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Spatial and Temporal Variations of Polychlorinated Biphenyls and Organochlorine Pesticides in Snow in Eastern Siberia

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Abstract: This study evaluated the spatial and long-term variations of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in the snow at 55 industrial, urban, rural, and remote stations in Eastern Siberia, Russia, in 2021 in comparison to data obtained from the 1990s to the 2010s. In 2021, the mean levels of the organochlorine compounds in snow amounted to 76 ng/L $\sum PCB_{36}$, 5.8 ng/L hexachlorobenzene (HCB), 0.02 ng/L α-hexachlorocyclohexane (HCH), and 1.01 ng/L dichlorodiphenyltrichloroethane (DDT) and its metabolites. The spatial distribution of organochlorines was shown to result from the presence of industrial and urban sources, as well as atmospheric transport. The PCB and HCB temporal distributions from the 1990s to the 2020s were represented as V-shaped curves. The PCB homological patterns show that, in some of the samples, the abundance of lower chlorinated homologues in 2021 is greater than in previous years. Over the last three decades, the HCH and DDT levels have significantly decreased. The relationship between PCBs and suspended particulate matter became stronger with the increase in PCB chlorination levels from lighter to heavier chlorinated congeners. Deposition with wet precipitation in the wintertime provided 3–8% of the annual deposition flux. Massive POP deposition with wet precipitation occurred in May (about 12–18%) and from July to September (60–65%).

Keywords: snow; persistent organic pollutants; Eastern Siberia; suspended particulate matter; deposition flux

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1. Introduction

Persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs), *p*,*p*′-dichlorodiphenyltrichloroethane (*p*,*p*′-DDT) and its metabolites, hexachlorocyclohexanes (HCH), hexachlorobenzene (HCB), and other organochlorine pesticides, are artificially created compounds that were not found in detectable quantities in the environment before their production and application by humans [1,2]. POPs are able to be transported over long distances via the atmosphere from the sources of their formation and/or application. POPs circulate in the abiotic components of the environment, are deposited from the atmosphere onto the soil, accumulate in the soil for some time, and then evaporate from the soil and are transported further into the atmosphere [3,4].

Snow cover is an indicator of land contamination by organic and inorganic pollutants [5–7], etc. Snow scavenges organic pollutants from the atmosphere more effectively than rain [8–10]. The removal of pollutants from the air occurs when organic compounds are incorporated into a snowflake as part of the core, forming ice, or as part of the cloud condensation nuclei that form the nuclei of supercooled water droplets [11]. Particles can be captured by falling snowflakes in the atmosphere when snowflakes filter the air away from the particles [11]. At high latitudes such as the Arctic and Antarctic areas, POPs are scavenged from the atmosphere by snowflakes and accumulate in preserved, non-melting snow cover. At lower temperate latitudes, snow is a transfer medium, scavenging POPs from the atmosphere during the cold season and supplying POPs to soils and water bodies, and partially to the atmosphere by evaporation, during snowmelt in the spring [10,12–14].

The industrial source of the PCBs, HCB and other industrial POPs in the Usol'e-Sibirskoe area, which affect the terrestrial environment of the adjacent territories, has been determined in previous studies [15,16]. There is also an accumulation of organochlorine pesticides (OCPs) in soil and agricultural products from the River Angara valley due to the application of OCPs in the past [17,18].

The first data on the OCP concentrations in the snow in the Lake Baikal Region, obtained in the 1980s, show the occurrence of these compounds, in spite of the fact that they were not officially applied there [19]. Atmospheric transport was suggested as a source of the pesticides in the background area of Lake Baikal and its adjusted protected areas [19]. In subsequent decades, investigations of POPs in snow water were performed in natural and anthropogenically modified environments in the southern part of Irkutsk Region, Eastern Siberia in 1994, 1996, 2003, 2009, 2011, and 2016 [16,20–24].

The aim of the study is to the present spatial and temporal variations of PCBs and OCPs in the snow cover of the southern part of Irkutsk Region, Eastern Siberia for the last three decades. We also focused on the relationship between POPs and suspended particulate matter in the precipitation in the winter, as well as on the access of the daily, monthly, and annual wet deposition fluxes of POPs. Data for non-Aroclor PCB-11 in snow were also obtained.

2. Materials and Methods

2.1. Sampling Location

The region under study is located in the southern part of the Irkutsk-Tcheremkhovo plain in the south of Irkutsk Region, along the valley of the River Angara outflowing from Lake Baikal, Eastern Siberia. The climate is sharply continental, with severe, prolonged low-snow winters with weak winds and frequent inversions of air temperature, and with warm summers with heavy precipitation and increased wind activity [25,26]. The prevailing wind directions are west and northwest [27].

The area consists of a zone of intensive industrial development including the regional center of Irkutsk, the towns of Angarsk, Schelekhovo, and Usol'e-Sibirskoe, and their districts, with a population amounting to over 1.1 million people out of the total population (2.3 million) in Irkutsk Region. Here, there are enterprises of the basic sectors of the economy of Irkutsk Region (oil refinement, the chemical industry, non-ferrous metallurgy, mechanical engineering, the production of building materials, etc.) [28]. The agricultural areas and territories of increased environmental requirements, including the towns of Baikalsk and Sludyanka, were amongst the areas under investigation as well.

In the southern part of Irkutsk Region, several enterprises have been founded in the last century and have stopped production at different times [29]. Currently, the hazardous waste and polluted industrial areas resulting from these enterprises pose a major problem. The chemical complex of Usol'ekhimprom is one such enterprise [30]. The industrial area of Usol'ekhimprom is located in the north-west of the residential area of the town of Usol'e-Sibirskoe. The enterprise of Usol'ekhimprom was founded in the 1930s and specialized in the production of organochlorine synthesis compounds, caustic soda, organosilicon synthesis products (varnishes and paints), etc. [30]. Until the 1980s, the town of Usol'e-Sibirskoe was one of the five most developed towns of Irkutsk Region. It accounted for about 10% of the overall industrial production in the region [29]. In the 2000s, the share of Usol'e-Sibirskoe already accounted for 2.1% of the overall regional volume of goods and services [29]. In the 1990s, the environmental pollution of the areas around the Usol'ekhimprom was revealed, which, in turn, led to the cessation of caustic soda production via mercury electrolysis [31]. In 2012, the operation of Usol'ekhimprom was completely stopped, and the enterprise was terminated. Since 2020, efforts to eliminate the accumulated environmental damage in the industrial area of Usol'ekhimprom have been made [32,33].

2.2. Snow Sampling

Fifty-five snow samples were collected in the late winter, not long before the beginning of intensive snowmelt (15–26 February 2021), from fifty-five stations along the roads running in the Irkutsk–Listvyanka, Irkutsk–Sludyanka, Irkutsk–Bayanday, Irkutsk–Bolshoe Goloustnoe, and Muruy–Zalary–Balagansk directions and within the towns of Irkutsk, Schelekhovo, Angarsk, Usol'e-Sibirskoe, Tcheremkhovo, and Baikalsk (Figure 1). The scheme of snow sampling established in 2021 takes into account the snow monitoring performed in 1994–1996 [20,21,34], changes made in 2003 within the framework of the INTAS 2000-00140 project [22], and additions in accordance with the simultaneous study of POPs in the atmospheric air and snow cover in the settlements of Irkutsk Region in the 2000s and the 2010s [23,24] (Figure 1). The snow was sampled with a metal shovel to the depths of the snow cover and stored in a polyethylene bag in an unheated location prior to analysis. Snow samples taken at stations outside of settlements were collected at least 100 m away from any roads and construction. The snow in settlements was sampled in recreational or residential areas of those settlements. Snow near the industrial area of Usol'ekhimprom was additionally sampled.

