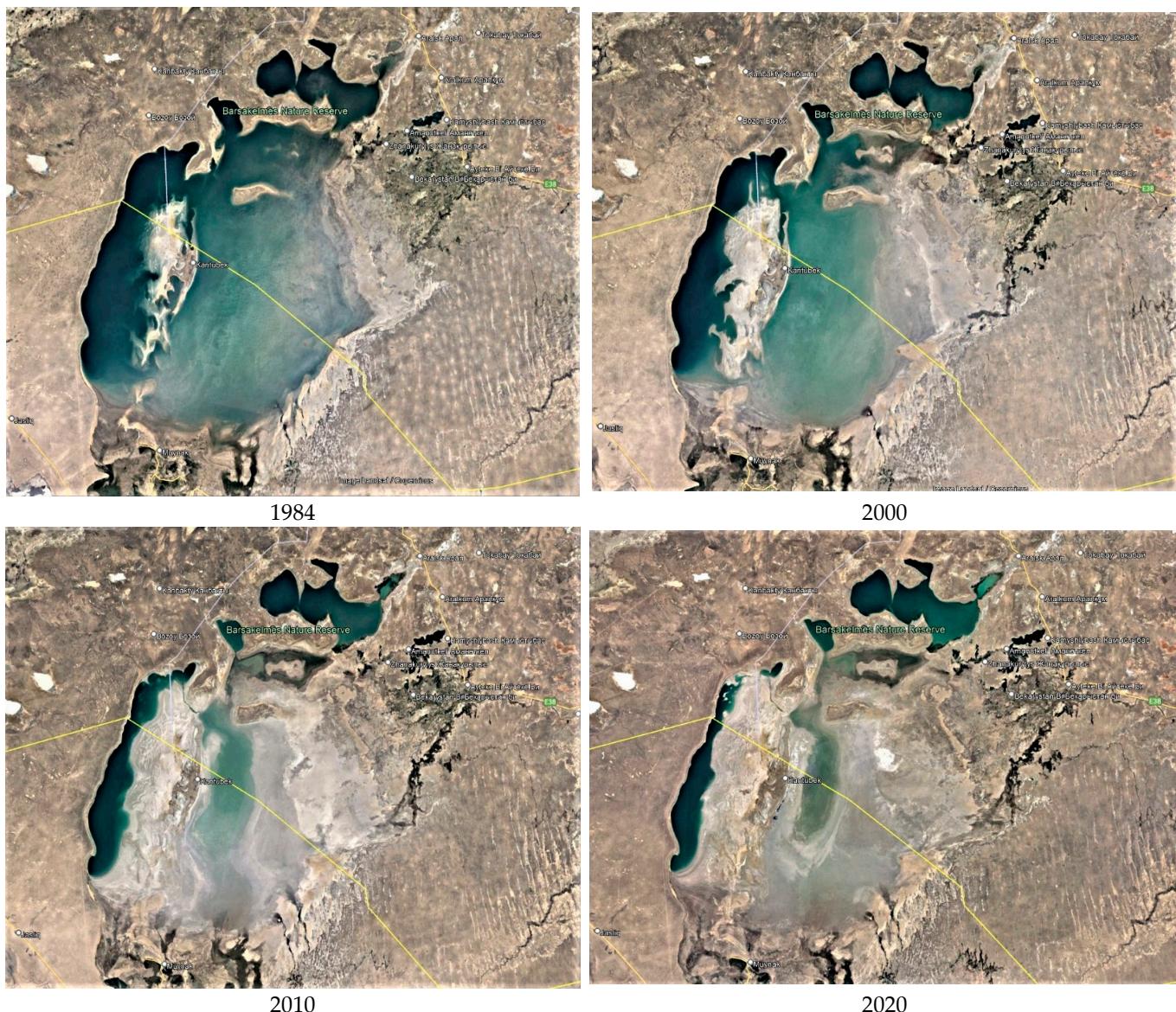


Figure 3. Aral Sea on satellite images (the period 1984–2020) [24]. <https://earth.google.com/web/@45.71179127,61.70799825,-2342.10771046a,1316012.72906139d,35y,0h,0t,0r/data=OgMKATA> (accessed on 6 October 2023).

It is known that water salinity is the most important indicator that limits the vital activity of water animals. During the period of the Aral Sea's conditionally natural regime (1951–1960), the average salinity of the lake was 10.08‰. In the early 1970s, the average salinity had already increased to 13–14‰. By the end of the 1970s, the water salinity had reached 15–16‰. In 1992, the average salinity of the lake water was 33.8‰ according to results based on 41 stations used in our own hydrochemical and toxicological studies of the Large Aral Sea, together with the Russian Oceanographic Institute. During our investigations in the Kazakh part of the water area in 1996, the lake's water salinity was found to be 42.1–84.3‰ [25–27]. According to Zholdassov I.M. et al. [28], the water salinity in the eastern part of the Large Aral Sea exceeded 100‰ in 2004.

The first powerful wave of loss of the hydrofauna composition of several invertebrates occurred in the early 1970s when the salinity reached 12–14‰ [29,30]. This barrier salinity separated the two main types of fauna: freshwater and saline. The next barrier salinity range came at around 24–28‰ [31] and 25–30‰ [32,33], and was the boundary of distribution for brackish species.

Most macrozoobenthos species had fallen by 1976 at salinity levels of 11.6–13.7‰ [34]. The reproduction of aboriginal ichthyofauna species inhabiting the Aral Sea had practically stopped at the salinity level of 15–16‰ by the end of the 1970s. In 1980, when the salinity exceeded 18‰, fishing in the lake ceased and it lost its fishery value [34].

1.2. Partly Successful Problem Management in the Kazakh Part of the Aral Sea Basin

The first step to save the Northern (Small) Aral Sea located in Kazakhstan was taken in 1992 when a temporary earthen dam was constructed in the Berg Strait. In August 2005, with the completion of the capital Kokaral dam, the Berg Strait was blocked at the level of the Small Aral Sea of about 39.0 m BS. The level of the Small Aral Sea was rising intensively as a result of large winter releases along the Syrdarya River, and it reached 42 m BS in April 2006. At this level, the Small Aral Sea had the following parameters: volume 27.07 km³, lake area 3288.0 km², maximum depth 12.5 m, and average depth 8.2 m [35]. As a result of a significant increase in the desalinized zone in the Small Aral Sea, the area of native commercial fish species expanded. The creation of this water body has played a positive role in the socio-economic development of this Kazakh part of the Aral Sea region.

As a consequence of the intensive development of irrigated agriculture and the construction of drainage systems in Central Asia, a rapid increase in the collector-drainage water (CDW) volume has taken place. According to the available data from Kipshakbaev N.K. and Getker M.I. et al. [35,36], the volume of return water in the Syrdarya River basin increased from 6.72 to 12.70 km³ per year from 1950 to 1970. The annual volume of return water in Central Asia between 1975 and 1990 was 33.1 km³, of which 13.1 km³ was in the Syrdarya River basin [37,38]. About two-thirds (or about 8.5 km³/year) of the drainage water is discharged into the Syrdarya River system annually. The Syrdarya River system carries the main mass of various pollutants and salts. Between 1960 and 1990, according to Kipshakbaev N.K. [39], the volume of CDW reached 13.5–15.5 km³/year in the Syrdarya River basin and 16.19 km³/year in the Amudarya River basin. As a rule, CDW contains increased concentrations of mineral salts, residues of nitrogen–phosphorus fertilizers, pesticides, and other toxic substances that significantly pollute the river water.

Thus, the formation of the hydrochemical regime and water quality indicators in the lower reaches of the Syrdarya River occurs under the influence of CDW and industrial, with domestic effluents entering the river network in the middle and lower reaches of the river. The most dangerous and widespread toxic compounds in the Aral Sea basin are pesticides, especially when widely used on irrigated lands in the years of maximum chemicalization of agriculture (1950–1990).

1.3. Water Pollution Problems

According to the available data from Glazovsky N.F. [10], more than 1,015,000 tons of pesticides were used in the Aral Sea region only from 1975 to 1990, with an annual average of 20–25 kg/ha. Back in the 1970s, 44,000 tons of organochlorine, 6000 tons of organophosphorus, and 15.4 tons of other pesticides were used in the Uzbek Socialist Soviet Republic. During 1970–1990, 118,000 tons of pesticides and herbicides were poured only on the land of Karakalpakstan (an autonomous territory within Uzbekistan), which amounted to 10 kg per capita per year. In Kazakhstan, 8500 and 7500 tones were used in 1990 and 1991, while in 1992 and 1993, 6300 and 5600 tones were used, respectively [39].

