

Article

Polychlorinated Biphenyls in the Snow Cover of South-Eastern Kazakhstan

Nariman Amirgaliyevich Amirgaliyev ¹, Akhmetkal Rakhmetullayevich Medeu ¹, Christian Opp ^{2,*}, Azamat Madibekov ^{1,*}, Roza Kulbekova ¹, Laura Ismukhanova ¹ and Askhat Zhadi ¹

¹ Institute of Geography and Water Security of the Ministry of Education and Science of the Republic of Kazakhstan, Nur-Sultan Z05K5K8, Kazakhstan

² Department of Geography, Philipps-University of Marburg, 35032 Marburg, Germany

* Correspondence: opp@geo.uni-marburg.de (C.O.); madibekov@ingeo.kz (A.M.);
Tel.: +49-6421-2824129 (C.O.); +7-7-017342176 (A.M.)

Abstract: The presence of large sources of environmental pollution due to persistent organic pollutants (POPs), in particular, polychlorinated biphenyls (PCBs), in Kazakhstan necessitates the assessment of pollution as a result of these toxicants. For this purpose, we chose snow cover as an indicator for assessing pollution status in the study area. An assessment of the PCB accumulation level included in the list of POPs was carried out for a snow cover (SC) study in south-east Kazakhstan. The content of PCBs with a wide congener composition was determined using the chromatographic analysis method. During the winter periods of 2014, 2015, 2018–2020 and 2021, the SC pollution of the study area from up to 25 individual PCB congeners was identified. These congeners included highly toxic dioxin-like congener PCBs 105; 108; 114; 118 and “marker” PCBs 52; 101; 138; 153. These congeners were mainly found in snow samples with a wide range of PCB congener compositions. The main PCB pollution sources were indicated. The analysis of the obtained results and structure of the congener composition of PCBs show that the SC contamination in this territory occurs under the influence of local and regional sources.

Keywords: snow cover; POPs concentration; congeners; toxicants; pollution sources

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1. Introduction

The SC analysis was carried out in the south-eastern region of Kazakhstan, which includes parts of the territories of three regions of the Republic of Kazakhstan (Almaty, Zhambyl, and Karaganda provinces) and occupies the northern slope of Ili-Alatau, including a vast foothill plain. The study area also includes the whole basin of the Ili (Ili) River with numerous tributaries. This south-eastern Kazakh region is densely populated and one of the largest and most economically significant territories in Kazakhstan.

The total length of the Ili River is 1439 km; the first 624 km is situated in China, and the rest in Kazakhstan. The total area of the basin is 140,000 km², of which 77,400 km² belongs to Kazakhstan [1,2]. The total runoff volume of the Ili River basin is 2287 km³/year, of which 174 km³/year is formed in China.

Sixty kilometers from Almaty, the Kapshagai Reservoir was built at the Ili River, one of the largest artificial waterbodies in Central Asia. Its area is 1450 km², and the water volume is 16.0 km³. Notably, 70% of the water inflow into the reservoir is from the Ili River. The left-side tributaries are the Shelek, Turgen, Esik, Kaskelen, and Talgar Rivers. Within the reservoir dam, the Kapshagai Hydro Power Plant (KHPP) was built with a capacity of 364 MW (rated capacity is 434 MW) [2].

The Ili River Delta is the largest natural inland delta of Central Asia (CA) with a total area of 20,000 km², of which 8000 km² belongs to the recent delta. The rest belongs to the ancient delta with branching channels (“Bakanasses”) [2]. Against the background of

globally widespread desertification and the degradation of river deltas (deltas of the rivers Syrdarya, Amudarya, Shu, etc.) [3], the area of the modern delta of Ili River is the only remaining river delta in Central Asia. The delta's area is included in the Ramsar convention and the list of wetlands of the international importance of the Convention on Wetlands of International Importance as waterfowl habitat (adopted in the city of Ramsar, Iran) [4,5]. In 2018, the Ili-Balkhash State Nature Reserve (SNR Ili-Balkhash) was created within the contact zone between the Ili Delta and Lake Balkhash. It has a protected reserve regime and it is a unique object in terms of ecological restoration.

The Almaty agglomeration was created on this territory, including five cities. Almaty is the biggest city and the core of the agglomeration. The total land area of the agglomeration is 939.5 thousand hectares, and 188 settlements of the Almaty region are located in this agglomeration zone, with a total population of 2.5 million people. An agrarian-industrial complex has developed outside the urban areas. There are rather large irrigation areas: Akdala (30.000 hectares), Shengeldy (18.000 hectares), and Kerbulak (1400 hectares) [6,7].

This vast territory is subject to significant anthropogenic impacts on transboundary and regional nature conditions. As a consequence, there is a need to study the ecological and toxicological effects of the natural conditions. Hence, this study's aim is to assess the level of environmental pollution of the snow cover in south-eastern Kazakhstan using the chromatographic determination of PCB content with a congener composition in the SC. This is because snow cover functions as a temporal storage medium for pollution inputs. Polychlorinated biphenyls (PCBs) are included in the list of persistent organic pollutants (POPs) which are recognized by the international community as substances that pose a great danger to people and the environment [8]. Even short-term human exposure to high levels of dioxins can lead to pathological changes to the skin, such as chloracne and focal darkening, as well as changes in liver function. Prolonged exposure damages the immune system, the emerging nervous system, the endocrine system, and reproductive function [8,9]. A global international agreement has been in force since 2001 (the Stockholm Convention on POPs [8] to protect human health and nature). This was ratified by the Republic of Kazakhstan in 2007.

In the frames of the Helsinki Commission (HELCOM) convention on the protection of the Baltic Sea from pollution, three main criteria are used to assess the hazard of substances: persistence, toxicity, and bioaccumulation. According to these characteristics, the work of [10], which assessed the dangerous substances polluting the Baltic Sea included in the HELCOM list, formulated priority groups of harmful substances. Such harmful substances include hazardous organic compounds, such as POPs and others. Consequently, the dangerous xenobiotics (PCBs) investigated in the current study are quite consistent in their properties with the three specified criteria.

PCBs are artificial organic compounds formed by biphenyls with a variable number of chlorine atoms alternating on two benzene rings of six carbon atoms. These compounds can have 10 homologs and 209 related compounds, recognized based on the number and position of the chlorine atoms. These contaminants are lipophilic chemicals commonly used in electronics manufacturing, pesticide carriers, and building materials [11]. The world production of PCBs is estimated to exceed 1.3 million tons per year [12,13]. Due to their toxicity and danger to human health, the use of PCBs has been prohibited in the USA and most industrialized countries of the world since the 1970s.

Some PCBs are called dioxin-like PCBs because they have similar chemical structures to dioxins and furans. In fact, 12 PCB congeners (PCBs 77; 81; 105; 114; 118; 123; 126; 156; 157; 167; 169 and 189) were selected as dioxin-like PCBs (DL-PCBs) because they were identified as hazardous for the environment and human health [14,15]. Thus, the toxicity equivalent (TEQ) established by the World Health Organization (WHO, 2005) was calculated by summing the congener-specific toxic equivalence coefficients (TEFs) [16]. TEFs are an integral part of the toxic equivalent (TEQ) concept and have been developed for dioxins/dioxin-like compounds over the past two and a half decades [17–26].