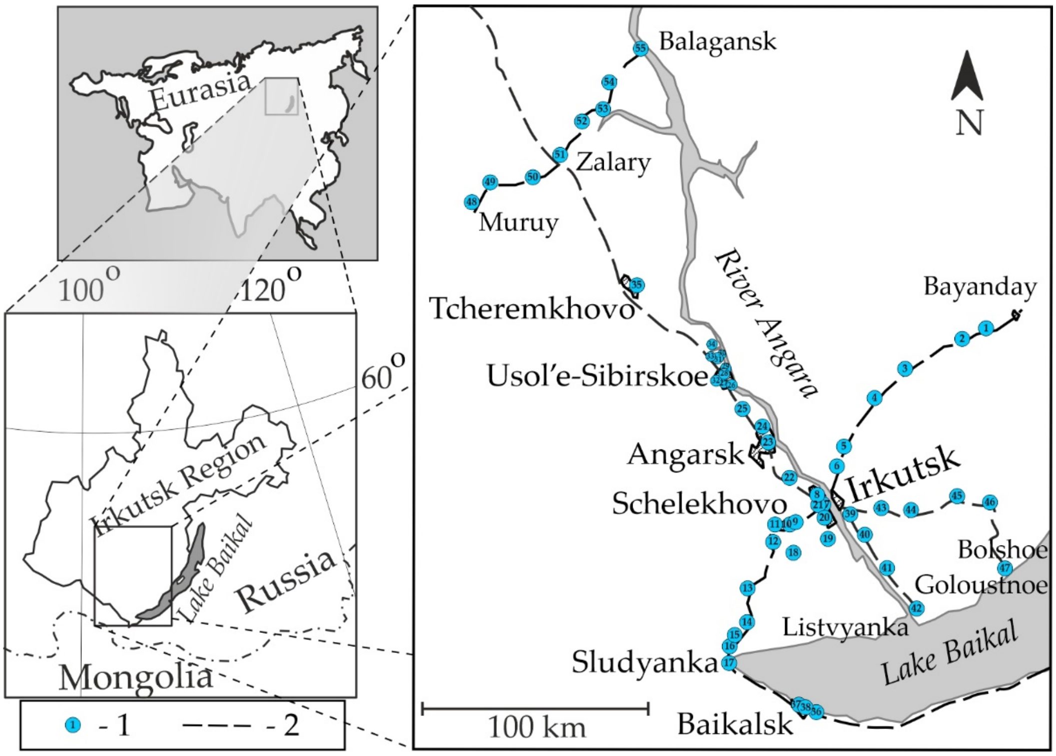

Figure 1. The scheme of snow sampling in the south of Irkutsk Region in 2021 (1—sampling site with the station number, 2—roads).

2.3. Sample Pretreatment and Analysis

OCP and PCB analyses were performed in the laboratory of the Institute of Geochemistry in Irkutsk using the method described in [17,35].

The snow samples were melted at room temperature. For melting, the snow samples were transferred in a metal reservoir, which was pre-washed with soap and water and rinsed with *n*-hexane:acetone (1:1). An amount of 0.9 L of snow water was transferred to a dark glass bottle, mixed with surrogate (35.7 ng PCB-14) and internal (15.2 ng PCB-65) standards, and extracted thrice using 20, 15, and 15 mL of dichloromethane, sequentially. Extracts of the snow samples were dried over Na_2SO_4.

The extracts of snow were cleaned using two liquid chromatography columns: a gel permeation chromatography (GPC) column filled with bio-bead S-X3 and a chromatographic column containing silica gel (3 g, activated at 400 °C), aluminum oxide (3 g, activated at 850 °C), and Na_2SO_4 (3 g). Large molecules in the extract were separated by a GPC column (fraction 1). Fraction 2 was eluted from the GPC column with 100 mL of DCM:hexane (3:7 *v*/*v*), which contained PCBs and OCPs. Fraction 2 was evaporated to 1–2 mL. In the next step, the extract was further purified on a column consisting of Al_2O_3–silica gel–Na_2SO_4. The columns were conditioned using 40 mL of DCM, followed by 10 mL of n-hexane. The sample extracts were loaded and eluted with 12 mL of n-hexane, followed by 40 mL of DCM/n-hexane (1:9 *v*/*v*). To prepare for gas chromatography, the fraction containing PCBs and OCPs was evaporated to 1 mL with a rotary evaporator, and then reduced further to a volume of 30 µL using a stream of nitrogen.

GC/MC analyses were performed on a Chromatec Crystal 5000 (Russia) gas chromatograph with a mass spectrometer operating in selected ion monitoring (SIM) and electronic ionization mode equipped with a DB-5 capillary column (J&W Scientific, Folsom, CA, USA; a 0.25 µm film thickness, a 0.25 mm inner diameter, and a 60 m length). The column temperature program started at 90 °C (2 min hold), increased to 170 °C at 22 °C min^{-1} and then increased to 265 °C at a rate of 1.3 °C min^{-1} (35 min hold). The temperature of the injector port was 270 °C. The transfer line and ion source temperatures were 265 and 200 °C, respectively. The carrier gas was He at a constant flow rate of 1 mL/min.

PCBs and OCPs were quantified in selective ion monitoring mode using characteristic ions (Table S1). All samples were analyzed with up to 36 congeners of PCBs including six indicator PCB congeners (IUPAC no.: 28, 52, 101, 153, 138, 180), hexachlorobenzene (HCB), *p,p*′- dichlorodiphenyltrichloroethane (*p,p*′-DDT), *o,p*′-dichlorodiphenyltrichloroethane (*o,p*′-DDT), *p,p*′-dichlorodiphenyldichloroethane (*p,p*′-DDD), *o,p*′-dichlorodiphenyldichloroethane (*o,p*′-DDD), *p,p*′-dichlordiphenyldichlorethylene (*p,p*′-DDE), *o,p*′-dichlordiphenyldichlorethylene (*o,p*′-DDE), α-, β, γ, and δ-isomers of hexachlorocyclohexane (HCH), heptachlor, aldrin, dieldrin, and endrin.

All solvents used were distilled and checked for interference prior to use. Standards of individual PCB congeners including PCB-65 and PCB-14 as internal and surrogate standards, the PCB mixture, and the OCP mixture were purchased from the Dr. Ehrenstorfer Laboratory (Ausburg, Germany). Aluminum oxide and silica gel for column chromatography were purchased from MERCK (Darmstadt, Germany).

In addition, the suspended particulate matter (SPM) in the snow water was determined by the method described in [20,36], which is filtration through nitrate cellulose membrane filters with a pore diameter of 0.45 µm.

2.4. Quality Control and Quality Assurance (QA/QC)

The PCBs and OCPs were quantified based on a ±3 s retention time between the analyte and the standard; the ratio of quantifier to qualifier ions had to be within ±15% of the theoretical values; the signal-to-noise ratio had to be at least 3.5; response factors were obtained from the standards for the individual compounds and the concentration of the internal standard (PCB-65).

Method recoveries were determined using spiked samples. They lay between 70% and 130% for the OCPs and 77% and 117% for the PCBs, with the only exceptions being β-HCH (3%), endrin (163%), *p,p*′-DDD (161%), *o,p*′-DDE (178%), *o,p*′-DDD (142%), and PCB-47 (67%). The β-HCH was excluded from consideration. Corrections for recoveries were not made.

Laboratory blanks were run with each batch of 10–12 samples to estimate the purity of the reagents and instruments. Only samples in which the level of the analyzed compound exceeded the level of the blank 3.5 times were taken into consideration. Corrections for blanks were not made. Method detection limits (MDLs) were derived from the blanks and quantified as the average of the blanks plus three standard deviations. The MDLs ranged between 0.003 and 0.069 ng/L for the OCPs and between 0.001 and 1.1 ng/L for the PCBs (depending on the congener) (Table S1). Concentrations below MDL were set to 1/2 MDL for the calculation of the sum, average, median, and standard deviation and for the statistical analysis. The recoveries for the PCB-14 surrogate that was added to each sample amounted to 50–138% (mean: 80%). No correction was applied to the samples.

2.5. Data Analysis

The suspended particulate matter (SPM) and organochlorine compound concentrations were expressed and discussed as ng (mg) per liter and ng (mg) per square meter (m^2).

The deposition fluxes of the POPs were calculated by two methods:

The first method was adapted from the calculation of the "dust load" or "SPM load" which is the ratio of the weight of the SPM in the snow sample to the square per the number of days from the date of a stable snow cover establishment to the date of snow sampling [37]. The "POP load" or daily deposition flux equation is as follows:

$$Load_{POPs} = \frac{C}{(S \times t)},$$

where $Load_{POPs}$ is the POP load or daily deposition flux (ng/m^2), C represents the POP levels (ng/m^2), S is the square (m^2), and t is the number of days from the date of a stable snow cover establishment to the date of snow sampling.