About 3% of the applied defoliants' mass, 2–3% of pesticides, and 10–15% of biogenic substances are removed with the drainage water in Central Asia [40]. These data show the enormous number of toxicants carried out annually from irrigated territories into the river network.

Persistent organic pollutants (POPs) are industrially produced chemicals. They are also formed as by-products of anthropogenic activities. POPs are highly toxic to living organisms at extremely low concentration levels. These xenobiotics are characterized by their high resistance to physical, chemical, and biological factors; global prevalence by air, water, and migrating species; high ability for accumulation in living organisms; and

active migration along trophic chains. At present, UNEP (United Nations Environmental Program) has included PCBs in the group of compounds that should be given priority attention in environmental research [41].

Polychlorinated biphenyls (PCBs) are biologically one of the most dangerous organochlorines. Polychlorinated biphenyls or polychlorinated biphenyls are a group of organic compounds comprising chlorinated biphenyl (diphenyl) derivatives, whose molecule is composed of two benzene rings containing from 1 to 10 chlorine atoms connected to any carbon atom, and corresponding to the general formula $C_{12}H_nCl_n$, where $n = 1 \div 10$ [42,43]. According to IUPAC (International Union of Pure and Applied Chemistry) recommendations, all of them are assigned numbers from 1 to 209 in ascending order of the degree of chlorination. PCBs are stable against external influences, have a high decomposition temperature and low reactivity and, as a consequence, are difficult to metabolize in natural environments. Hydrolysis and oxidation processes in water do not destroy PCBs. The only real chemical process that destroys PCBs is photolysis. The half-life of mono-, di-, tri-, and tetrachlorinated biphenyls in surface water (depth less than 0.6 m) in summer in bright sunlight is 17 to 210 days [44], but more highly chlorinated PCBs poorly absorb sunlight. The biodegradation of PCBs in water by aerobic and anaerobic microorganisms is very slow, starting with tetra- and pentachlorosubstituted biphenyls, they are almost not biodegradable. The solubility of PCBs in water depends on the number of chlorine atoms in the molecule and varies from 0.00076 mg/L (for dechlorobiphenyl) to 4 mg/L (for monochlorobiphenyl) [45]. Industrial mixtures of PCBs present in water therefore have a variable composition both in terms of the origin and as a result of changes that occur in the environment. According to various literature sources, values of background concentrations of PCBs vary from 0.5 ng/L to 20 ng/L [45,46]. For the analysis of such complex multicomponent mixtures as PCBs, a determination method is used based on several (from four to nine) individual PCBs. Their content is used to identify an industrial mixture of PCBs or the composition of these mixtures and to calculate the total PCB content. The determination method of the sum of PCBs by conversion of all individual PCBs with different content of chlorine atoms to dechlorobiphenyl is also known [46]. However, this method demands complex sample preparation via perchlorination and gives overestimated results due to possible chlorination to dechlorobiphenyl and other compounds, such as biphenyl, naphthalene, and terpenes. The dioxin-like PCBs 60, 77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167, and 189 are a special group. Due to their dioxin-like structure, they have increased biological activity and toxic (dioxin) equivalents have been established for them in relation to the most dangerous 2,3,7,8-tetrachlorodibenzo-p-dioxin [42,43].

POPs are recognized by the international community as substances of great danger to both human health and the environment. A global international agreement, namely, the Stockholm Convention on POPs, was adopted in 2001 to take measures to protect humans and the natural environment [47]. The Convention came into force in 2004 and Kazakhstan ratified it in 2007 [48]. The Convention sets goals to stop the production of POPs immediately, to stop using them by 2025, and to destroy all wastes no later than 2028 using environmentally safe methods [49]. The problem related to POPs is quite acute in Kazakhstan as well. During the Soviet period, no investigations were carried out to detect POPs in and around the Aral Sea basin. That is why our research on this problem in the Aral Sea basin started in 1991. Initially, in 1991 and 1992, the research was conducted mainly in the Large Aral Sea. Other water bodies and watercourses of the basin were studied in subsequent years. Taking into account the current ecological situation in the Aral Sea basin, our long-term studies were devoted to the problem of water pollution by persistent organic pollutants (POPs). The first objective of this study was the status quo analysis of the POPs, including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), belonging to the group of POPs in water bodies of the Aral Sea basin, namely, (1) in the Large Aral Sea, (2) in the Syrdarya River basin, and (3) in the Small Aral Sea, during different years. A second objective was to detect the dynamics of POPs pollution

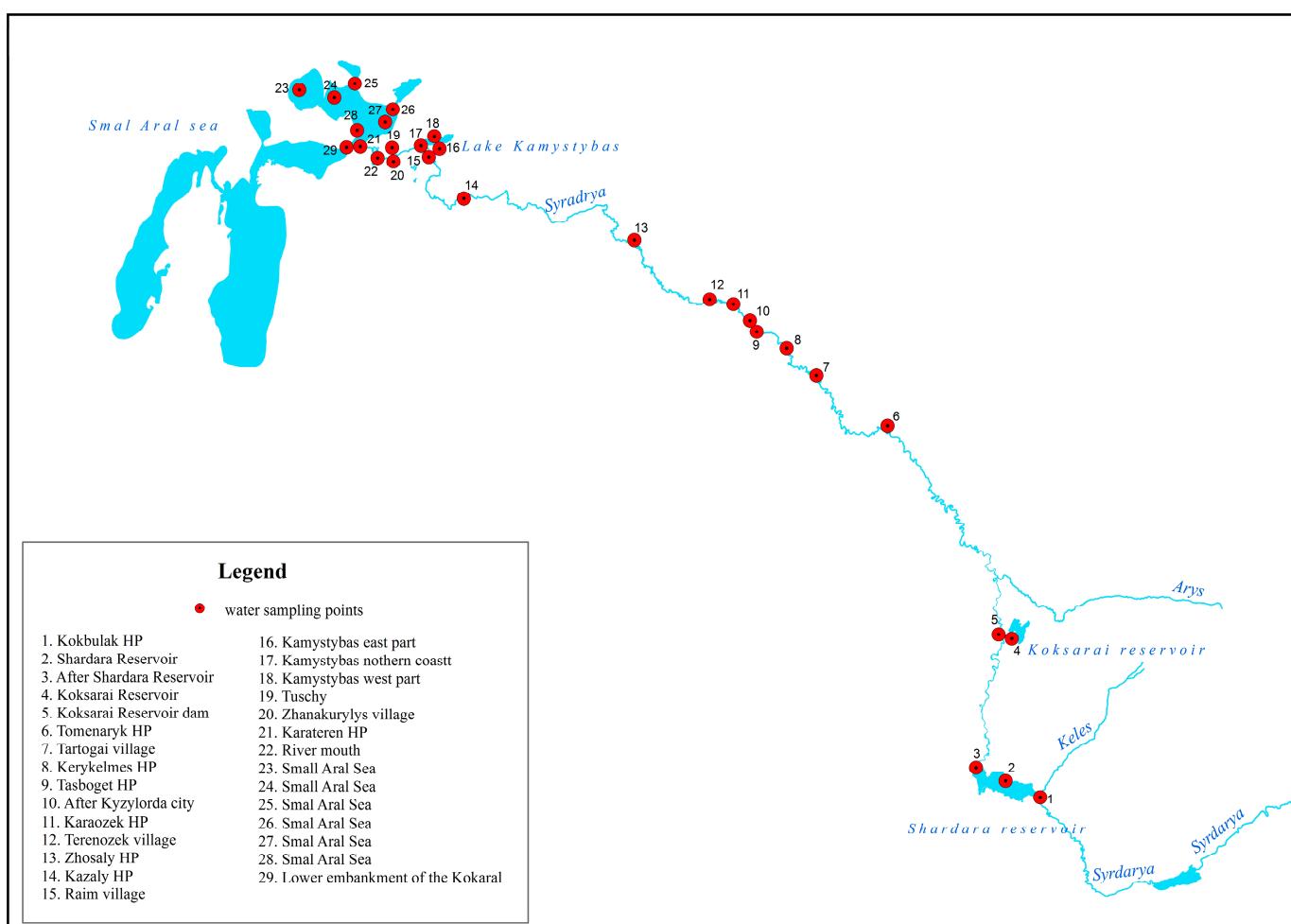
compared to the 1990s and the 2020s in these water bodies and to investigate the changes. A third objective was the presentation of these materials obtained over a multi-year period.

2. Materials and Methods

Water sampling was carried out according to generally accepted methods [50,51] in 2021 at 29 points and in 2022 at 22 points in the ASSB. The locations of the sampling points were chosen by considering the influence of natural and anthropogenic factors on the POP concentrations (Figure 4).