The coverage of this SC analysis includes almost the whole south-eastern territory of Kazakhstan. It differs from several scientific analyses devoted to SC studies only in urban areas. However, it is appropriate to refer to well-known work that has drawn attention to the predominance of urban areas as objects of study based on a statistical analysis of publications related to the study of snow cover [27]. The results of the study of snow cover worldwide show high efficiency in determining the sources and level of air pollution [28]. Researchers have proven the influence of urbanized areas on the content of individual ions in the snow [29–31].

In the area of atmospheric precipitation research, attention should be paid to the statement of the authors of review articles about the small number of analyses on organic xenobiotics in SC, including especially dangerous ones, and the need to extend research in this direction [27].

In other studies, it has also been emphasized that the high toxicity of POPs and their ability for bioaccumulation makes this problem particularly relevant [32,33]. Their long period of existence in the atmosphere and ability to be transported over long distances are determining factors in the global distribution of PCBs. Literature data have indicated the presence of POP compounds in the Arctic in relatively high concentrations [34,35]. The presence of POPs, including PCBs, in the snow cover and fresh waterbodies of the Arctic is also known from more recent studies [36,37].

The protection of both the environment and the population from the impact of POPs, including PCBs, is one of the most acute problems in Kazakhstan. In terms of POP waste reserves, Kazakhstan ranks second after Russia among the countries of Central, Eastern Europe and CIS [38]. According to the available literature information, there is no production of POPs in Kazakhstan [38,39]. The total volume of identified POP-containing wastes is estimated at 250.000 tons. Kazakhstan, as a supporter of the Stockholm Convention, has committed to eliminating all wastes containing POPs using environmentally friendly methods by 2028. In April 2010, the Ministry of Environmental Protection and Water Resources of the Republic of Kazakhstan (MEP and WR RK) together with the United Nations Development Programme (UNDP) started a joint project of a comprehensive plan for PCB management. The Kazakh government implemented the UNDP-Kazakhstan Project “Initial assistance to the Republic of Kazakhstan to fulfill obligations under the Stockholm Convention on POPs”. In 2004, in the frame of this project, a quantitative assessment of the existing equipment containing PCBs was carried out [40].

One of the most toxic and globally widespread representatives of POPs is PCB. PCB-containing equipment at the amount of 116 transformers and about 50.000 condensers has been identified in Kazakhstan. Such transformers and condensers contain PCBs of approximately 800 tons. Such equipment threatens potential hazards if it is depressurized [41,42].

Eight PCB-contaminated areas were identified in Kazakhstan. The total area of those contaminated territories is about 2500 hectares. There are some allocated plots (13.0 hectares) with heavily polluted soils. Those foci include a vast territory on the western and northern shores of Balkhash Lake, where large metallurgical enterprises, mines, and many military facilities of Kazakhstan and the Russian Federation, are located [38,39,42–44]. Obviously, some other sources located in south-east Kazakhstan can influence the accumulation of PCBs in the SC of the considered territory.

In natural objects and waterbodies of Kazakhstan, PCBs have been practically unstudied until recently. These xenobiotics are not monitored by the net of the Kazakh Hydro-Meteorological Survey (KazHydroMet) or other state agencies. Some information about PCBs in natural objects is available from the region of Ust-Kamenogorsk [43,44]. Limited materials about their accumulation in the SC of certain territories of Kazakhstan are provided in our publications [45–47].

The above-mentioned overview and the ongoing pollution in Kazakhstan due to the transboundary transfer of toxicants necessitate the continuous monitoring and evalua-

tion of PCB distribution. The main objective of the current study is to make a substantial contribution to these research gaps.

2. Materials and Methods

The present study was carried out in the winter periods of 2014, 2015, 2018–2020 and 2021. Snow sampling was realized in January–February of each sampling year at 22 and 30 points in 2018, 2019, and 2020. For a more detailed ranking of the Almaty agglomeration regarding PCB distribution, snow samples were taken at 41 points. The scheme of snow sampling points by the example of 2020 is shown in Figure 1. SC sampling points were chosen considering the degree of anthropogenic load and expected sources of technogenic pollution, in accordance with methodological recommendations [48].



Figure 1. Scheme of snow sampling points in 2020 (authors Madibekov A.S., Zhadi A.).

2.1. Sampling Technique

During field research, snow sampling was carried out according to the generally accepted methods [49]. To study the level of PCB accumulation in SC, sampling was carried out in an open flat area. Snow sampling was carried out by the pit method for the full capacity of the SC, except for a 5 cm layer above the ground, on an area of 1×1 m². Samples were placed in plastic bags [49]. The ingress of foreign substances into the sample was excluded, both at the time of sampling and during their storage and transportation to the laboratory. Since the content of substances dissolved in sediments is small and measured in milligrams per liter of water, strict observance of the conditions for sampling, storage, and the analysis of samples was required. The samples were delivered to the laboratory, where they were stored at temperatures between -5 and -15 °C until they were processed. To melt the snow, samples were placed overnight in pre-prepared con-

tainers. The settled samples were filtered through a paper filter for further chemical and toxicological analyses.

2.2. Methodology of Toxicological Analysis

For chromatographic analysis, snow sample extraction was made by n-hexane for PCB determination. About 50 mL of extract from each sample was analyzed in an accredited testing laboratory “Nutritest”. Chromatogram reports are available under “Supplementary Materials”.

Modern methods and approaches used for the determination of PCB content allow the determination of all congeners, even though no single chromatographic column can currently separate all 209 PCB components. The dominant methods are:

- (1) Gas-liquid chromatography (GLC) using an electron-capture detector (ECD) selective for chlorine-containing compounds [50,51];
- (2) A combination of low-resolution GC-MS (gas chromatography-mass spectrometry) for measuring PCBs (No. 105; 114; 118; 123; 156; 157; 167 and 189) [52,53]. This was applied in our study. For the rest of the PCBs (i.e., No. 77; 81; 126; 169) a combination of GC with high-resolution MS [54,55] was applied.

The determination of PCBs in SC was carried out according to the Standard of the Republic of Belarus (STB) International Organization for Standardization (ISO) 6468-2003 using a Khromos GH-1000 gas chromatograph with software, an electron-capture detector (ECD) and a capillary column 30 m × 0.32 mm long [27,56] (ISO 6468-2003 is identical to ISO 6468:1996 “Water quality-Determination of certain organochlorine insecticides, polychlorinated biphenyls, and chlorobenzenes-Gas chromatographic method after liquid-liquid extraction”. Determination of certain organochlorine insecticides, polychlorinated biphenyls, and chlorobenzenes. Gas chromatographic method after liquid-liquid extraction. For the chromatography conditions, the column temperature was 220 °C, the evaporator temperature was 240 °C, the detector temperature was 300 °C, and the carrier gas flow rate (“high purity nitrogen”) was 38 mL/min. The state standard sample (SSS) of the Sovol solution composition in hexane, a mixture of PCB-52, PCB-101, PCB-138, PCB-153, and the sum of tetra-, penta-, and hexachlorobiphenyls were used as a standard.