The second method included the calculation of annual and monthly POP deposition fluxes with all types of wet precipitations. These values were calculated as concentrations on the square (ng/m^2) multiplied by the annual and monthly precipitation volumes (mm) and divided by the snow water equivalent (SWE, mm) at the time of sampling.

Meteorological parameters, including the annual and monthly precipitation volumes, and the characteristics of the snow cover (the date of a stable snow cover establishment) in the town of Irkutsk and the settlement of Bolshoe Goloustnoe were downloaded from the Federal Service for Hydrometeorology and Environmental Monitoring website (Roshydromet) [38,39].

2.6. Statistical Analysis

Statistical analyses were performed using STATISTICA 6.0 software for Windows. The concentrations of PCBs, OCPs, and particulate matter were reported as the mean and median, with the standard deviation (SD), standard error (SE), and ranges. For statistical analyses, the data were ln-transformed. The significance of the difference in the POP levels in snow from different sampling profiles or settlements was assessed using Student's *t*-test in independent groups. Linear regression was used to analyze the dependence of the POP levels on the SPM concentrations in snow water. The Spearman test was conducted to evaluate the correlations between compounds found in the snow. The relative PCB homological patterns were analyzed using the cluster method. A confidence level of $p < 0.05$ was used as the criterion for statistical significance.

3. Results and Discussion

3.1. Characteristics of Snow Cover at the Time of Sampling in 2021

The characteristics of snow cover, including height, density, snow water equivalent (SWE), and suspended particulate matter (SPM), are presented in Table S2. The distribution of snow cover height and SWE on the area investigated was typical of Irkutsk Region [25,26]. The spatial distribution and values of the SPM concentrations are in line with the results obtained in our previous studies at the same location [16,20–22]. More information on the characteristics of the snow cover is presented in the Supplementary Material (Text S1).

3.2. Organochlorins Levels in Snow from the Southern Part of Irkutsk Region and Its Comparison with Data from Other Locations

Individual PCB congeners levels above MDL were found in 12–100% of the snow water samples with the exception of PCB-126, 169, 196, and 194, which were determined in a few samples. HCB, *p,p′*-DDE, and *p,p′*-DDT levels above MDL were determined in 96%, 91%, and 82% of samples, respectively, followed by *o,p′*-DDT, *p,p′*-DDD, α-HCH, and *o,p*′-DDD (48%, 16%, 5%, and 2%, respectively). γ- and δ-isomers of HCH, *o,p*′-DDE, heptachlor, aldrin, dieldrin, and endrin levels below MDL were found in every sample.

In 2021, the mean levels and ranges of the organochlorine compounds in the snow amounted to 70 ± 89 (9–628) ng/L for total PCB_{36}, 0.62 ± 1.44 (bdl–7.39) ng/L for HCB (without highest value), 0.02 ± 0.09 (bdl–0.66) ng/L for α-HCH, and 1.01 ± 1.44 (bdl–9.8) for the sum of DDT and its metabolites (Table 1).

Table 1. The mean, median, range (min-max), standard deviation (SD), and standard error (SE) of organochlorines levels in snow found in 2021 (ng/L and ng/m^2).

Compound	Mean	Median	Min–Max	SD	SE	Mean	Median	Min–Max	SD	SE
			ng/L					ng/m^2		
HCB	5.80	0.15	bdl-286	38.8	5.28	341	9.51	bdl-16,700	2270	309
HCB *	0.62	0.15	bdl-7.39	1.44	0.19	33	9.50	bdl-360	77	10
α-HCH	0.02	0.01	bdl-0.66	0.09	0.01	0.70	0.42	bdl-11.8	1.59	0.22
p,p′-DDT	0.51	0.24	bdl-8.47	1.17	0.16	21	14	bdl-260	36	4.92
p,p′-DDE	0.40	0.33	bdl-1.52	0.34	0.05	20	18	bdl-66	16	2.11
p,p′-DDD	0.01	0.004	bdl-0.07	0.01	0.002	0.48	0.23	bdl-2.88	0,65	0.09
o,p′-DDT	0.09	0.002	bdl-0.87	0.15	0.02	4.61	0.18	bdl-22	6.81	0.93
o,p′-DDD	0.01	0.004	bdl-0.06	0.01	0.002	0.31	0.23	bdl-3.81	0.51	0.07
∑DDTs	1.01	0.66	bdl-9.80	1.44	0.20	47	37	bdl-301	47	6.42
PCB-8	4.24	2.22	bdl-23	5.07	0.68	245	120	bdl-2470	382	51
PCB-11	0.22	0.22	bdl-0.85	0.22	0.03	12	9.80	bdl-66	14.0	1.88
PCB-31	8.77	3.92	bdl-58	10.9	1.46	501	272	bdl-5950	857	116
PCB-28	11.7	4.9	bdl-76	14.2	1.9	642	342	bdl-5870	918	124
PCB-52	5.06	3.75	0.76–36	5.65	0.76	294	185	24–2400	382	52
PCB-49	2.04	1.36	bdl-12.4	2.19	0.30	115	71	bdl-726	138	19
PCB-47	0.37	0.27	bdl-1.90	0.38	0.05	21	14.2	bdl-127	24	3.27
PCB-44	2.51	1.82	0.46–11.5	2.29	0.31	144	96	12–771	153	21
PCB-74	2.00	1.33	bdl-16.5	2.52	0,34	116	76	bdl-1105	168	23
PCB-66	0.38	0.27	bdl-2.57	0.49	0.07	22	14.9	bdl-170	31	4.16
PCB-91	0.63	0.39	bdl-7.31	1.06	0.14	36	21	bdl-427	64	8.67
PCB-56	0.10	0.07	bdl-0.84	0.15	0.02	5.70	2.93	bdl-49	9.04	1.22
PCB-101	5.29	3.24	0.45–66	9.41	1.27	303	164	23–3880	566	76
PCB-99	4.35	2.87	0.39–38	5.93	0.80	248	145	26–2220	364	49
PCB-97	1.30	0.81	bdl-18.6	2.55	0.34	73	40	bdl-1090	151	20.4
PCB-87	0.18	0.11	bdl-2.56	0.35	0.05	10	5.4	bdl-150	21	2.81
PCB-85	1.11	0.65	bdl-14.2	2.00	0.27	63	35	bdl-833	119	16.1
PCB-77	0.08	0.04	bdl-0.66	0.11	0.02	4.06	2.29	bdl-20	5.23	0.71
PCB-110	4.70	2.80	0.36–72	9.75	1.31	268	142	19.8–4210	577	77.8
PCB-149	1.37	0.63	bdl-31	4.14	0.56	76	36	bdl-1810	242	32.6
PCB-118	5.02	2.85	0.41–81	10.9	1.47	283	159	17.7–4740	639	86.2
PCB-153	2.09	0.96	0.09–47	6.27	0.85	117	55	5.0–2730	365	49.2
PCB-132	0.60	0.23	bdl-15.6	2.09	0.28	34	12	bdl-910	122	16.5
PCB-105	1.71	0.84	bdl-32	4.32	0.58	96	46	bdl-1880	252	33.9
PCB-141	0.26	0.05	bdl-7.87	1.06	0.14	14.2	3.04	bdl-460	62	8.36
PCB-138	3.10	1.17	0.11–78	10.5	1.42	174	65	6.7–4590	616	83
PCB-126	0.004	0.001	bdl-0.14	0.02	0.003	0.21	0.05	bdl-8.21	1.10	0.15
PCB-187	0.08	0.002	bdl-3.11	0.42	0.06	4.44	0.12	bdl-182	24.6	3.31
PCB-183	0.06	0.005	bdl-2.30	0.31	0.04	3.38	0.29	bdl-134	18.1	2.45
PCB-128	0.49	0.16	bdl-14	1.89	0.25	27	8.31	bdl-816	110	14.8
PCB-177	0.04	0.001	bdl-1.93	0.26	0.04	2.49	0.04	bdl-113	15.3	2.06
PCB-156	0.22	0.003	bdl-8.09	1.10	0.15	12	0.19	bdl-473	64	8.65
PCB-180	0.26	0.001	bdl-9.63	1.30	0.18	14	0.09	bdl-563	76	10.3
PCB-170	0.14	0.002	bdl-5.77	0.78	0.11	7.73	0.12	bdl-337	45	6.15
PCB-196	0.02	0.002	bdl-0.98	0.13	0.02	1.14	0.08	bdl-57	7.74	1.04
$\sum PCB_{36}$	70	46	9.0–628	89	12	3990	2620	274–36,700	5520	744
$\sum PCB_7$	27	18	3.1–228	33.5	4.5	1545	1060	93–13,350	2060	277

bdl—below detected level; * description statistic for the HCB dataset without one highest datum.