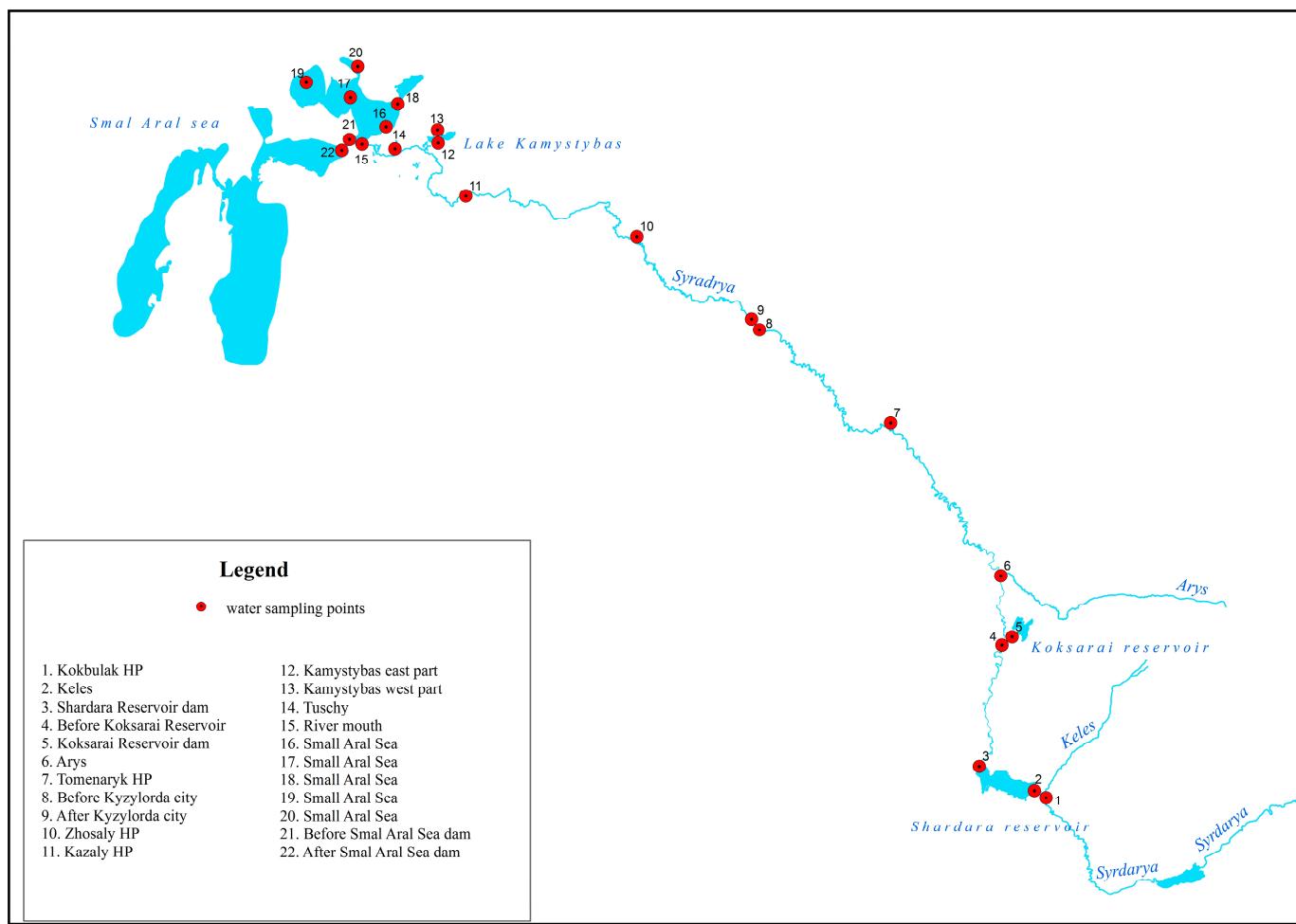
Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) were determined in each selected water sample. A total of 20–30 cm³ of extractant (n-Hexane) was added to 50 mL of water sample, corked and shaken for at least 20–30 min, then poured into a separating funnel and incubated until the phases separated. The aqueous (bottom) layer was poured back into the container. The extraction was repeated twice. After the extraction and separation, the extract was dried with anhydrous sodium sulfate.

The essence of this method is to extract pollutants from the sample of analyzed water using an organic solvent (n-Hexane), concentrate and purify the extract from concomitant compounds, and analyze the extract via gas chromatography using an electron capture detector (ECD), followed by determining the mass concentration of individual pollutants using the method of absolute calibration.



(a)

Figure 4. Cont.



(b)

Figure 4. Map of the water-sampling points: (a) 2021 and (b) 2022.

Gas chromatographic analysis was conducted in accordance with STB ISO 6468-2003 [52]. A concentrated sample extract of the analyzed water (1–2 mm³) was injected with a microsyringe and the chromatographic signal (peak area or peak height) was measured, and the retention time of the analytes was recorded from the obtained chromatogram. Chromatograms from the analyses performed are given in the Supplementary Materials.

The determination of PCBs and OCPs in the collected water samples was carried out according to STB ISO 6468-2003 [52] using a gas chromatograph “Chromos GC-1000” with software (GCMS solution workstation software Chromos. Program for controlling the chromatograph, collecting and processing chromatographic data. Version 2.22.31.) and an electron-capture detector (ECD) using a capillary column of 30 m × 0.32 mm length. The chromatographic conditions were as follows: column temperature 220 °C, evaporator temperature 240 °C, detector temperature 300 °C, and carrier gas flow rate (“Highly pure” nitrogen) 38 mL/min. As a standard, we used a GSO of Sovol solution in hexane, which is a mixture of PCB-52; PCB-101; PCB-138; PCB-153; and a sum of tetra-, penta-, and hexachlorobiphenyls.

For the separation of OCP and PCBs, different ratios of OCPs and PCBs to the sorbent (silicon dioxide) for phosphors were used, on which their separation was performed. The prepared extract was passed through a chromatographic glass column with a dropper filled with the sorbent. PCBs were eluted with petroleum ether of a certain volume (I fraction), and OCPs were eluted with a methylene chloride-hexane 4:1 mixture, also of a certain volume (II fraction). Each of these fractions was chromatographed on a GC-1000 gas

chromatograph, taking into account different chromatographic conditions for PCBs and OCPs, as well as the retention time of each congener.

Hydrometeorological observations and research work on the Aral Sea unfortunately took place discontinuously when the environmental crisis developed. In 1991 and 1992, we conducted studies of the Large Aral Sea. During the autumn expedition in 1991, water samples for pesticide determination were taken at 18 points of the Large Aral Sea. In 1992, during the most recent detailed study of the Large Aral Sea in the 20th century that was carried out jointly with the Russian Oceanographic Institute, samples were taken at 41 stations covering all characteristic points of its water area.

Along the Syrdarya River catchment, we determined the pollution of river water and reservoir water by organic substances in four river sections—namely, Kokbulak, Shardara, Kyzylorda, and Amanotkel, all of which are located in Kazakhstan starting during the Soviet period (1979–1989) by ourself—including the measurements taken by the Kazak Hydrometeorology Survey in 1992, 1993, 2004, and 2005. In 1993–2005, we carried out studies in the mouth of the Syrdarya River at its inflow into the Small Aral Sea. Some water bodies in the lower reaches of the Syrdarya River were examined in the winter of 2013. After a relatively long lack of investigations and information, our sampling campaigns in 2021 and 2022 allowed us to obtain information on the current level of POP contamination of the main current watercourses and water bodies of the Aral Sea basin within the territory of Kazakhstan.

Therefore, POPs in the water of the Small Aral Sea were studied from 1991 to 2006, as well as in 2021 and 2022. Chromatographic analysis was performed in the accredited testing laboratory Nutritest at the Kazakh Academy of Nutrition of the Republic of Kazakhstan (Accreditation certificate No. KZ.T.02.E0177 dated 5 June 2021).

3. Results and Discussion

3.1. Large Aral Sea

In 1991 and 1992, we conducted studies of the Large Aral Sea. Some results of the 1991 and 1992 studies are briefly described in several papers, e.g., [26,53–55].

In March 1991, the total pesticide content in water ranged from 0.01 to 1.46 $\mu\text{g}/\text{L}$. The analytical data obtained from the 1991 and 1992 expeditions and sampling are shown in Figure 5.