3. Results

3.1. Pollution of Snow Covers by Polychlorinated Biphenyls in Talgar City and Almaty City (2014 and 2015)

For the determination of PCBs during the winter periods of 2014 and 2015, we took SC samples from the territory of the Institute of Geography of the Ministry of Education and Science of the Republic of Kazakhstan. This is located 25 km from Almaty in the central part of a large metropolis (the city of Almaty) and the satellite town of Talgar. At the same time, the task was to obtain real values of concentrations to provide an understanding of the PCB contamination level of solid precipitation within a densely populated area with developed infrastructure.

The obtained results (Tables 1 and 2) show that the fresh solid precipitation in the territories of Almaty and Talgar cities is subject to PCB contamination. The absence of PCBs in snow samples was noted on January 29 and November 1, 2014, at both observation points, and on February 21 in the precipitation in Almaty. The highest concentrations of the toxicant were recorded at both points on December 8 of the same year: 0.8 µg/L in the precipitation in Talgar and 3.79 µg/L in Almaty. In 2015, the maximum PCB content of 0.33 µg/L was found in the snow from Talgar and 0.65 µg/L in the snow from Almaty. Increased levels of snow pollution at both sampling points were noted in December and January.

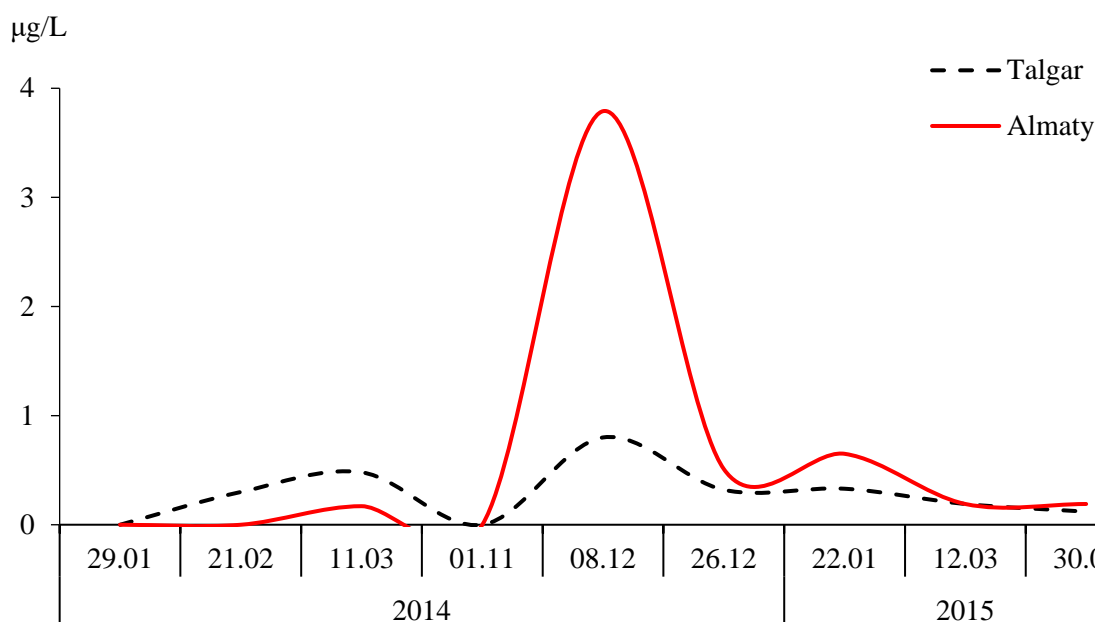
Table 1. Content and congener composition of PCBs in solid precipitation in the territory of Talgar city.

Indicators	Sampling Date					
	2014					
	29.01	21.02	11.03	01.11	08.12	26.12
PCB congeners	Not found	52; 66	52; 66; 138	Not found	52; 66	52; 66
Total PCB, µg/L	Not found	0.30	0.48	Not found	0.80	0.32
	2015					
	22.01		12.03		30.03	
	52; 66; 70		66; 82		66; 151	
Total PCB, µg/L	0.33		0.19		0.12	

Table 2. Content and congener composition of PCBs in solid precipitation in the territory of Almaty city.

Indicators	Sampling Date					
	2014					
	29.01	21.02	11.03	01.11	08.12	26.12
PCB congeners	Not found	Not found	66; 70	Not found	66; 118; 146	41; 44; 66; 70; 87; 101; 105; 110; 129; 151
Total PCB, µg/L	Not found	Not found	0.17	Not found	3.79	0.51
	2015					
	22.01	11.02	12.03	30.03		
	44; 66; 70; 74; 85; 87; 118; 146; 155	52; 66; 105; 110	66; 97; 137	66; 151		
Total PCB, µg/L	0.65	0.66	0.19	0.19		

The observed synchronism in the dynamics of the toxicant concentration in solid precipitations of Almaty and Talgar can be more clearly seen in Figure 2.

**Figure 2.** PCB content changes in the snow samples at the observation points of Almaty and Talgar cities.

Despite the general pattern of fluctuation synchronism of the toxicants, the level of PCB contamination in Talgar city in the 1st quarter of 2014 was higher than in Almaty city. In the snow samples taken at the end of 2014 and during the first quarter of 2015, the

toxicant concentration in Almaty was significantly higher than in the Taglar precipitation. This is probably an indicator of more sources of PCB air pollution from numerous industrial enterprises, transport, municipal, and private emissions in Almaty. At the same time, the synchronous fluctuations of the toxicant concentrations at selected observation points can be understood as an effect of toxic component formation in solid precipitation in this foothill area. The time accumulation inequality of anthropogenic components in precipitation depends on several meteorological characteristics such as wind direction and wind speed, relief, urban air corridors, and both construction and biologic barriers.

In the snow of Talgar city, three individual congeners were registered in 2014 and five in 2015, belonging to the homologous groups of tetrachlorobiphenyls (TCBs) (PCB congeners 52; 66; 70), pentachlorobiphenyls (PCBs) (PCB congener 82), and hexachlorobiphenyls (HCB) (PCB congeners 138 and 151) (Table 1).

Structurally, PCBs 66 and 52 dominated among the identified congeners, and only in precipitations of the year 2015 were congeners PCB 70; 82, and 151 present. A characteristic pattern of the congener composition of the toxicants in the snow cover of Talgar is the presence of widespread and strictly controlled “marker” PCB congeners 52 and 138, the first of which was found in almost all snow samples taken in 2014 and in the sample taken on 22 January 2015.