The PCB and OCP levels in the snow water found in our investigation were compared with values from other areas of the world in Tables 2 and 3.

Table 2. The comparison of PCB levels in snow water from different areas of the world.

Site of Sampling	Time of Sampling	Type of Area	Instrumental Method	Number of PCB Congeners	Total PCB, ng/L	Reference
Russia, Irkutsk Region	II.2021	industrial+ urban + rural + remote	GC-MS	36	70 (9–628)	this study
				6	27 (3–228)	this study
Spain, Pyrenees, Lake Redo	II.1998	remote	GC-MS	7	0.22	[40]
Alps, Lake Gossenkolle	III,V.1997	remote	GC-MS	7	0.73	[40]
Switzerland, Alps, Lake Jori III	II.1997, II.1998	remote	GC-MS	7	2.2	[40]
Slovakia, Lake Starolesnianske	III.1998	remote	GC-MS	7	0.2	[40]
Norway, Ovre Neadalsvatn	III.1997/1998	remote	GC-MS	7	0.73	[40]
Alps, Monte Rosa massif, Colle del Lys	VII.2003	remote	GC-MS	31	0.091	[41]
Slovakia, Tatra Mountains	IV.2005	remote	GC-µECD	7	0.55–1.63	[42]
Austria, Tyrolean Alps	III.2006	remote	GC-µECD	7	0.46–0.9	[43]
The East Rongbuk Glacier, Mt. Everest	IX.2005	remote	GC–HRMS	7	0.016 (0.003–0.048)	[7]
Russia, Moscow	III.2011	urban	GC-MS	13	280–560	[44]
Kazakhstan: -Talgar -Almata	2014–2015	urban	GC-ECD	16	120–800 nd-3790	[45]
Kazakhstan, Almaty	2018–2020	urban	GC-ECD	22	9–71	[45]
Kazakhstan	2021	remote	GC-ECD	25	88–397	[45]
Canada	III.1997	urban, industrial	GC-ECD	100	0.7–45	[46]
Minneapolis/St. Paul	winter 1991–1993	suburban	GC-ECD	87	7.9; 4.6; 1.9	[10]
Arctic, Russia, the Ob–Yenisey watershed	winter 1992–spring 1993	remote	GC-ECD+ GC–MS	9	0.5	[47]
	winter 1993–spring 1994		GC-ECD+ GC–MS	9	0.4	[47]
Arctic, Russia, Taimyr	1995	remote	GC-ECD+ GC–MS	7	0.005	[47]
Arctic, the Barents Sea and the North Pole area: -dissolved -particulate	VI–VIII.2001	remote	GC–HRMS	15	0.002–0.007; 0.001–0.002; 0.099	[48]
Finland, Pallas; Evo	III.2003, 2004	rural	HRGC–HRMS	7	0.264; 0.285	[49]
Canadian High Arctic	V-VI.2016	remote	GC-MS/MS	70	0.233–0.788	[50]
Antarctica, South Shetland Archipelago, King George Island	XI-XII.2007	remote	GC-ECD	51	0.156	[51]
	XII.2008	remote	GC-ECD	51	0.144	[51]
	II-III.2010	remote	GC-ECD	51	0.138	[51]
The western Antarctic Peninsula	X-XI.2010	remote	HRGC–HRMS	29	0.77 (0.3–1.1)	[52]
Antarctic (from Northern Victoria Land to the East Antarctic plateau)	austral summer 2011–2012	remote	HRGC–HRMS	127 7	0.11–0.58 0.018–0.19	[53]
Antarctic, South Shetland Archipelago, Livingston Island	XII.2014–III.2015	remote	GC-µECD	41	0.19 (0.078–0.417)	[54]

The PCB levels obtained in the urban, suburban, rural and remote areas of the southern part of Irkutsk Region in 2021 were found to be higher than the levels determined in the snow from the Arctic and subarctic regions [47–50], from Antarctica [51–54], and from high-mountain areas of Europe [40–43] and Asia [7]. The lowest PCB levels in snow from the southern part of Irkutsk region were observed at the stations along the road between the settlements of Muruy and Balagansk ($\sum PCB_{36}$ = 28.5 (9–52) ng/L) and at some stations in rural areas along the road from the settlement of Baynday to the town of Irkutsk ($\sum PCB_{36}$ =12–20 ng/L). These values were comparable to or higher than the levels found in the suburban areas of Minnesota [10]. The highest $\sum PCB_{36}$ levels were found in the snow from the industrial towns of the southern part of Irkutsk Region (Irkutsk: 68 (44–95) ng/L;

Angarsk: 119 (96–142) ng/L; Schelekhovo: 62 ng/L; Baikalsk: 83–102 ng/L; Tcheremkhovo: 44 ng/L; Usol'e-Sibirskoe: 162 (39–628) ng/L). These values were comparable to the levels in the snow cover from urban and industrial areas in Eurasia [44,45] and North America [46].

Table 3. The comparison of OCP levels in snow water from different areas of the world (ng/L).

Site of Sampling	Time of Sampling	N	∑DDTs	∑HCHs	HCB	Reference
Russia, Irkutsk Region	II.2021	industrial+ urban + rural + remote	1.01 (bdl-9.80) #	0.02 (bdl-0.66) **	5.8 (bdl-286)	this study
Spain, Pyrenees, Lake Redo	II.1998	remote	bdl	0.52 *	na	[40]
Alps, Lake Gossenkolle	III,V.1997	remote	0.33 @	1.1 *	na	[40]
Switzerland, Alps, Lake Jori III	II.1997, II.1998	remote	bdl	0.49 *	na	[40]
Slovakia, Lake Starolesnianske	III.1998	remote	0.073 @	0.022 *	na	[40]
Norway, Ovre Neadalsvatn	III.1997/1998	remote	bdl	bdl	na	[40]
Alps, Monte Rosa massif, Colle del Lys	VII.2003	remote	0.001 (nd-0.004)	0.088 (0.011–0.25) *	0.004 (0.003–0.006)	[41]
Slovakia, Tatra Mountains	IV.2005	remote	na	0.026–0.075 *	0.0034–0.0099	[42]
Austria, Tyrolean Alps	III.2006	remote	na	0.027–0.057 *	0.037–0.055	[43]
The East Rongbuk Glacier, Mt. Everest	IX.2005	remote	0.024 (nd-0.043)	na	0.033 (nd-0.14)	[7]
Arctic, Russia, the Ob–Yenisey watershed	winter 1992–spring 1993	remote	0.6 #	1.7	trace	[47]
	winter 1993–spring 1994	remote	0.9 #	1.5	trace	[47]
Arctic, Russia, Taimyr	1995		2.06	5.61	0.76	[47]
Canadian High Arctic	V-VI.2016	remote	na	0.0027–0.020 ***	0.0006–0.002	[50]
Antarctica, South Shetland Archipelago, King George Island	XI-XII.2007	remote	0.024 #	0.004 **	0.004	[51]
	XII.2008	remote	0.015 #	0.003 **	0.003	[51]
	II-III.2010	remote	0.005 #	0.001 **	0.001	[51]
The western Antarctic Peninsula	X-XI.2010	remote	na	na	0.010–0.046	[52]
Antarctic, South Shetland Archipelago, Livingston Island	XII.2014–III.2015	remote	na	0.018 ** (0.001–0.030)	0.008 (0.005–0.015)	[54]

(#—*p,p'*-DDT + *p,p'*-DDD + *p,p'*-DDE + *o,p'*-DDT + *o,p'*-DDD + *o,p'*-DDE; @—*p,p'*-DDT + *p,p'*-DDE; * α + γ-HCH; ** α + γ+β + δ-HCH; *** α + γ+β-HCH; na—not analyzed.