In autumn 1991, Hexachlorocyclohexane (HCCH) isomers were present in all samples (frequency of occurrence—100%), with concentrations from 0.001 to 0.440 $\mu\text{g}/\text{L}$. In 1992, the area of their spreading over the lake surface noticeably decreased (frequency of occurrence—65%), with average concentrations from 0.02 $\mu\text{g}/\text{L}$ to 0.09 $\mu\text{g}/\text{L}$. The average concentrations of DDT were 0.24 $\mu\text{g}/\text{L}$ in 1991 and 0.08 $\mu\text{g}/\text{L}$ in 1992. In 1992, the percentage of their occurrence also decreased. Organophosphorus pesticides and toxicants of other classes were found only in waters of some lake areas (occurrence 20–45%), with a generally low concentration. In 1992, PCBs were present in the water and their concentrations ranged from 0.1 to 26.0 $\mu\text{g}/\text{L}$ across the Aral Sea. No notable regularities in the PCBs distribution and accumulation levels in the Aral Sea water were detected.

The low pesticide contamination of the Aral Sea water was compared with other large fishery water bodies in Kazakhstan. This low contamination can be explained by the fact that river runoff that entered the lake previously reduced the pesticide concentration, and by the increased intensity of degradation processes of toxicants in water. A similar explanation of this issue is given in the work of Bortnik V.N. et al. [56] on the basis of data from the Russian Hydrometeorological Service network.

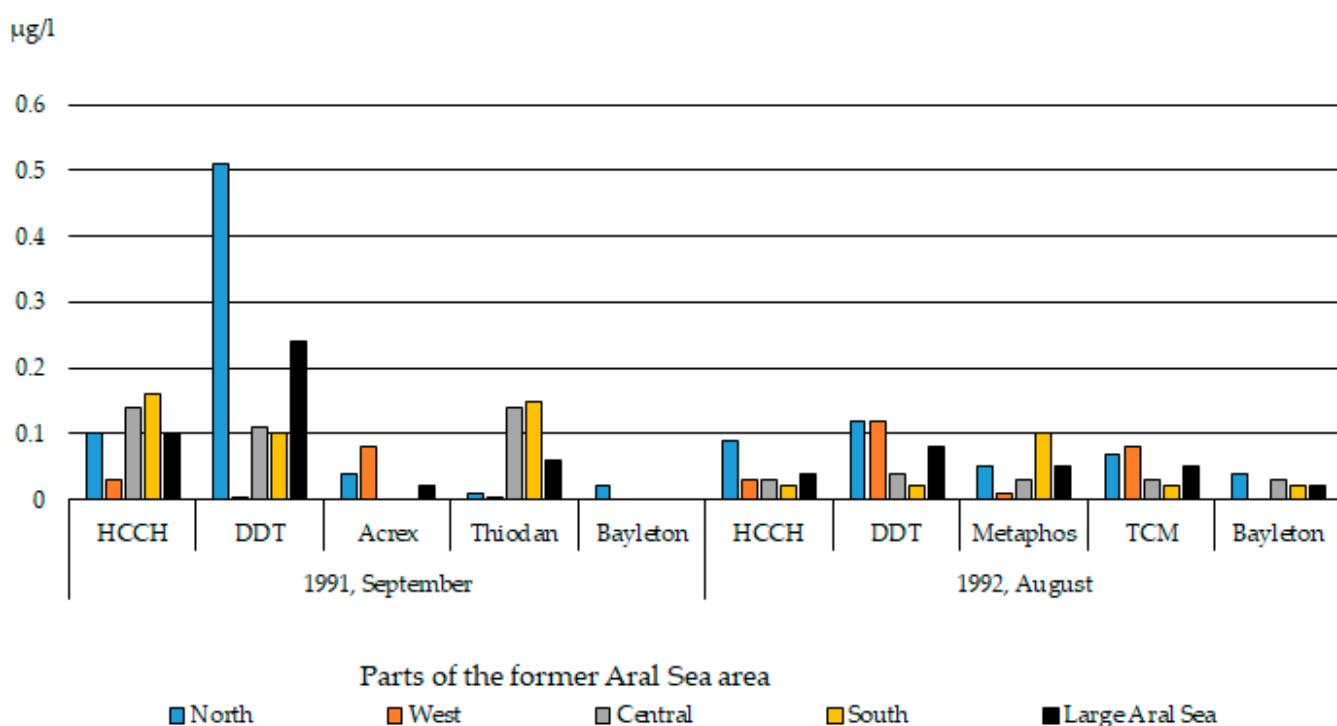


Figure 5. Average pesticide contents in parts of and the whole Large Aral Sea water in 1991 and 1992.

3.2. Syrdarya River Basin

The qualitative composition of water resources of the Syrdarya River depends on the flow formation zone and also on anthropogenic impacts. In the upper flow formation zone, within the territories of Tajikistan and Kyrgyzstan, the composition is predominately influenced by natural factors. In the lower flow zone of transition and dispersion, within Uzbekistan and Kazakhstan, it is mainly influenced by anthropogenic factors, such as river pollution by CDW and industrial effluents that contain various pesticides, metals, fertilizers, and mineral salts. Excessive deterioration of the natural water quality was one of the significant factors of the ecological crisis in the region.

The highest level of pesticide pollution in the Syrdarya River was observed in 1979–1988. The maximum contents of toxicants in $\mu\text{g}/\text{L}$ were as follows: the sum of HCCH isomers 3.575, DDT 13.386, DDE 1.096, and DDD 4.153. Among the organophosphorus pesticides (OPPs), the contents of metaphos and Rogor reached 3.579 and 176.25 $\mu\text{g}/\text{L}$, respectively [57].

According to annual surface water quality data from Kazhydromet [58], the contents of hexachlorocyclohexane (HCCH) and DDT were 0.376 $\mu\text{g}/\text{L}$ for 1986 and 0.397 $\mu\text{g}/\text{L}$ for 1987 in the Syrdarya River at the transboundary site of Kokbulak. This content was up to 0.860 $\mu\text{g}/\text{L}$ in the Shardara Reservoir, and downstream of this reservoir, it was 0.544–0.633 $\mu\text{g}/\text{L}$. DDT was registered in concentrations up to 0.546–1.225 $\mu\text{g}/\text{L}$. Maximum concentrations of DDT up to 1.939–4.906 $\mu\text{g}/\text{L}$ were recorded in the summer of 1985 near Kyzylorda, and the HCCH content was 0.824 $\mu\text{g}/\text{L}$. Downstream, near Kazaly, HCCH and DDT were detected in amounts up to 1.022 and 0.892 $\mu\text{g}/\text{L}$, respectively, i.e., a substantial increase in the content of organochlorine toxicants from the downstream river to its estuary zone occurred, which was the result of considerable pollution of the river within the Kazakhstan territory.

Therefore, the reviewed information of the Background State of the Environment [59] shows that the content of organochlorine pesticides in the water in 1980–1989 exceeded the background concentration for the Central Asian region by 1–2 orders of magnitude (DDT 1.6–48 $\mu\text{g}/\text{L}$, HCCH 0.5–84 $\mu\text{g}/\text{L}$) in the lower reaches of the Syrdarya and Amudarya.

HCCH and DDT are the main substances of pesticide pollution in the Shardara Reservoir water. The sums of the discovered pesticides of different classes were 0.007–10.2 $\mu\text{g}/\text{L}$ in 1992 and 0.28–3.94 $\mu\text{g}/\text{L}$ in 1993, with an average of 0.92 $\mu\text{g}/\text{L}$, i.e., in 1993, trends of

their concentration reduction were observed [60]. In the Syrdarya River water and the Shardara Reservoir, the PCBs were recorded in concentrations up to 2.0 $\mu\text{g}/\text{L}$ and 8.0 $\mu\text{g}/\text{L}$ in the spring and autumn of 1992, respectively, but in 1993, they were recorded only in a single sample with a concentration of 0.006 $\mu\text{g}/\text{L}$.

The analysis of intra-annual dynamics of organochlorine pesticides in river water near the Kokbulak boundary section revealed the dependence of these toxicants' concentrations on water discharge [61].

The pesticides inflow into the river network and their transformation within the water basin obviously depended not only on the water volume or discharge in a particular river basin. The dynamics of toxicant removal from irrigated massifs are caused by several factors, including the amounts of pesticides used in the basin; soils; orographic, hydrogeological, and drainage conditions of irrigated massifs and river valley sections, including the hydromorphological features; temperature regime; and precipitation in some seasons.

Our analysis of Kazhydromet data for several years on four river sections located in Kazakhstan, namely, Kokbulak, Shardara, Kyzylorda, and Amanotkel, established two peaks in the intra-annual regime of pesticide concentrations in the river water. The first one was in September–November, which was caused by the intensive inflow of CDW to the river network from irrigated areas. The second one was in early spring (March, April, rarely a slight rise in May), which occurred as a result of pesticide washout from the surface of the catchment area and irrigated lands during winter thaws and spring snowmelt. Autumn witnessed a rise in pesticide concentrations in the river mouth water 1 and 2 months later than in the upstream sections, which depended on the time of arrival of more contaminated water, the filling of the Shardara Reservoir, and the water discharge in the river [62].