The snow precipitation in Almaty is characterized by a wider composition of congeners. In the twelve samples from 2014 and the fifteen samples from 2015, individual congeners were identified (Table 2). At the same time, the largest number of PCB isomers was registered in solid precipitation in the third part of December 2014 and January 2015.

The founded congeners in the snow precipitation of Almaty are also included in the homologous groups of tetraCB (PCB 44; 52; 66; 70; 74), pentaCB (PCB 85; 87; 97; 101; 105; 110; 118) and hexaCB (PCB 129; 137; 146; 151; 155). Among the detected congeners are “markers” (PCB 52; 101 and 138), and the most dangerous and highly toxic for living organisms are the dioxin-like congeners PCB 105 and 118 (registered in the snow samples taken in December 2014 and January 2015).

The analysis of the relative content of congeners is shown in Figures 3 and 4. The highest relative share in the snow cover of both Talgar and Almaty belongs to congener PCB 66 from the homologous group of tetrachlorobiphenyls. The content of this congener was from 6 to 87% in the snow of Talgar, and from 47 to 98% in Almaty.

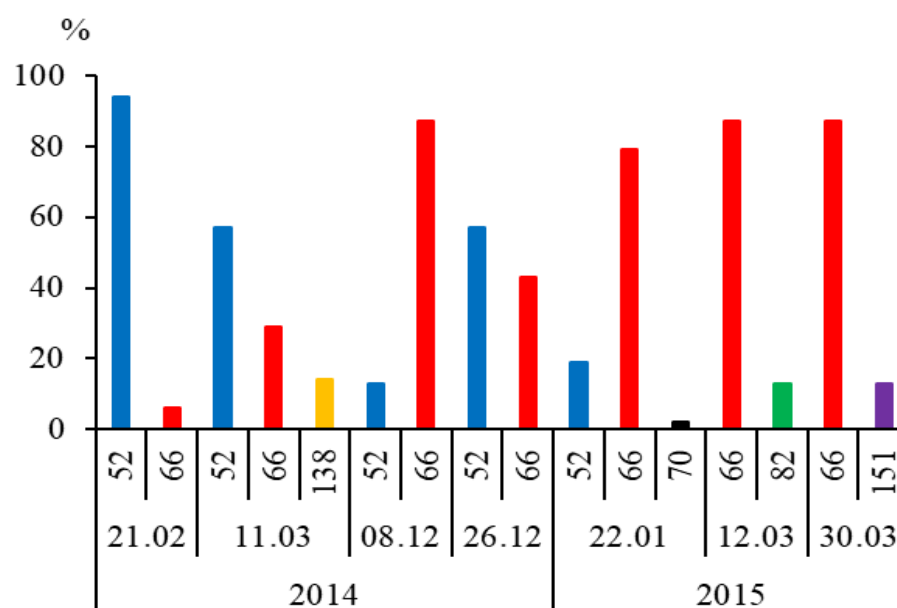


Figure 3. Relative content of PCB congeners in solid precipitations in the territory of Talgar city.

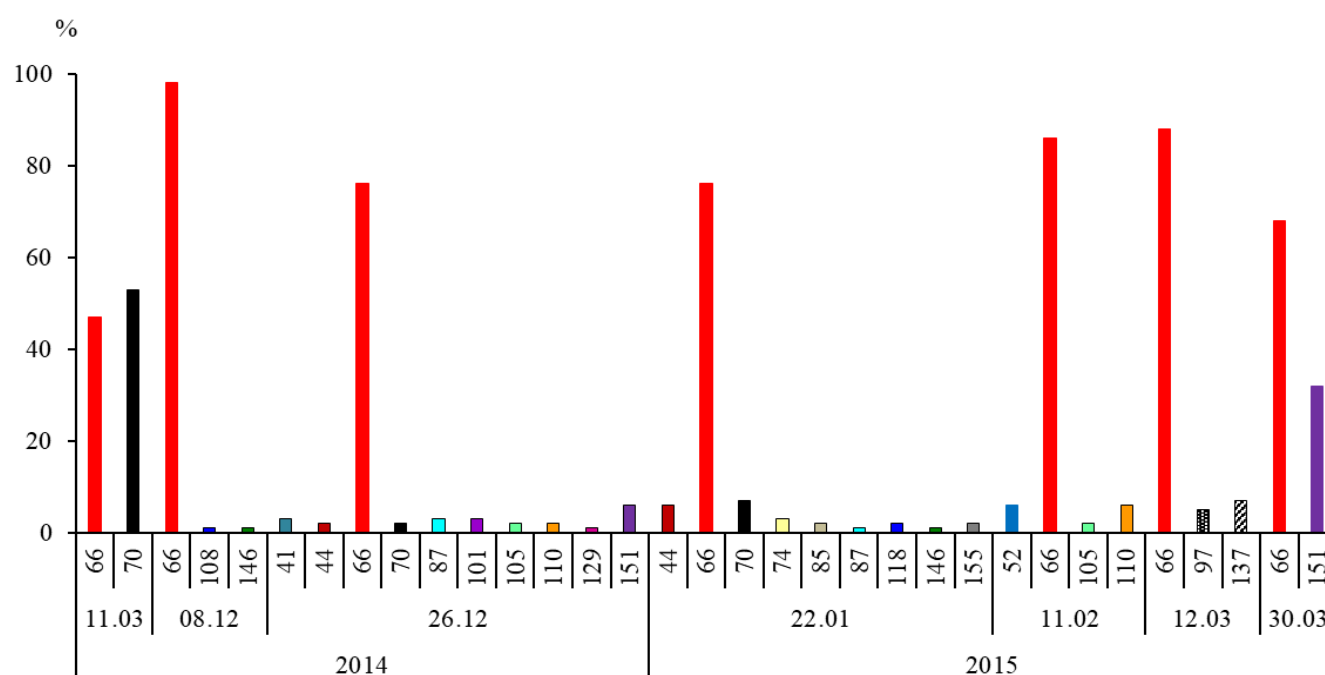


Figure 4. Relative content of PCB congeners in solid precipitations in the territory of Almaty city.

The concentration of “marker” PCB congeners reached high values in the solid precipitation of Talgar, where PCB 52 was registered in an amount from 13 to 94%, and PCB from 138 to 14%. In the snow cover of Almaty, the relative content of “marker” (PCB 52 and 101) and dioxin-like congeners (PCB 105 and 108) was low: from 3 to 6% and from 1 to 2%, respectively.

Thus, fresh solid precipitation in the territory of Talgar is characterized by significant unevenness during the winter period both in terms of the PCB accumulation level and the content of highly toxic isomers. In the snow of Almaty, dioxin-like congener PCBs 105 and 118 were predominantly present in samples with a wide spectrum of PCB congener composition. This is a distinctive feature of the structural indicator of PCBs that accumulate in solid precipitations in the territory of Almaty. This feature of the congeneric composition of PCBs in precipitation is due to the presence of various sources of pollution of the city’s atmosphere by those pollutants.