The mean ∑DDT levels in snow water from the southern part of Irkutsk Region in 2021 were comparable to ∑DDT values in snow sampled in the 1990s in the Arctic and temperate latitudes [40,47] and higher than the levels found in the 2000s in high-mountain areas [7,41] and Antarctica [51].

In the current study, the HCH levels measured in 2021 were lower than the values found in the 1990s in the Arctic and in Europe [40,47] and were comparable to the data obtained in the 2000s and 2010s in remote areas [42,43,50,51].

On the other hand, the HCB levels in snow from the southern part of Irkutsk Region were considerably higher than the HCB levels found in other areas around the world in the 1990s and 2000s [7,41–43,47,50–52,54]. The highest HCB and PCB levels in snow water were observed at the station near the industrial area in Usol'e-Sibirskoe, which has been associated with the reemission of these compounds from the surfaces of buildings and the sites of industrial waste storage, when work on the elimination of accumulated environmental damage to the territory of the Usol'ekhimprom industrial area began.

Maximum permissible levels (MPLs) are used for the evaluation of the potential effects of pollutants contained in environmental media on living organisms and human health. In Russia, MPLs for PCB, HCB, HCH, and DDT in snow are absent. Pollutants are contained in snow after snowmelt enters into water bodies [11–13]. Assuming that the levels of pollutants in the snow water remain permanent during the snowmelt process, and taking into account the possible household usage of snow water by some residents, we can compare the data obtained with the MPLs for water. The Russian MPLs for HCB in drinking water, groundwater, and surface water for households and drinking and cultural purposes amount to 0.001 mg/L [55]. In surface water, the Russian MPLs for HCHs and DDTs are up to 0.002 mg/L [55] and 0.1 mg/L [56], respectively. All data regarding the HCB, HCHs, and DDTs found in the snow water in Irkutsk Region were considerably lower than these Russian MDLs. The HCH levels in snow water in this study are also lower than the Russian MPLs for HCH in freshwater water bodies for fishery purposes (0.00001 mg/L [57]). There are no MPLs for PCB in freshwater water bodies in Russia.

3.3. Temporal Trend of PCBs and OCPs in Irkutsk Region, Eastern Siberia in 1994–2021

The PCB and OCP levels obtained from the 1990s to the 2020s in the southern part of Irkutsk Region were compared for data expressed as a square to avoid the effect of the interannual variation in precipitation volume. While the number of snow sampling sites was different from the 1990s to the 2020s, the snow was sampled in urban, rural, and remote areas during every sampling expedition.

3.3.1. PCBs

The total PCB temporal distribution from the 1990s to the 2020s is represented as a V-shaped curve with minimum PCB concentrations in 2009 (1855 ± 3250 ng/m^2) (Figure 2a). The mean total PCB levels in snow in 2021 (3990 ± 5520 ng/m^2) were comparable to the mean PCB levels obtained in 1994 (4585 ± 6455 ng/m^2).

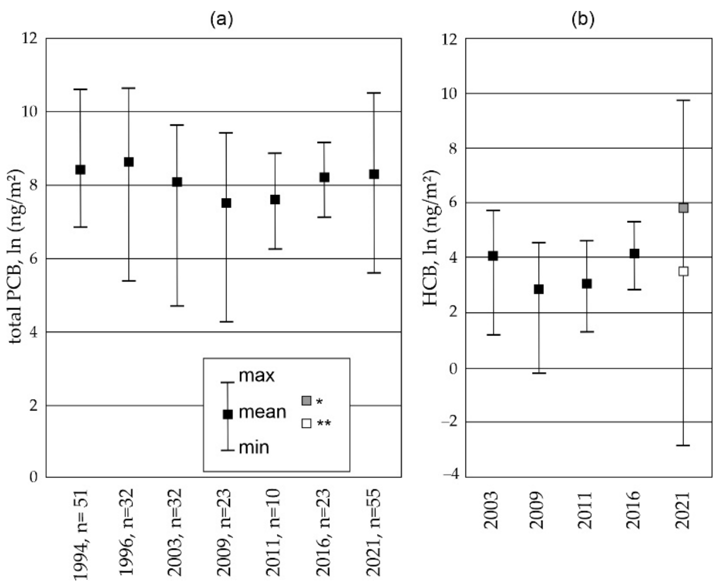

Figure 2. The comparison of the total PCB (**a**) and HCB (**b**) levels in snow from the 1990s to the 2020s (ln (ng/m^2)) (* mean HCB levels including data for Site # 31 near the industrial area of Usol'ekhimprom; ** mean HCB levels without data for Site # 31) [16,21–24], and present study.

The PCB decrease in the late 2000s was caused by the collapse of industrial production in Irkutsk Region and across the Russian Federation in the 1990s [29], as well as by the continuous, gradual reduction in operation or stopping of individual technological processes in Usol'ekhimprom enterprises in the 2000s due to the mercury pollution resulting from chlor-alkali production via mercury electrolysis [29,31]. In 2020, efforts to eliminate the accumulated environmental damage in the territory of the Usol'ekhimprom industrial area began [32,33]. This activity resulted in secondary emissions of PCB and other organic pollutants from the soil and the surfaces of industrial constructions, despite the restrictive measures taken. Water curtains were one of these measures [33]. The abundant wetting of surfaces with water can lead to intense PCB reemission from contaminated surfaces during water evaporation [58] as well as leading to the increase in PCB entrance into the River Angara with sewage from the industrial area of Usol'ekhimprom.

In 2021, the spatial distribution of the total PCBs and the sum of six indicator PCB congeners in the snow in the southern part of Irkutsk Region (Figure S1) were similar to those found in previous studies from the 1990s to the 2010s [16,20,22–24], which were conditioned by the presence and influence of PCB emissions from a terrestrial source located in the industrial area of Usol'ekhimprom [59,60]. The highest PCB levels were found in the town of Usol'e-Sibirskoe and in the surrounding area, followed by those in other industrial towns (Irkutsk, Baikalsk, and Schelekhovo). The lowest levels were detected in rural areas along the roads from Irkutsk to Bayanday and from Muruy to Zalary (Figure S1).

It should be noted that, in 2021, compared to the previous data, the PCB concentrations were found to vary differently at different locations. In 2021, the total PCB levels in almost all of the snow samples from the Usol'e-Sibirskoe area appeared to be the highest among all of the measurements obtained previously from this area (Figure 3). At the same time, in 2021, the total PCB levels in the snow sampled in remote sites along the roads from Muruy to Zalary were lower than those measured in 1994, whereas the total PCB levels in remote and rural areas located in touristic zones on the shores of water bodies (near the settlements of Balagansk located on the shore of the River Angara and near the settlement of Bolshoe Goloustnoe located on the shore of Lake Baikal) appear to be higher than those in samples taken in 1994 (Figure S2). Rising traffic congestion and increasing tourist and recreational activities in some areas near water bodies in the 2010s [61] likely resulted in additional new local sources of PCB emissions in these areas on the shores of Lake Baikal and the River Angara.