In the spring and fall of 2004 and 2005, only organochlorine forms were found in the transboundary flow of the Syrdarya River out of the 17 pesticides of various classes that we determined. Out of them, metabolites of DDT were not detected, but isomers of HCCH were constantly present, in particular, their increased concentrations were registered in the spring of 2005.

The received data also followed the increased level of HCCH concentration, as well as the occurrence of DDT in rather high concentrations (up to 1.36–1.40 $\mu\text{g}/\text{L}$) in the water of the central and near-drainage parts of the Shardara Reservoir. Such phenomena, registered both in 2004 and in 2005, were obviously caused by the accumulation of these toxicants in the reservoir in autumn–winter and early spring periods during its filling due to releases from upstream reservoirs and CDW coming to the river network from irrigated areas. During these periods, a large number of suspended solids also accumulated in the reservoir, which was brought by the river from the adjacent territories during high winter and early spring water discharges. It is known that toxic compounds, such as metals and pesticides, are transported in considerably larger amounts with suspended and carried river loads in the adsorbed state [2,63].

The accumulation of these persistent organochlorine pesticides, both in the water column and in the bottom sediments of the reservoir, as a result of these processes is a constant source of pollution to the ecosystem of the reservoir and the river. Despite the fact that various pollutants accumulate in the reservoir itself, the downstream Syrdarya River is also contaminated by these toxic compounds under the influence of sources in the Kazakh part of the river, such as pesticides and heavy metal ions.

The obtained results for the mouth of the Syrdarya into the Small Aral Sea (Figure 6) indicate that HCCH isomers were present in the water of this section almost continuously in these years, except for 2000 and 2003. DDT metabolites were recorded inconstantly, and they were not detected in 2002–2005.

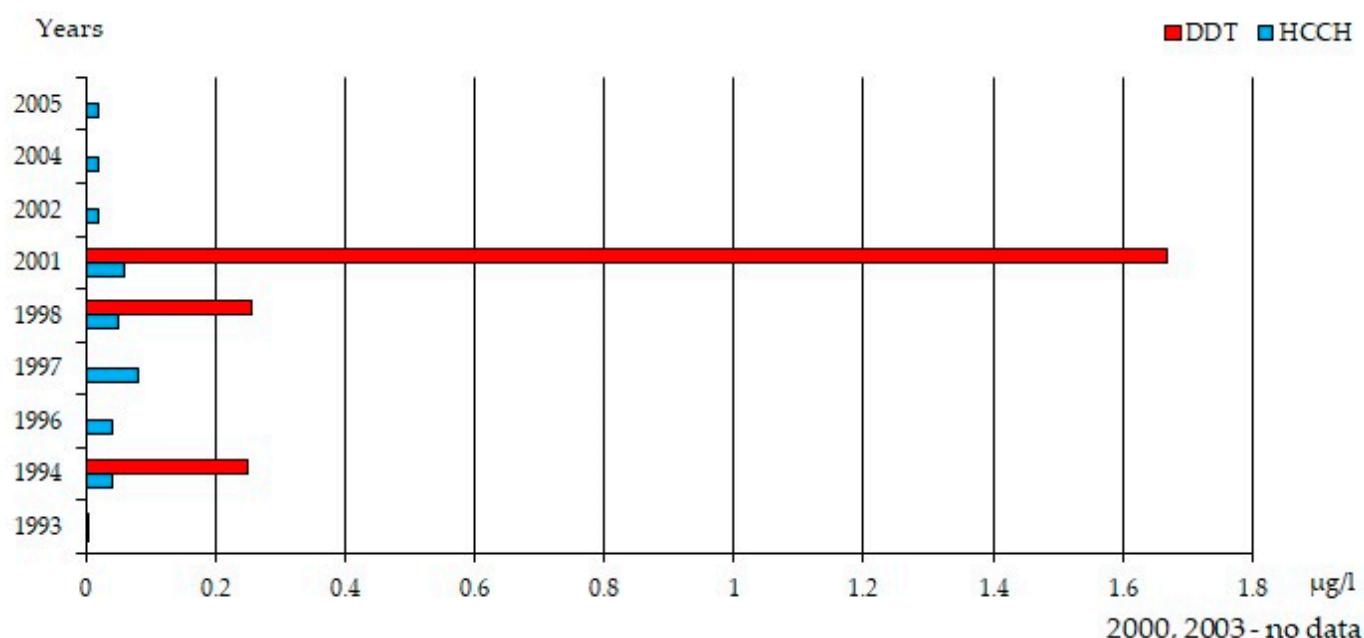


Figure 6. Pesticide content in the water of the Syrdarya River mouth.

The highest concentrations of pesticides in the river water of this section were found for HCCH isomers before 2001, and for DDT metabolites in 1994, 1998, and 2001, which was associated with their continued use in the Syrdarya River basin.

Thus, besides the transboundary inflow of pesticides, there were local sources of pesticide pollution of the river in Kazakhstan, as evidenced by the results of our studies along the entire river flow within the Kazakh Republic, long-term observations in the estuary zone, and available information from the literature.

The last 15 years have been characterized by the absence of reliable data on pesticide pollution of water bodies in this basin. Our studies conducted in 2021 and 2022 allowed us to obtain materials on the current level of POP contamination of the main current watercourses and water bodies of the ASSB within the territory of Kazakhstan (Figure 4). Taking into account the significant reduction in pesticide load on irrigated lands of Central Asian republics in recent decades because of a markable decreasing use of pesticides in agriculture, special attention in the given years was paid to the study of industrial pesticides, namely, PCBs, which are the most toxic compounds from the group of POPs. It is also known that in the basin of the Syrdarya River in the territories of the Central Asian states, several cities, industrial enterprises, and energy facilities serve as pollution sources.

Further, continuing the discussion of the organochlorine pesticides (OCPs) dynamics in the Syrdarya River water, we note first of all the presence of DDT and HCCH in all water samples taken in 2022. The analysis of other toxicants of the OCP group showed the presence of heptachlor and aldrin in water samples (Table 1).

The contents of registered pesticides in the water of all the water bodies we studied were generally low: DDT metabolites varied from 0.001 to 0.015 and 0.016 µg/L, with maximum concentrations found in the water of the Syrdarya River mouth. Increased concentrations of HCCH up to 0.002–0.003 µg/L were observed in the transboundary river flow near the cities of Kyzylorda and Kazaly. The content of aldrin varied within narrow limits of 0.001–0.002 µg/L; low concentrations of DDT and HCCH were also found in the waters of different small lakes within the catchment.

The comparison of the data in Table 1 with the long-term data given above clearly shows a decrease in pesticide concentrations in the water courses and water bodies of this basin by tens and hundreds of times. Apparently, this was primarily the result of the reduction in the volume of pesticide application on agricultural fields of the river basin in the Central Asian countries, including Kazakhstan. However, the fact that pesticides such

as DDT and HCCH, the use of which have been prohibited all over the world for a long time, are still used in the agricultural fields of the ASSB was also evident.

Table 1. Concentrations of organochlorine pesticides ($\mu\text{g/L}$) in the Syrdarya River water and its tributaries in 2022.

Sampling Site	DDT (Metabolites)	Heptachlor	Aldrine	HCCH (α , β , γ -Isomers)
Kokbulak HP	0.007	n/d	0.001	0.003
Tributary of the Keles River	0.006	0.001	0.002	0.002
Shardara Reservoir—dam	0.006	n/d	0.002	0.001
Before Koksarai Reservoir	0.003	0.001	0.001	0.001
Koksarai Reservoir—dam	0.003	n/d	n/d	0.001
Tributary of the Arys River	0.011	0.001	n/d	n/d
Tomenaryk HP	0.002	n/d	0.002	0.001
Before Kyzylorda city	0.007	n/d	0.001	0.001
After Kyzylorda city	0.004	n/d	0.001	0.002
Zhosaly HP	0.005	0.001	0.001	0.003
Kazaly HP	0.005	n/d	0.001	0.001
River mouth	0.015	n/d	0.001	0.001
Lakes in the Syrdarya delta				
Kamystybas—eastern part	0.001	n/d	n/d	0.002
Kamystybas—western part	0.006	n/d	0.001	0.002
Tuschy	0.007	n/d	0.001	0.001

Note: HP—hydrological post, n/d—no data (no toxicant).