3.2. Pollution of Snow Cover by Polychlorinated Biphenyls in Almaty Agglomeration (2018–2020)

From 2018 to 2020, the object of the study of PCBs in the SC was the territory of the Almaty agglomeration (AA), created in 2016 within the south-eastern part of Kazakhstan. The AA covers the northern slope of the Ili Alatau Mountains up to an altitude of 2755 m above sea level and a foothill plain with a minimum altitude of 487 m above sea level. There are many rivers of different water content. Tributaries of the Ili River, which is one of the main transboundary rivers in Kazakhstan, feed the unique Balkhash Lake. The territory of AA includes the near-dam part of the water area of the Kapshagay Reservoir that was built on the Ili River.

The analysis of the results obtained over the years primarily shows the distribution of PCBs in SC in the whole AA, except for cases of their temporary absence at certain sampling points (Table 3). In 2018, the highest concentrations of the toxicants in the SC of the AA exceeding 0.1 µg/L, i.e., 100 pg/L, were noted at nine points during the first survey, and four points during the second survey out of 22 studied sampling points. The maximum PCB accumulation level was recorded during the second survey in the snow

water of a mountain point (mountain skiing sports base (MSSB) “Shymbulak”), located at the altitude of 2755 m above sea level (1.942 µg/L) and at the area of Shamalgan Station with an amount of 1.283 µg/L. In total, 22 individual PCB congeners were registered in the snow samples.

Table 3. Average content and congener composition of PCBs in snow cover of the Almaty agglomeration in 2018–2020.

Zone	PCB Congeners			PCB Concentration, µg/L				2020
	2018	2019	2020	2018		2019		
				1 *	2 *	1 *	2 *	
1. Mountain territory	40; 42; 44; 49; 151	40; 42; 48; 86	44; 49	0.031	1.942	0.026	0.0	0.005 (0.038)
2. Territory of Almaty city	41; 44; 49; 52; 66/95; 87/115; 101; 110; 118; 119; 138; 151	40; 41; 44; 64; 71; 86; 101; 114	44; 74; 114; 137	0.066	0.058	0.044	0.009	0.071
3. Small towns and urban-type settlements	40; 44; 49; 52; 85; 97; 110; 118; 119; 128; 138; 151; 155	42; 44; 74; 86	44; 66/95; 74; 97	0.129	0.225	0.039	0.016	0.207
4. Small settlements	40; 44; 49; 97; 118; 121; 151	42; 44; 86	44; 48; 49; 74; 97	0.093	0.028	0.016	0.007	0.068

Note: * = number of field trips for sampling; AA = Almaty agglomeration.

It is known that the presence of several congeners in SC samples is an indicator of the presence of various sources of PCB air pollution in an area. Many researchers came to this conclusion by studying the soil cover in cities [57,58]. These conclusions are also confirmed by our studies [48]. Strictly controlled “marker” (indicator) PCB congeners 101 and 138, as well as PCB congener 118, belonging to the group of highly toxic dioxin-like congeners, were registered in a wide range of PCB congener compositions in the snow samples taken at the indicated points. The “marker” congener PCB 52 and dioxin-like congener PCB 118 were also found in the SC of Almaty city. Highly toxic congeners were not found in the SC of the mountain zone.

The concentrations of PCBs in the SC of small towns and urban-type settlements varied in a wide range from zero to 1.283 µg/L. The highest values of the average content of PCBs (0.129 and 0.225 µg/L) were registered in the SC of this zone.

The maximum values of the relative content of PCB congeners in SC were noted for PCB 44 and 155; “marker” congeners PCB 52 and 138 were registered in the amount of 100 and 15%, respectively, as well as dioxin-like PCB 118 (39%). These isomers were present in the SC of Talgar and Kapshagay cities.

In the snow water of small settlements, the content of PCBs reached 0.192 and 0.205 µg/L. The dominant position in relative concentration had light congeners PCB 44 (up to 97 and 100%) and PCB 49 (up to 77%) and also PCB 151 (from 64 to 100%). The only case of the presence of dioxin-like congener PCB 118 was noted at the point close to the territory of Almaty city.

Based on the 2019 results, we note a relatively low level of agglomeration SC contamination from the studied pollutants. The maximum concentrations of PCBs in the SC of certain points in the territory of Almaty and small towns were 0.140 and 0.148 µg/L during the first survey and 0.039 and 0.044 µg/L during the second.

A decrease in the level of SC pollution by PCBs in 2019, compared with the data received in 2018, can presumably be explained by the fact that the winter of 2019 in the studied region was characterized by little snow and frequent thaws. As a result, fresh precipitation which was less exposed to the influence of local sources of pollution was taken for analysis. The indicator congener PCB 101 (0.017 µg/L) and dioxin-like congener PCB 114 (0.038 µg/L) were registered in the SC of two points in the urban area. In the SC

of Almaty city, which is the center of the agglomeration, we detected the dominance of the highly toxic dioxin-like isomer PCB 114 at 53% (Figure 5).

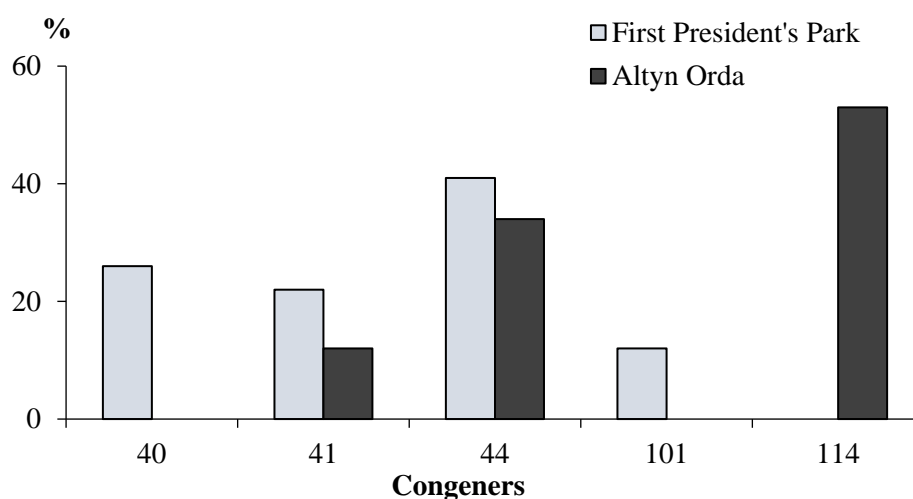


Figure 5. Relative content of PCB congeners in the SC of Almaty territory.

The PCB concentration distribution in the SC of the entire territory of the AA in 2020 (Figure 5) showed that PCBs were registered in the SC at 27 out of 41 sampling points. Out of seven points chosen in 2020 in the mountainous area, PCBs of 0.038 $\mu\text{g/L}$ were found only in the snow of the ski resort “Shymbulak” (Figure 6).