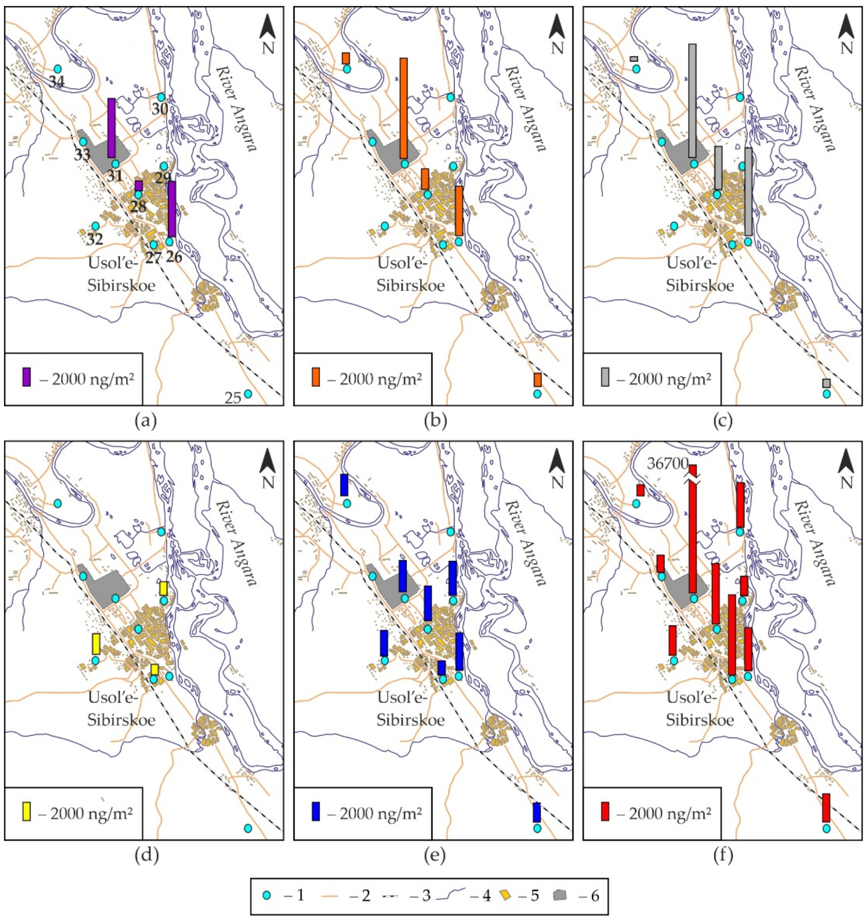

Figure 3. The total PCB levels in the snow in the town of Usol'e-Sibirskoe and the surrounding area in 1996 (**a**) [20,21], 2003 (**b**) [22], 2009 (**c**) [23], 2011 (**d**) [24], 2016 (**e**) [16], and 2021 (**f**) (ng/m^2).

On the other hand, in 2021, the PCB homological and congener patterns changed as compared to those from the previous studies.

From 1996 to 2016 [16,20–24], the PCB homological patterns in snow corresponded to those in Sovol (PCB technical mixtures analogous to Aroclor 1254 produced in the former USSR [62,63]) (Figure S3). In 2021, the sampling sites were divided into two groups with different PCB homological and congener patterns (Figures 4 and 5 and Table S3). The first group included sites located near industrial areas and surrounding territories and was characterized by a predominance of pentaCB (PCB-99, PCB-101, PCB-110, and PCB-118), followed by tetraCB (PCB-52 and PCB-44) or hexaCB (PCB-138 and PCB-153). The second group included the majority of the sampling sites, where the homological PCB pattern was similar to triCB (PCB-28 and PCB-31) and diCB (PCB-8). Thus, in 2021, the shift to a predominance of lower chlorinated homologous and congener PCBs increased compared to previous years. These changes in PCB patterns, as well as total PCB concentrations, are associated with the complete cessation of organochlorine production in the former enterprises of Usol'ekhimprom and with efforts made to eliminate the accumulated environmental damage in the industrial area of Usol'ekhimprom [32,33]. Thus, we observed changes in the total PCB levels and in the PCB homological and congener patterns in the snow samples during the periods of the high and low activity of enterprises producing organochlorines, a standstill period (2012–2020), and a period of the liquidation of the construction and waste of Usol'ekhimprom (starting in 2020). More information about homological and congener PCB patterns in snow from 1994 to 2021 is presented in Text S2.

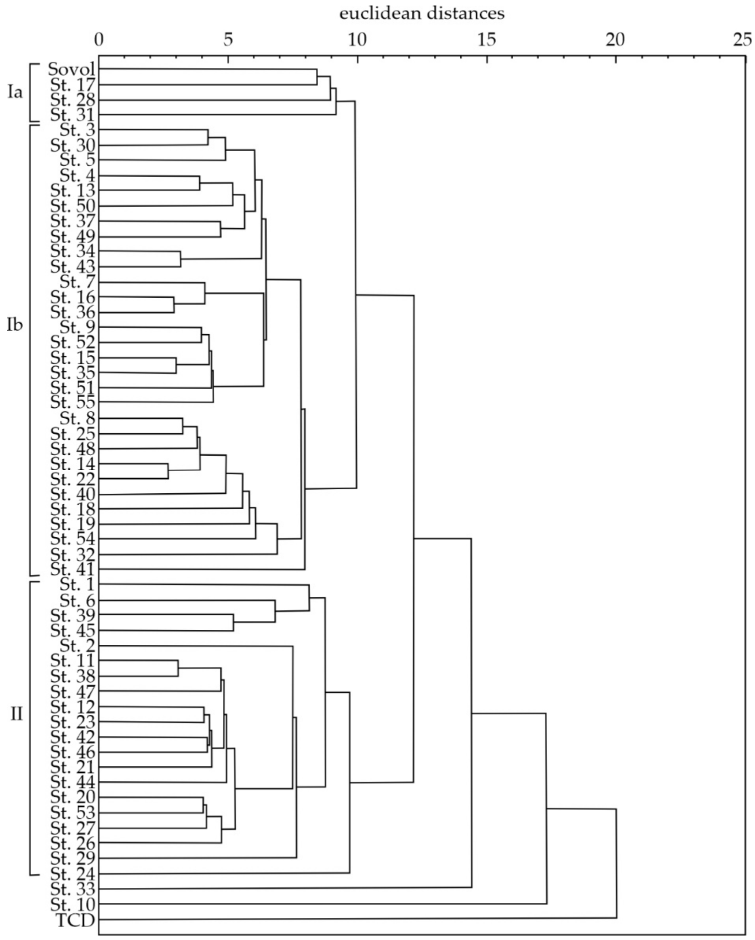

Figure 4. The grouping of snow sampling sites by relative PCB homological patterns using the cluster method.

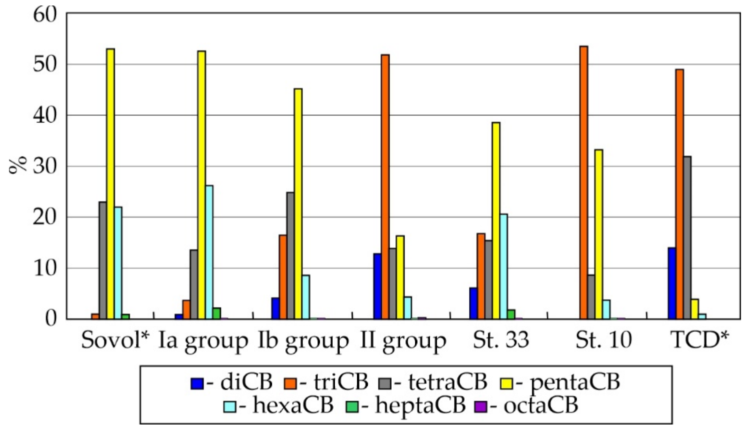

Figure 5. The PCB homological patterns (%) in groups obtained by the cluster method in comparison to homological patterns in technical mixtures of PCB (Sovol and trichlorodiphenyl (TCD); * [61]).

The dominant low chlorinated (for example, PCB-28 in the Himalayas [7]) and higher chlorinated (for example, PCB-101 and PCB-138 in mountains in Slovakia [42]) PCB congeners in the total PCB have also been found in snow in other regions of the world. The prevalence of higher chlorinated PCB congeners is likely due to the snow aging when high volatile congeners are evaporated and low volatile congeners are gathered in snow [42,64]. There were several small snowfalls during our snow sampling campaigns (Figure S4) [38] that could have resulted in the additional enrichment of fresh snow with high volatile PCB congeners. However, the snow sampling campaign of 2021 was performed in conditions of seasonal snowfalls similar to those of the previous snow studies in Irkutsk Region [16,21,22], and the precipitation volume had no significant effect on the PCB levels and patterns in 2021. In addition, the snow samples in Usol'e-Sibirskoe and the adjacent area were taken within a day (in a similar condition of precipitation volume), but the homological and congener patterns in these samples varied depending on the prevalence of both lower and heavier chlorinated PCBs. This suggests that snowfalls have no considerable effect on PCB levels and that the homological and congener patterns mainly depend on the PCB source.

3.3.2. PCB-11

In 2021, the non-Aroclor congener PCB-11 was first determined in snow samples from Irkutsk Region. PCB-11 was found in 64% of the snow samples analyzed. The mean PCB-11 level amounted to 0.22 ± 0.22 (bdl-0.85) ng/L or 9.8 ± 14 (bdl-66) ng/m^2 (Figure 6). The mean contribution of PCB-11 in the total PCB made up 0.55%, and it did not exceed 2.64%. The same contribution of PCB-11 to the total PCB was found in the Arctic snow [50,65,66].