According to the results of the chromatographic analysis, PCBs were registered in all water samples taken in September 2021 and May 2022 along the Syrdarya River. The contents of the toxicants in the river water in 2021 varied from 0.130 to 0.479 $\mu\text{g/L}$, and in 2022, from 0.355 to 1.080 $\mu\text{g/L}$ (Figure 7). In May 2022, compared with the data from 2021, the concentration of PCBs in the Syrdarya River water was significantly higher, especially in the lower reaches of the river and in the estuary zone.

The results of the analysis show that the pollution of the Syrdarya River due to PCBs occurred in the territory of Kazakhstan. Figure 7 clearly shows that the maximum concentrations of the toxicants were registered in the water of the border zone and Shardara Reservoir due to PCB contamination of the transboundary inflow. But along the course of the river in the territory of Kazakhstan, their concentrations in the river water increased near the cities of Kyzylorda and Kazaly. No significant decrease in the level of water pollution in 2021 as far as the mouth of the river was determined.

The congener composition of PCBs in river waters was very broad. In 2021, 33 individual PCB isomers were recorded, belonging to homologous groups from tetrachlorobiphenyls (PCBs 40 and 49) to heptachlorobiphenyls (PCB 171). In 2022, 20 congeners were found that were within these homologous groups. Among the congeners found were strictly controlled “marker” congeners, namely, PCBs 52, 101, 138, and 153, and highly toxic dioxin-like congeners, namely, PCBs 105, 114, and 118, belonging to the pentachlorobiphenyl homology group. Eleven congeners were registered in the waters of the Shardara and Koksarai reservoirs.

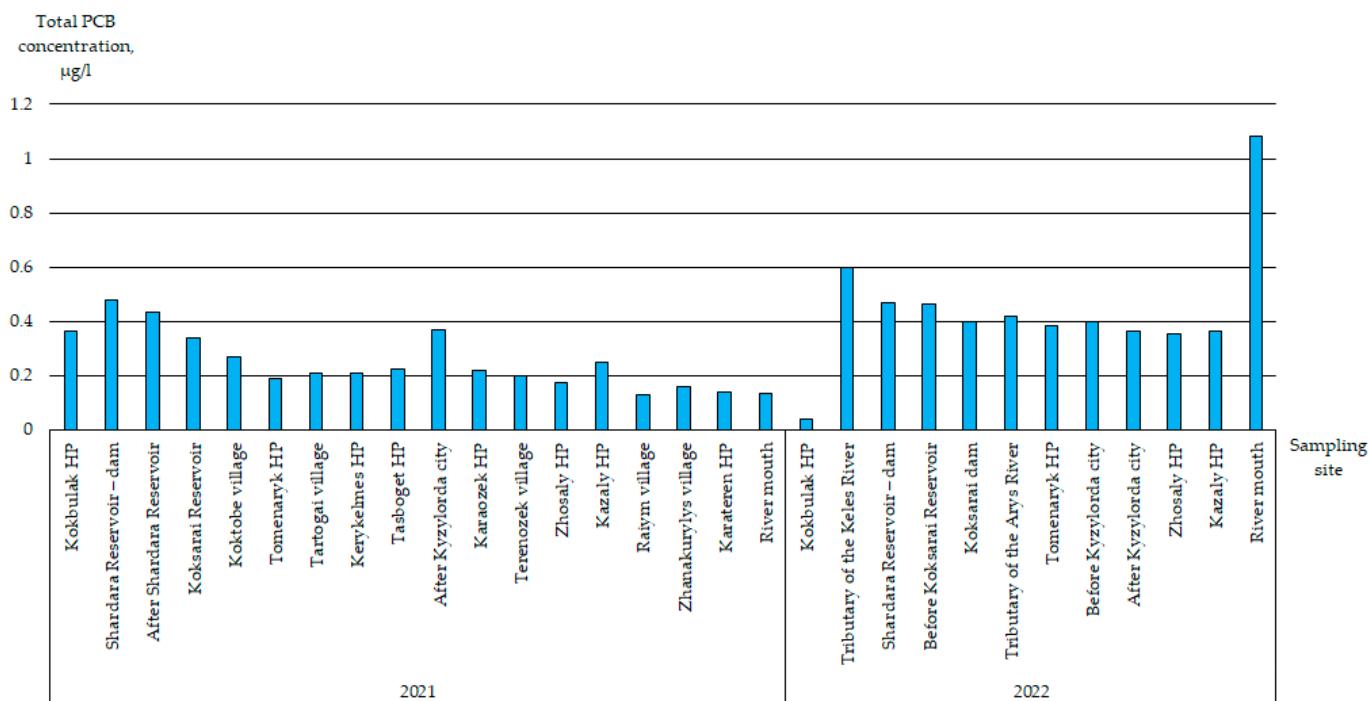


Figure 7. Total PCBs concentration changes along the Syrdarya River in September 2021.

We have not found such a large number of PCB congeners, 33 in the waters of the Syrdarya River (Figure 7), in other water bodies of Kazakhstan. According to Agapkina G.I. and Kannan N. [64,65], a wider structural diversity of PCB congeners is a sign that sources of different origins are involved in the pollution of the water body and the watercourse with these toxic compounds. These may include contamination by industrial PCB mixtures, atmospheric transport, and pyrogenic origin, for instance, as a consequence of reed burning, due to industrial and domestic waste incineration processes.

The toxicity of natural waters in relation to PCBs is obviously determined not only by the total concentration of a toxicant but also by the content in them with more toxic “marker” congeners, especially dioxin-like ones. The content of the “marker” congeners in 2021 varied in the river water samples from 0.032 to 0.053 µg/L, and their relative contents in some samples ranged from 15 to 35%. The highest relative proportion of the PCB 153 congener was found in the water of the Syrdarya River mouth. Similar data were obtained in May 2022, where the concentrations of the “marker” congeners in the river and reservoir waters were found to range from 0.030 to 0.059 µg/L, and their relative contents in some samples ranged from 9 to 17%.

The concentration of highly toxic dioxin-like congeners in 2021 ranged from 0.038 to 0.056 µg/L. Their relative concentrations varied in separate samples ranging from 8% in the water of Shardara Reservoir to 41% and in the water samples taken in the river delta near the Karateren hydrological post. It should be also noted that increased concentrations of PCBs (0.370 µg/L) were detected in the water samples taken from the Syrdarya River downstream of Kyzylorda. Dioxin-like congeners PCB 114 and the “marker” PCB 138 were registered in this sample, representing 37% of the total PCB amount. The analysis of water samples collected in 2022 showed that the contents of dioxin-like isomers ranged from 0.031 to 0.052 µg/L, and their relative contents were in a range from 8 to 11%.

Thus, the absolute and relative contents of the “marker” and dioxin-like congeners in the Syrdarya River water and reservoirs in 2021 and 2022 were characterized by close values, which allowed for general assumptions about the close levels of river water toxicity in these years with respect to PCBs.

In 2022, two main tributaries of the Syrdarya River, namely, Keles and Arys, were studied. The chromatographic analysis of the collected water samples showed PCB con-

tamination of these rivers as well (Figure 7). The total concentration of toxicants in the Keles River water was $0.600 \mu\text{g/L}$, and $0.420 \mu\text{g/L}$ in the Arys River water, i.e., within the maximum values registered in the water of the Syrdarya River. The Syrdarya River and other water bodies of the basin were exposed to pollution by the effluents of their tributaries within the territory of Kazakhstan. Ten congeners, including the “marker” congener PCBs 138 and 153 with concentrations of $0.048\text{--}0.055 \mu\text{g/L}$ and the dioxin-like PCBs (PCBs 105, 114, and 118) with concentrations from 0.031 to $0.046 \mu\text{g/L}$ were registered in the water of the tributaries.

Among the lakes located in the delta zone of the Syrdarya River, water samples were taken from the largest lake Kamystybas and the periodically through-flowing lake Tushchy. PCBs were present in all water samples taken from these water bodies, despite the fact that Kamystybas Lake is a non-flowing water body. The total PCB content in the water of these lakes was found in 2021 within $0.093\text{--}0.220 \mu\text{g/L}$, and in 2022 within $0.324\text{--}0.648 \mu\text{g/L}$ (Figure 8). Fifteen individual congeners were found, including the dioxin-like congeners PCBs 118, 105, and 114 and the “marker” PCBs 101, 138, and 153. In lake waters, the total content of toxicants in 2022 was almost twice as much as in 2021. The maximum content of PCBs was found in the water of the flowing lake Tushchy.