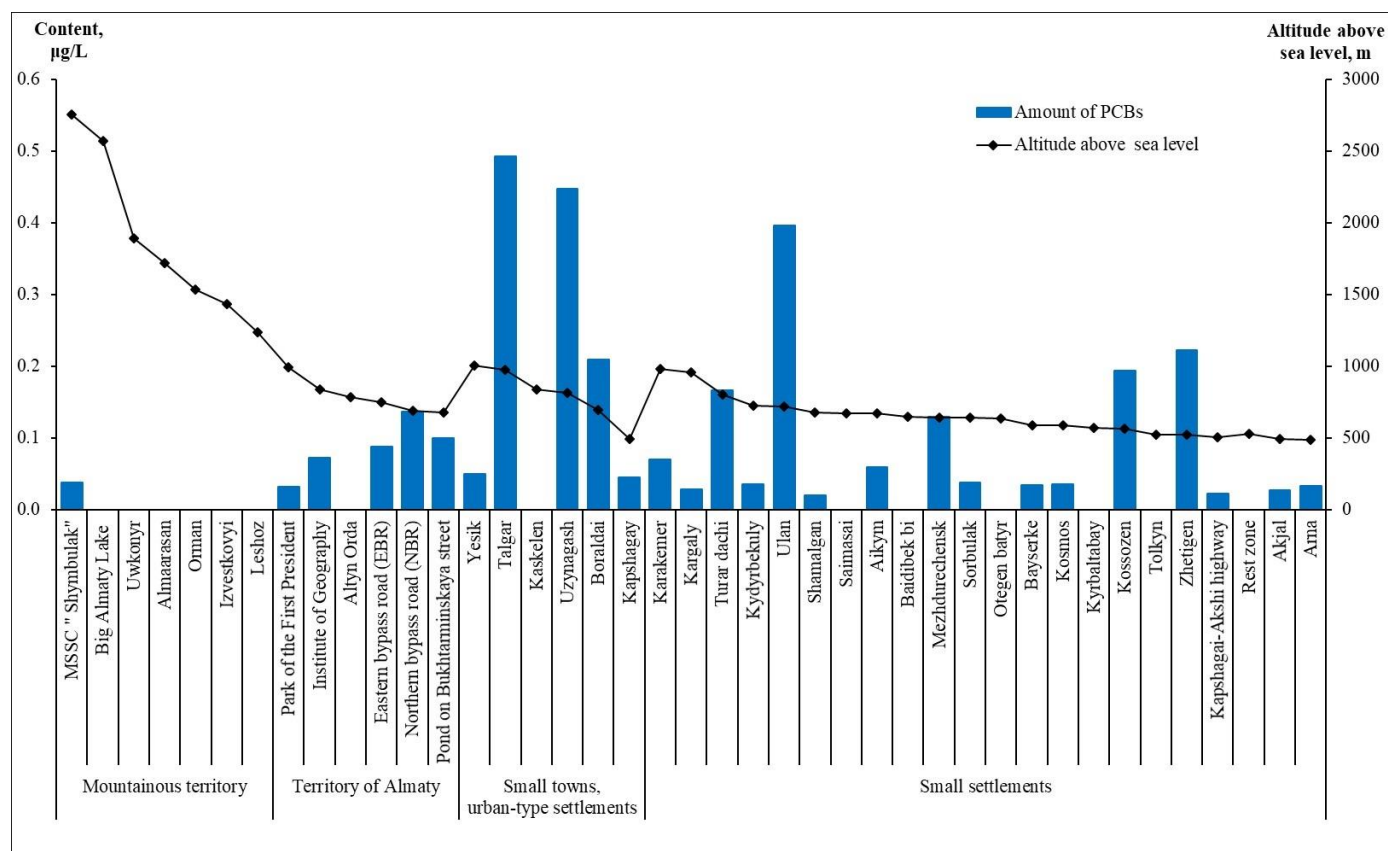


Figure 6. Content of PCBs in the snow cover of Almaty agglomeration (AA) depending on the altitude.

Such relatively high concentrations can be attributed to the fact that the ski resort “Shymbulak” is situated closer to the territory of Almaty city compared to the other sampling points, which are situated at a considerable distance in the east and south-west directions from the ski resort. Consequently, convective air flow from the mountain valley circulation raises polluted aerosols above the city to the ski resort altitude and to the higher layers of the atmosphere. At the same time, solid precipitation in this zone accumulates a certain part of the pollutants, including PCBs.

As shown in Table 3, the average PCB content in the SC of Almaty city in 2020 was 0.071 µg/L. This was the highest average concentration of PCBs (0.207 µg/L), which turned out to be a characteristic of the SC of small towns and urban-type settlements zones. The highest content reached 0.209, 0.447, and 0.492 µg/L in the SC of Boraldai village, Talgar city, and Uzynagash village, respectively (Figure 6).

Pollution sources of the SC of these settlements resulted from emissions from industrial facilities and from the Central Heating and Power Plant Number 2 located close to Boraldai village.

PCBs were registered in the SC of 16 small settlements (SS) out of 22 surveyed. Their highest concentrations were in the SC of Ulan village (0.396 µg/L). The average toxicant content indicators in the SC of this zone (0.068 µg/L) were approximately equal to those of the territory of Almaty city in 2020. Possible pollution sources of the SC of this zone include the production facilities of small- and medium-sized businesses, autonomous utilities often operating on high-ash coal (up to 40%), and railway and coal handling facilities. The atmospheric transport of pollutants from the territory of nearby cities such as Almaty and others is not excluded.

In 2020, PCB congener composition in the AA did not differ significantly from that observed in 2019. In total, seven individual PCB congeners were registered. Light congeners 44 and 49, which belong to the homologous group of tetrachlorobiphenyls, were dominant. The relative share of PCB 44 congener in the urban area ranged from 35 to 53% (Figure 7). The most toxic congener PCB 114 was present in the SC of the Northern bypass road in an amount of 33%.

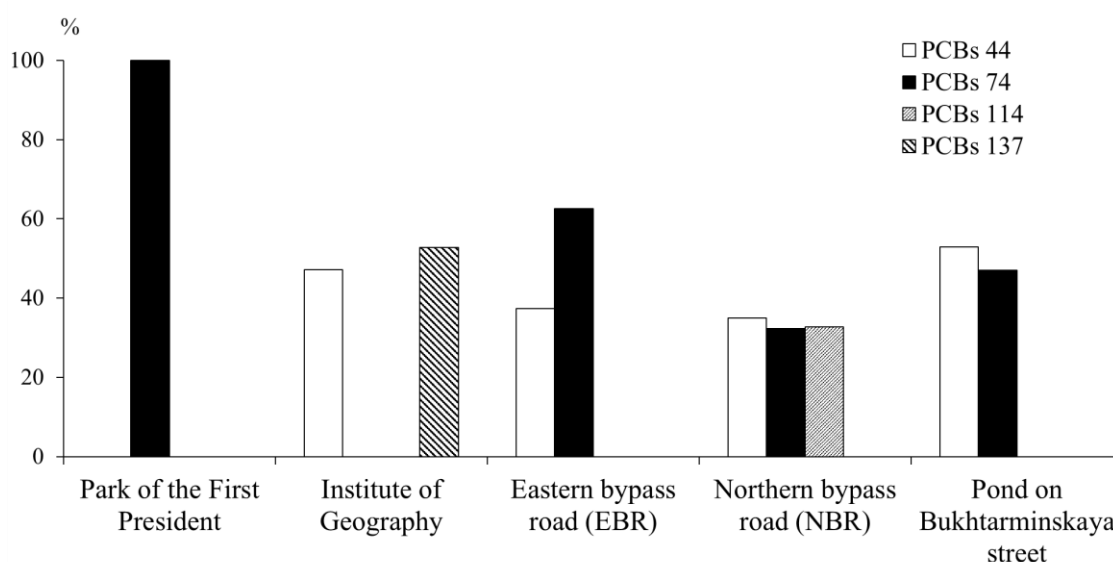


Figure 7. Relative content of PCB congeners in the snow cover of Almaty city in 2020.