In this study, the spatial distribution of PCB-11 in snow was irregular. The highest PCB-11 levels were found at one sampling site along the road from Irkutsk to Sludyanka, followed by the levels at several sites in Irkutsk and Usol'e-Sibirskoe and near the town of Baikalsk. The PCB-11 levels within individual settlements or along the investigated road were either below detectability or considerably high, except for the PCB-11 concentrations found along the road from Muruy to Balagansk (Figure 6). PCB-11 was found in every snow sample in that location (9.8–19 ng/m^2). The mean PCB-11 along the road from Muruy to Balagansk was significantly higher than the PCB-11 mean values in the industrial towns of Irkutsk, Angarsk, Schelekhovo, and Baikalsk ($p > 0.05$). PCB-11 was likely transferred by air masses from the northwest towards Muruy-Balagansk with dominated wind in the southern part of Irkutsk Region.

It should be noted that the mean PCB-11 levels in the town of Usol'e-Sibirskoe and the surrounding area (19 ng/m^2) were significantly higher than those in Schelekhovo, in Baikalsk, and along the road from Irkutsk to Bolshoe Goloustnoe ($p < 0.05$). The abundance of PCB-11 in the Usol'e-Sibirskoe area was likely the result of a paint factory located in the industrial area of Usol'ekhimprom in the past. It is known that PCB-11 is unintentionally formed during the production of pigments for paints [67].

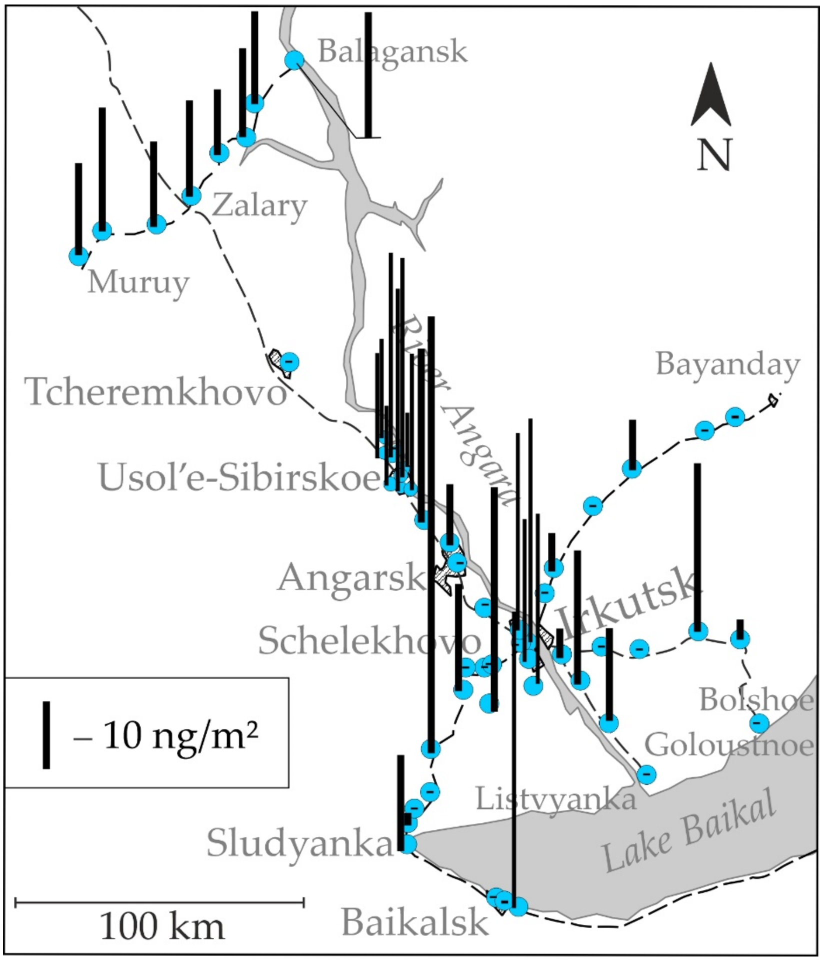

Figure 6. PCB-11 in snow in the southern part of Irkutsk Region in 2021 (ng/m^2).

There is no significant correlation between the spatial distributions of PCB-11 and the other PCBs, either in the total dataset or in separate groups of samples combined along the roads and areas of towns ($p > 0.05$) (Figure S5).

3.3.3. HCB

As in the case of the PCB distribution, the temporal distribution of HCB levels in the period between 2003 and 2016 represents a V-shaped curve (Figure 2b). If all data concerning HCB concentrations are used for calculation, the HCB mean in 2021 is higher compared to the 2003–2016 period [16,22–24]. If the maximum HCB level found near the industrial area of Usol'ekhimprom (Site #31 from Figure 1) is excluded from the calculation of the HCB mean for 2021, the HCB level in 2021 is lower than that obtained in 2016 (Figure 2b).

In 2021, the highest HCB levels in snow were found at the location near the industrial area of Usol'ekhimprom (16700 ng/m^2), followed by the sites in the town of Usol'e-Sibirskoe (up to 360 ng/m^2) (Figure S6). The highest HCB levels, compared to other locations of Irkutsk Region, were also found in the soil, vegetation, and food items from the Usol'e-Sibirskoe area [16,18]. This can be associated with an HCB source located in the industrial area of Usol'ekhimprom, as HCB is known to be an unintentional product of some processes of organochlorine synthesis [68,69]. In the past, the production of trichloroethylene at Usol'ekhimprom [30] could have been one of the chemical processes during which HCB was formed as a by-product [69]. The association of the locations of the HCB and PCB sources at the industrial area of Usol'ekhimprom is also supported by a significant correlation between the HCB and total PCB concentrations in snow in 2021 (0.59, $p < 0.001$).

3.3.4. DDTs and HCHs

The DDTs and HCHs in snow from the Lake Baikal Region were first analyzed in the 1980s [19]. The total DDT and total HCH concentrations in the snow water sampled in the remote areas of the Lake Baikal region amounted to 31.5 and 13.5 ng/L, respectively [19]. In Russia, the application of DDTs was banned in 1970 [70]. The authors considered long-range transport of DDT from developing countries where the pesticide was applied [19]. However, in Russia, HCH was used in agriculture until the late 1980s [70]. The HCH load per unit of arable land in 1981–1985 was 0.34 kg of active substance per hectare [71]. In addition, the entrance of pesticides into the environmental media from the storage of obsolete pesticides in subsequent years was also possible [72]. From 2003 to 2021, the concentrations of DDTs and HCHs in snow water were lower (2–35 and 2–675 times, respectively) than those found in the 1980s.

The DDT and HCH concentrations also decreased during 2003–2021 (Figure 7). Overall significant decreases were found for HCHs. The sum (±SD) of the α- and γ-isomers of HCHs decreased from 187 ± 152 (13–604) ng/m^2 in 2003 [22] to 25 ± 18 (7–58) ng/m^2 in 2011 [24] and 57 ± 27 (17–109) ng/m^2 in 2016 [16]. In 2021, only α-HCH was determined sporadically, whereas the other three HCH isomers were generally below the detected limit. The sum of *p,p*′-DDT, *p,p*′-DDE, and *p,p*′-DDD decreased from 910 ± 885 (11–3165) ng/m^2 in 2003 to 40 ± 44 (0.6–300) ng/m^2 in 2021.

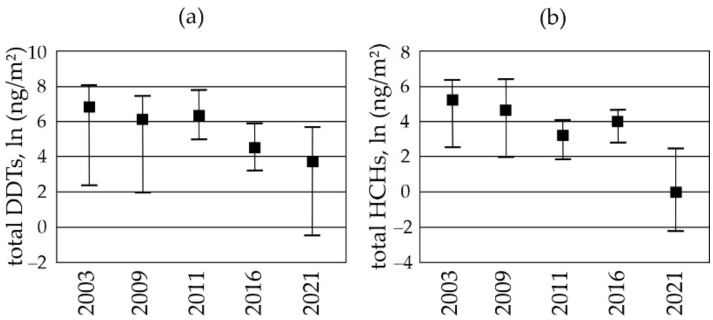

Figure 7. Comparison of total DDT (**a**) and HCH (**b**) levels in snow in 2003–2021 (ln (ng/m^2)) [16,21–24].