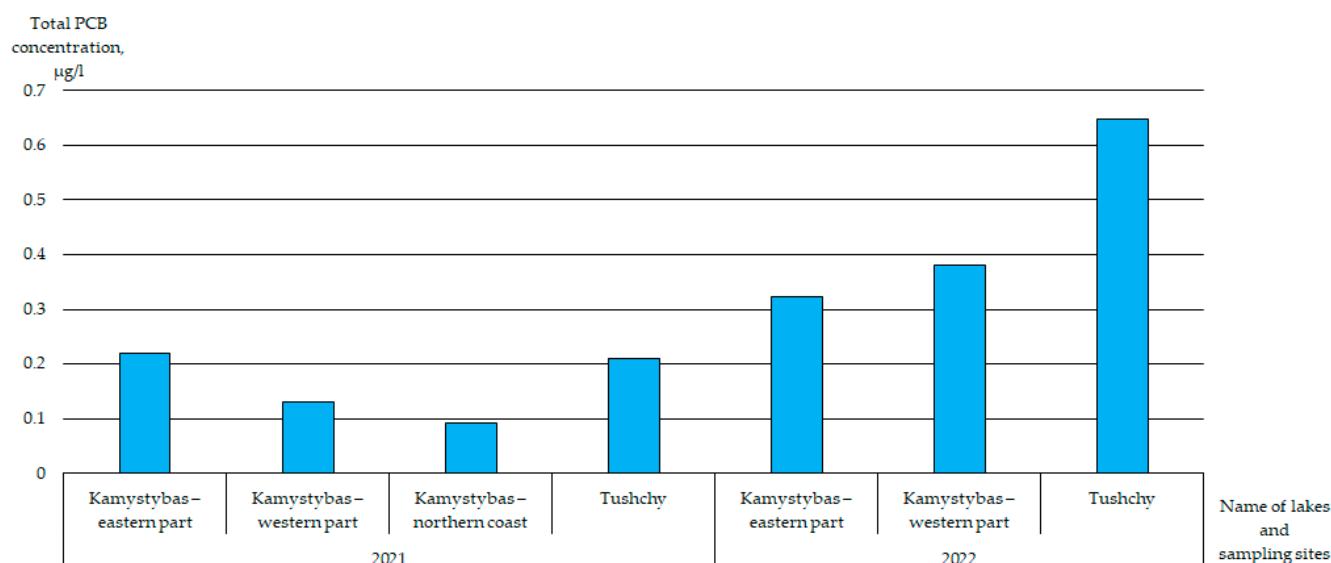


Figure 8. PCB contents and their congeners in the water of the Syrdarya River delta lakes.

The results of the 2013 winter campaign in the lower reaches of the Syrdarya River show the presence of PCBs in the water of the Syrdarya River in the amount of $0.083 \mu\text{g/L}$. In the Tushchy and Laikol lakes, the levels of accumulation of pollutants were significantly higher (2.18 and $4.70 \mu\text{g/L}$, respectively) than in the river water. PCBs were not detected in the water of Kamystybas Lake.

After the Kokaral dam of the Small Aral Sea was built, a water body formed, which has a non-permanent connection with the northern end of the Large Aral Sea. This water body has no connection with the Syrdarya River. At the same time, a quite high accumulation of PCBs up to $23.12 \mu\text{g/L}$ was registered in this water body during winter time. It is difficult to name direct sources of PCB pollution in this water body. However, one can only assume the influence of the so-called “historical” sources, such as military facilities that functioned for many years during the Soviet Union period on “Vozrozhdenie” Island (Renaissance Island) and other parts of this region and the atmospheric removal of pollutants from the surface of the dried lakebed.

All the abovementioned data is an indicator of significant variability in the level of pollution of the deltaic lakes of the Syrdarya River by PCBs over time. This variability depends on the nature of their connection with the river, as well as the influence of

atmospheric transfer of the toxicant from the surface of the dried bottom of the Large Aral Sea.

3.3. Small Aral Sea

POPs in the waters of the Small Aral Sea were studied from 1991 to 2006, as well as in 2021 and 2022. The sum of pesticides in the Small Aral Sea water was 0.22–1.58 µg/L in 1991 (HCCH, DDT, and some organophosphorus compounds were present). In 1992, only HCCH isomers in concentrations up to 0.09 µg/L were detected here. In 1993, the species diversity of pesticides in water was significantly higher than in previous years. This was mainly due to the inflow of a significant volume of the Syrdarya runoff. Ten species were detected: HCCH, DDT, metaphos, TCM, and others. The average concentrations of HCCH and DDT were 0.022 and 0.130 µg/L, respectively, and the sum of all pesticides reached 1.58 µg/L, with 0.460 µg/L on average.

In June 1994, 12 pesticide species were detected in the water of the Small Aral Sea and 7 were recorded in autumn, and in 1996 and 1997, 6 species were detected. HCCH (68%) and DDT (52%) were usually the most common pesticides. Their concentrations in the water of the river flow distribution zone were one and two orders of magnitude higher than in its central and western parts. During 1996–2006, there was a clear trend of decrease in the level of pesticide pollution in the lakewater, primarily due to the decrease in number of recorded species (Table 2).

Table 2. Concentrations of pesticides in the water of the Small Aral Sea (average values).

Year, Month	Number of Pesticides Found	HCCH (Isomers)		DDT (Metabolites)		Sum of Organochlorine and Organophosphorus Pesticides, µg/L
		µg/L	% Occur.	µg/L	% Occur.	
1993, June	10	0.022	82	0.130	91	0.506
1994, June	12	0.100	81	0.270	75	0.800
1994, September	7	0.020	75	0.174	33	0.799
1996, July	6	0.050	58	0.052	37	0.128
1997, June	6	0.080	68	0.279	52	0.421
1998, June	3	0.015	83	0.138	93	0.163
2000, August	3	0.020	71	0.030	12	0.032
2001, June	3	0.015	60	0.480	40	0.495
2002, July	3	0.017	67	0.120	8	0.137
2003, July	1	0.019	92	Absent	-	0.019
2004, August	1	0.006	73	Absent	-	0.006
2005, April	1	0.010	50	Absent	-	0.010
2005, May–June	2	0.011	24	0.0–0.0870	14	0.058
2006, June	1	0.046	73	Absent	-	0.046
2006, August	1	0.028	100	Absent	-	0.028

In 1992–1997, the concentrations of PCBs in the water of the Small Aral Sea were extremely unstable. In 1992, they were registered in the amount of 7–9 µg/L. In 1993, the PCBs concentration was 0.04 µg/L at only one station. In 1996, 1997, and 2000, these toxicant concentrations were 0.04–0.4, 0.1–1.0, and 2.0 µg/L, respectively [66].

Thus, the level of the Small Aral Sea pollution by toxic chemicals was characterized by significant fluctuations due to the volume of incoming and accumulated river flow, the amount of toxic substances used in the basin, the rate of their destruction in the aquatic environment, and their biogenic migration.

The results of the study of OSPs in the water of the Small Aral Sea in 2022 are presented in Table 3.

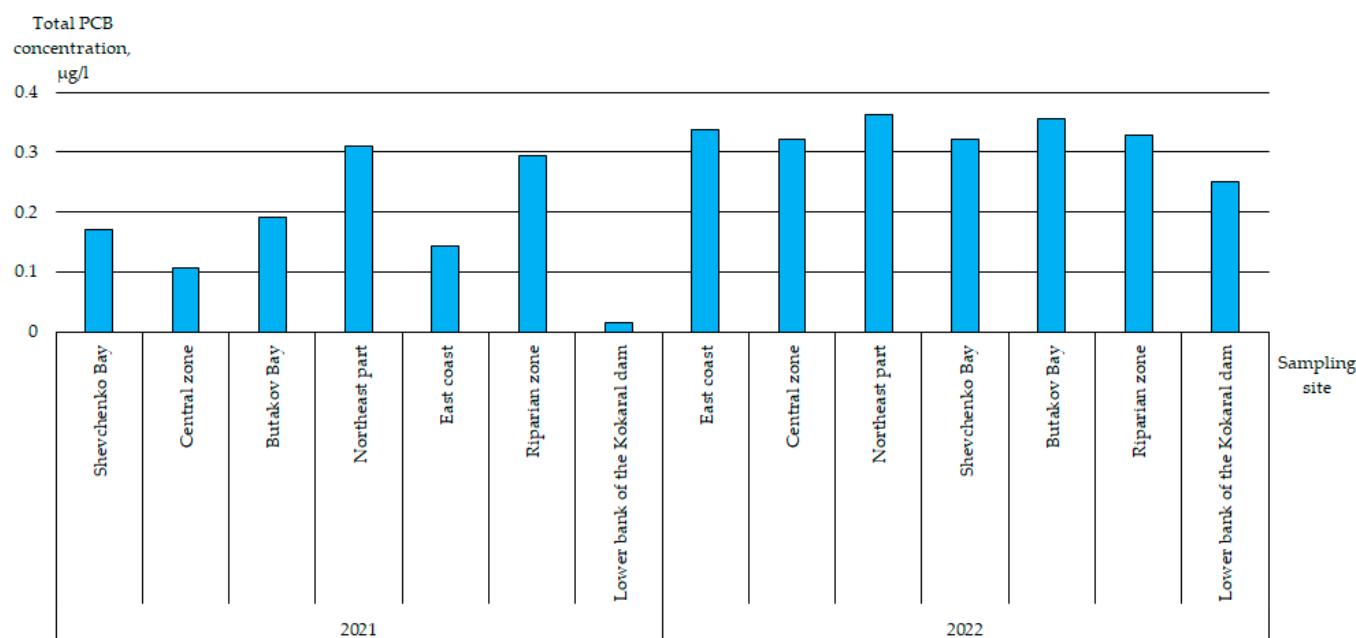
Table 3. Organochlorine pesticides in the water of the Small Aral Sea ($\mu\text{g/L}$).