According to studies in this field, the content of POP compounds in precipitation is influenced by two main types of pollution sources: local sources and global transport [32]. The predominance of low-chlorinated congeners (dichlorobiphenyls and trichloro-

biphenyls) in the composition of PCBs indicates the long-range transport of toxicants to the sampling area [59–61]. The dominance in the total concentration of PCBs of congeners belonging to the homologous group of tetra-, penta-, and hexachlorobiphenyls indicates a similar composition of the detected PCBs with the composition of the main mixture “Sovol”, which was used in the Soviet Union [50]. Therefore, this indicates the participation of mainly local or regional pollution sources in the sampling area for forming PCB composition. The coverage of the territory including a large number of snow sampling points allowed us to study the toxicants’ distribution in characteristic zones, i.e., urban, mountainous, and flat areas, with different anthropogenic loads to reach a relatively detailed conclusion.

3.3. Pollution of Snow Cover by Polychlorinated Biphenyls in the Territory of Ili River Delta and Ili-Balkhash State Natural Reserve (2021)

The objects of the study in 2021 were the delta of the Ili River and the territory of the State Nature Reserve “GNR Ili-Balkhash”, with a total area of 415 thousand hectares, situated in south-eastern Kazakhstan. The reserve is located in the ancient delta of Ili River and the southern Balkhash Lake region (Figure 8). The study aimed to obtain scientific data on the level of SC contamination by PCBs in this vast and important natural area, which had not been previously studied regarding this issue.

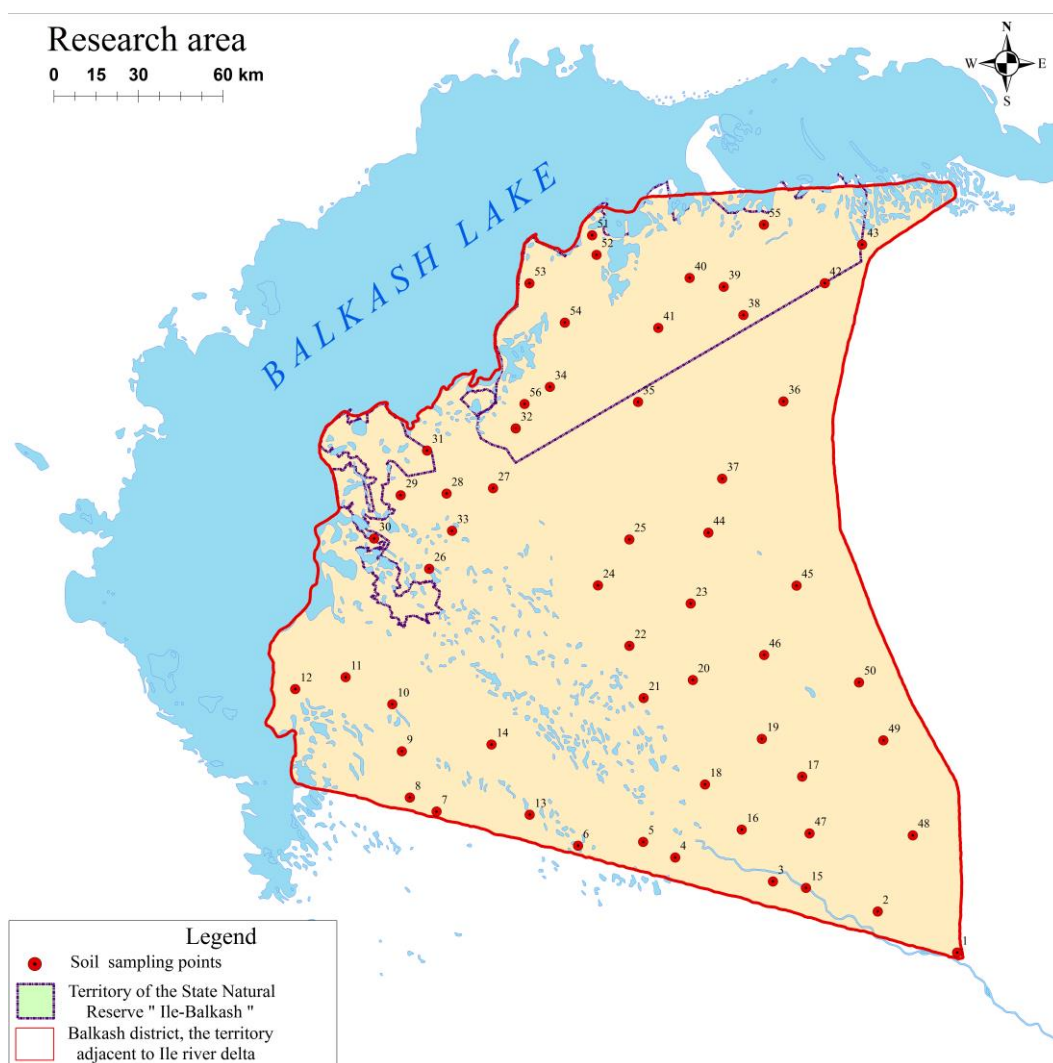


Figure 8. Delta of Ili River and the territory of “Ili-Balkhash Lake” reserve (authors Madibekov A.S., Zhadi A.).

According to the obtained data, it should be noted that PCBs were registered in the SC of all sampling points. The total concentration of PCB in the SC of the Ili River Delta was in the range of 0.088–0.397 µg/L. At the points located in the Ili-Balkhash Lake SNR zone, the content of toxicants in snow water reached 4.750 and 20.71 µg/L. Such a high concentration of PCB, according to our studies, was not registered on the northern slope of the Ili Alatau Mountains or in the territory of the Almaty agglomeration. The average concentration of PCB in the SC of the entire study area, excluding two samples with a high content of the toxicant, was 0.227 µg/L.

In the upper part of the Ili River Delta, there were areas with higher values of the total concentration of PCBs. The largest number of congeners (seven) from all the taken samples, including strictly controlled “marker” (PCB 153) and highly toxic dioxin-like (PCB 105) congeners, were found here.