Sampling Sites	DDT (Metabolites)	Hexachlorobenzene	Heptachlor	Aldrine	HCCH (α , β , γ -Isomers)
East coast	0.006	n/d	n/d	n/d	0.002
Central zone	0.007	n/d	n/d	0.001	0.001
Northeast zone	0.012	n/d	n/d	0.001	0.001
Shevchenko Bay	0.002	n/d	n/d	0.002	0.003
Butakov Bay	0.016	n/d	n/d	0.001	0.003
Near the Kokaral dam	0.006	0.001	0.001	n/d	0.002
Lower embankment of the Kokaral dam	0.001	n/d	n/d	n/d	0.002

Note: n/d—no data (no toxicant).

The data in Table 3 show the presence of DDT and HCCH in all lakewater samples. Hexachlorobenzene, heptachlor, and aldrin were detected in the waters of some parts of the Small Aral Sea. A comparison with the results in Tables 2 and 3 shows a significant decrease in HCCH and DDT concentrations in 2022 compared with data from 1993–2006.

Surveys in 2021 and 2022 have detected PCB pollution in the whole water area. Their concentrations in 2021 ranged from 0.108 to 0.310 $\mu\text{g/L}$ and in 2022 from 0.321 to 0.362 $\mu\text{g/L}$. A higher content of the toxicants was registered in the water of the near-river zone and bays (Figure 9).

**Figure 9.** PCB contents and their congeners in the water of the Small Aral Sea and the Kokaral dam downstream.

PCBs found in the Small Aral Sea water were characterized by a wide range of congener compositions (Figure 9). Twenty-one individual congeners were registered in 2021 and 14 congeners in 2022. Among these were “marker” PCB congeners 52, 138, and 153 and dioxin-like PCB congeners 105, 114, and 118. “Marker” congeners comprised 7 to 37% of the individual samples in 2021 and 9 to 19% in 2022; dioxin-like congeners comprised 12 to 15% in 2021 and 9 to 16% in 2022.

The protection of the natural environment and the population from the POPs’ impact is one of the most acute problems for the whole territory of Kazakhstan. In terms of POP waste stockpiles, Kazakhstan ranks second among Central, Eastern Europe, and CIS countries after Russia. At the present time, a large amount of PCB-containing equipment

at 8 PCB-contaminated sites (areas) of about 2500 ha was identified in the territory of the Kazakh Republic.

In other natural objects and ecosystems of water reservoirs of Kazakhstan, POPs are practically not studied. These xenobiotics are not monitored by the Kazakh Hydrometeorological Survey and other authorities of the Republic of Kazakhstan. However, the results of studies conducted in some years show the stable pollution of PCBs and OCPs in the water resources of the main transboundary river basins of Kazakhstan [2,66,67].

4. Conclusions

The Aral Sea disaster, also known as Aral Sea syndrome and ecological crisis has a special place among the global catastrophes of the world. It is one of the largest anthropogenic interferences with and destruction of the natural environment. There is no analog in the world where these profound processes and changes took place in the aquatic ecosystem of such large inland lakes. The catastrophic drop in the Aral Sea level and the intensive pollution of the entire Aral Sea region caused deep degradation of the natural environment and created environmental, social, and economic problems unprecedented in their acuteness and urgency.

The widespread expansion of irrigated areas in Central Asia, including Kazakhstan, was accompanied by an increase in the use of water resources. Since 1961, when the runoff of the Amudarya and Syrdarya rivers, the two only tributaries into the Aral Sea lake, was dramatically reduced, the water level of the Aral Sea dropped down, and the lake was divided into two water basins: the Large Aral Sea and the Small Aral Sea. Intensive salinization continued, its salinity exceeded 100‰ by 2004, and it lost its fishery value.

One of the most negative consequences of the Aral Sea desiccation is the wind-driven removal of salt and dust aerosols to the atmosphere from the dried lakebed [66]. One of the main causes of the deep degradation of the natural environment of the Aral Sea basin was the excessive use of pesticides in irrigated lands, i.e., their contamination of soils, drainage waters from irrigated areas, and all surface water resources in this basin.

In 1991 and 1992, HCCH and DDT were detected in the water of the entire water area of the Large Aral Sea, while PCBs and low concentrations of POPs were also registered. The highest level of contamination of the Syrdarya River with OCPs and PCBs was registered in 1979–1988. At the same time, a significant increase in the content of toxicants was registered downstream of the river to the estuary zone due to increased pollution by such toxicants in the territory of Kazakhstan.

Two peaks in the intra-annual regime of pesticides in river water were identified in the territory of Kazakhstan: the first one in September–November was caused by an intensive inflow of toxicants into the river system as part of CDW from irrigated areas, and the second one in early spring (March–May) was a result of pesticide washout from the surfaces of the catchment area and irrigated lands during winter thaws and spring snowmelt.

The studies in the present period (in 2021 and 2022) showed the presence of pesticides, such as HCCH, DDT, heptachlor, aldrin, and PCBs, in the Syrdarya River water, the Small Aral Sea, and the reservoirs. The content of the PCBs in the river water in 2021 varied from 0.130 to 0.479 µg/L and in 2022 from 0.355 to 1.080 µg/L of the Syrdarya River. The average concentrations of HCCH and DDT were 0.022 and 0.130 µg/L, respectively, and the sum of all pesticides reached 1.58 µg/L, with 0.460 µg/L on average for the Small Aral Sea and the reservoirs. The comparison of these data with the given multi-year material clearly shows a decrease in pesticide concentrations in the water of all water bodies of the Aral Sea basin by tens and hundreds of times. This was, first of all, the result of the reduction in the volume of pesticide applications used in the river basin by the Central Asian countries, including Kazakhstan. However, pesticides such as DDT and HCCH, the use of which has been prohibited in the world for a long time, are still used in the agricultural fields of the basin. Maximum concentrations of PCBs were registered in the transboundary flow, the Shardara Reservoir, and near the cities of Kyzylorda and Kazaly, indicating the presence of sources of pollution near them in the territory of Kazakhstan as well.

Thus, all water bodies in this basin were polluted with POPs. The levels of their pollution were extremely variable in time, which was caused by irregularities in the quantities and types of pesticides used in agriculture, fluctuations of the river flow entering the water bodies, and seasonality of CDW entering the river system.

The main sources of pollution of water bodies with PCBs in the ASSB include the transboundary inflow along the Syrdarya River; cities and settlements located in the river basin; and salt and dust outflow from the dried bottom of the Large Aral Sea, including "historical" sources formed on the former "Vozrozhdenie" Island or "Renaissance" Island.

Guided by the main provisions and requirements of the Global Stockholm Convention on POPs, the following are recommended:

- Take effective measures for the early elimination of hazardous sources of POPs in the territory of Kazakhstan by relevant state authorities;
- Devote comprehensive research programs for the science-based assessment of POP pollution levels in water, biological, and food resources to prevent their movement into the food chain and to achieve a development of state monitoring of POPs with the aid of the RSE "Kazhydromet";
- Establish strict control over the quality of the transit flow at the Syrdarya River (Kokbulak outlet) by installing a modern automatic water quality control station;
- Evaluate the impact of the Baikonyr cosmodrome on the natural environment and water quality of the Syrdarya River. The impact of the Baikonyr cosmodrome on the environment and water quality of the Syrdarya River should be analyzed and assessed, and a detailed study of its wastewater and atmospheric emissions should be organized in the near future.

This work constitutes a comprehensive study that emphasizes the imperative need for immediate actions to mitigate environmental challenges within the Aral Sea basin and safeguard its natural environment for future generations.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app132011453/s1>.

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