Twenty-five PCB congeners in total were registered in the SC of this study area. In certain samples, their number varied from 1 to 7. A more frequent presence in snow water is typical for light congeners PCB 44 (53%) and PCB 97 (82%), which are included in the homologous groups of tetra- and pentachlorobiphenyls. The relative proportion of the founded PCB isomers was between 6% and 12%.

In the snow samples of the study area, the more toxic PCB congeners were “marker” PCB congeners 52, 138, 153, and dioxin-like PCB 105 and 114. The congeners of the first group were founded in SC with concentration ranges of 0.027 µg/L to 0.082 µg/L, while dioxin-like ones were found in concentration ranges of 0.058 to 0.068 µg/L. It is known that the level of general toxicity of the total concentrations of PCB depends mainly on the congener content belonging to the categories of “marker” and dioxin-like congeners, which have higher toxic properties.

The highest relative content of dioxin-like congeners PCB 105 and 114 was noted in snow water (up to 25%), and the relative proportion of “marker” PCBs 52, 138, and 153 reached 21%. In the SC of certain points of the delta, the sum of “marker” and dioxin-like congeners was 43% and 38%, respectively. Therefore, those samples can be considered the most toxic. Among the samples with a high toxicity level are the samples at certain points of the Nature Reserve that had the highest total concentrations of PCBs.

Thus, the SC of the territory of the Ili River Delta and “Ili-Balkhash Lake” reserve is contaminated to highly contaminated by PCBs.

The main reason for the rather high PCB pollution of the SC of the considered territory is the long-term exposure of the north-western Balkhash region (including Balkhash Lake) to the anthropogenic load due to many large sources of PCB pollution. According to the available official data, the largest volume of contaminated soil is concentrated in the territory of former and existing military bases such as “Daryal-U” and other military training grounds of the Russian Federation, located near the Balkhash Lake coast [42,62]. Heavily polluted soils with PCB content of up to 50 mg/kg are located near the shore zone of the lake. The atmospheric transfer of the toxicant to the adjacent territories from these sources seems to be the major cause of pollution of natural objects in the region. It is also impossible to exclude the influence of sources available in the foothill territory (cities, industrial and energy facilities, urban wastewater storages) on the ecological condition of the natural objects of the Ili-Balkhash basin.

4. Discussion

Considering the importance and need to fulfill the obligation to monitor persistent organic pollutants, particularly polychlorinated biphenyls, we concentrated on the implementation of the plans of the Stockholm Convention for the assessment of PCBs in the environment [63–65]. Thus, the results of this study will fill the gaps both in this field of research and in the study area that have arisen as a result of the absence of state monitoring of the mentioned toxicants in Kazakhstan. Therefore, this study will help to ensure the protection of the population and the environment against the adverse effects of such compounds. To solve these problems, the authors systematized observations, selected

optimal methods, and studied the experience of PCB monitoring in other countries [66–68]. Data on the presence of PCBs in snow cover were first identified during the implementation of several scientific projects, for example: “Monitoring of the level of concentration and distribution of toxic compounds in snow cover in the territory of Almaty agglomeration and assessing their impact on natural objects”, carried out within the frames of grant funding number AP05133353 (2020) and “Geoenvironmental Monitoring of Depositing Environments in the Territory of Ili River Delta and State Natural Reserve “Ili-Balkhash”, carried out under grant funding number AP09260361 (2021). These projects were essentially innovative, differed in their complexity, and covered large areas and various natural landscapes, including urbanized areas. A wide range of determined parameters were studied, including PCBs. However, when carrying out research in the frame of the mentioned projects, it was also noticeable that, at the present stage, the processes of exchange and access to information were poor. Researchers have to solve the problem of access to information on their own. As a result, interested participants are not provided with access to social–economic and environmental information, and the objectivity of decisions made at all levels of administration leaves much to be desired. There is a significant lack of information and lack of awareness among decision-makers and the public. Among other problems, one can also note the low efficiency of the system for the protection of aquatic ecosystems, based mainly on measures of prohibitions and restrictions. In this regard, the authors believe that efforts should be directed towards effective public participation in activities related to the implementation of the Stockholm Convention, and a complete inventory of PCBs through the implementation of larger research projects should be established. The disadvantages of the performed work are that these projects do not include issues of soil and water remediation because of limited capacity. This should be a task for future research.

Despite the mentioned disadvantages, the resulting picture of PCB distribution allows us to show the significant influence of local air transport on significant pollution from local sources, considering the significant influence of climatic factors (temperature, direction of prevailing winds, moisture) on the features of the congener-specific distribution of toxicants under various conditions. Clarification is required for the higher concentrations of PCBs found on the east coast of the Balkhash Lake compared to the territory of the Almaty agglomeration. Whether such an increase in concentration is a consequence of growing technogenic load or whether the reason lies in the features of the redistribution of toxicants within the ecosystem remains to be determined. In general, snow cover is a convenient accumulative matrix for assessing air pollution during the winter period. Such investigations also make it possible to detect sources of pollutants in the controlled area. Taking into account the status of the study area, including the unique Lake Balkhash, it is necessary to carry out systematic research on PCBs, including an additional inventory of PCB-containing equipment.

5. Conclusions

Considering the presence of PCBs in the snow cover, it can be concluded that there is a threat of contamination to the whole ecosystem of the study area. It is necessary to strengthen the monitoring control of PCBs to prevent their release into the environment. All possible methods of research, education and enforcement should be used in this case. Due to concern about the impact of POPs on public health and the environment, the authors of this manuscript consistently carry out research to deliver complete, reliable and timely information to the public on POP issues. The results of the study show the PCB contamination of the SC within the whole studied territory of southeastern Kazakhstan. This endangers the population of many cities and settlements, as well as objects of the agrarian–industrial complex. The largest sources of PCB contamination are located at the north-western coast of the Lake Balkhash and within the northern slope of the Ili-Alatau Mountains. They continue to negatively affect the natural environment of this region.

The results of the study show the need to devote large, comprehensive research programs to the problem of POPs for a scientifically based assessment of the PCB pollution level of water, biological, and food resources, especially within the existing eight “hot spots” and trans-boundary basins to mitigate the existing danger to the population of Kazakhstan and to develop measures to protect the environment from these xenobiotics.

The active work of state environmental protection agencies is required to establish the control and systematic monitoring of the mentioned toxicants. The state bodies for nature protection, including the Ministry of Ecology, Geology and Natural Resources of the Republic of Kazakhstan, are recommended to take measures to assess the level of PCB pollution of natural objects and large industrial cities with the involvement of the RSE “Kazgidromet”. This is to assess the impact on the water resources of highly contaminated PCB “hot spots” existing in Kazakhstan.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app12178660/s1>. Supplementary material provides an example of a PCB test result (chromatograms).

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Institutional Review Board Statement: We did not use humans or living animals in the research process. For the analysis, individual dead fish samples were used to analyze their contamination with toxicants.

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