In Russia, the agricultural application of lindane and technical HCH was banned in 1990 and 1986, respectively [67]. HCH is less stable in the environment than DDT [73]. Therefore, we have observed a decrease in the HCH concentration in snow and in other environmental media of the region [74] over the past three decades after the HCH ban.

When studying POPs in the atmospheric air at several stations in the Asian part of Russia and in Mongolia, a considerable entrance of DDTs from an unknown source was found in the late 2000s [75,76]. The mean *p,p*′-DDT/*p,p*′-DDE ratio in snow changed from 11 in 2003 [22] to 41 in 2011 [24] and to 1.1 in 2021, thus confirming the decrease of the effect of short-term "fresh" DDT input in the environment in the southern part of Irkutsk Region as well as other areas of Asia during the 2010s.

3.4. The Relationship of Suspended Particulate Matter and Organochlorines Levels in Snow

The effect of the suspended particulate matter (SPM) content on organochlorines concentrations was studied by linear regression analysis between POPs versus SPM levels. The concentrations of POPs and SPM were expressed as a square and ln-transformed. The significant results of the linear regression analysis are presented in Table S4. A significant positive relationship was found between SPM and HCB, between SRM and $\sum PCB_{36}$, and between SRM and $\sum PCB_6$. The linear regression model describes only part of the dataset relationships, which could be associated with emissions from the former industrial area of Usol'ekhimprom, which was recultivated at that time. The variety of POPs and SPM sources, which may be unrelated to each other, in the southern part of Irkutsk Region results in weak or medium relationships between SPM and POP distribution.

The relationship between PCBs and SPM in snow becomes stronger with the increase in PCB chlorination levels from lighter to heavier chlorinated PCB congeners/homologues (Figure 8). This is in line with the ability of lighter PCB congeners to be transported in a gas phase, whereas heavier PCB congeners/homologues are transported more readily with air particles [77].

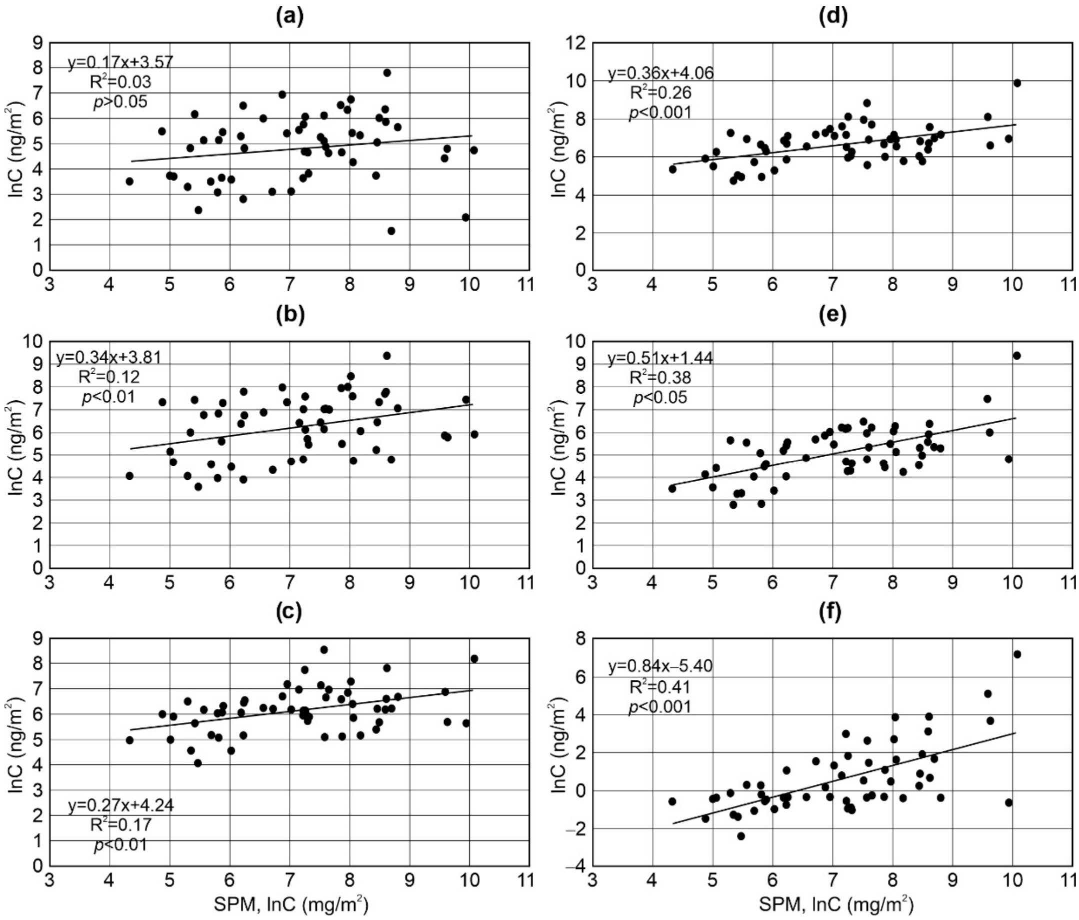

Figure 8. Relationship between the ln-transformed levels of suspended particulate matter (SPM) and PCB homologues ((**a**)—diCB; (**b**)—triCB; (**c**)—tetraCB; (**d**)—pentaCB; (**e**)—hexaCB; (**f**)—heptaCB) in snow in the southern part of Irkutsk Region in 2021.

3.5. The Deposition Fluxes of Organochlorines

In the winter of 2020–2021, the POP loads or daily deposition fluxes of total PCBs, HCBs, the sum of DDTs, and α-HCH amounted to 42 (2.9–386) ng/m^2 per day, 3.5 (0.001–175) ng/m^2 per day, 480 (1–3170) pg/m^2 per day, and 7 (0.7–124) pg/m^2 per day, respectively. The highest PCB loads were found in two areas near the former Usol'ekhimprom industrial area (St. 31: 386 ng/m^2 per day) and the former Baikalsk pulp and paper mill (St. 38: 204 ng/m^2 per day). Currently, the Usol'ekhimprom industrial area is being reclaimed [32], but the problems of eliminating waste and of the production facilities of the Baikalsk pulp and paper mill, which was closed in the early 2010s, still need to be solved [78]. The highest HCB load was also found near the former Usol'ekhimprom industrial area (St. 31: 175 ng/m^2 per day). The HCB load at the rest areas varied from 0.001 to 3.8 ng/m^2 per day with a mean of 0.36 ng/m^2 per day. It should be noted that the POP load characterizes the pollution of the area with POPs in the winter only and is quite similar to the POP concentrations expressed as a square when studying the interannual changes in POP loads (Figure S7).

Taking into account the features of the climate in Irkutsk Region (the precipitation volume in winter is much lower than that in summer [25,26,39]), annual deposition fluxes calculated on the base of annual precipitation volume give more information about the POP fallout from the atmosphere in the region under consideration.

The precipitation volumes from 2020 to 2021 of the hydrometeorological stations located in the town of Irkutsk and the settlement of Bolshoe Goloustnoe can be found in [39]. Taking into account the fact that the mean snow water equivalents for the dates of snow sampling in 2021 at the Irkutsk and Usol'e-Sibirskoe stations were similar to each other (51 and 53 mm respectively), we assumed that the precipitation volume in the town of Usol'e-Sibirskoe was equal to that in Irkutsk, and the value of the precipitation volume in Irkutsk was used for the calculation of the deposition fluxes in Usol'e-Sibirskoe. Thus, the deposition fluxes of PCBs and OCPs in 2020–2021 were calculated for the industrial town and regional center of Irkutsk, the settlement of Bolshoe Goloustnoe located within the recreational area of the central ecological zone of Lake Baikal Natural Territory, and the industrial town of Usol'e-Sibirskoe, which was highly polluted with PCBs.

In 2021, the annual OCP deposition fluxes in Usol'e-Sibirskoe and Irkutsk were twice as high as those in the settlement of Bolshoe Goloustnoe (Figure 9) due to the proximity of these towns to agricultural areas, whereas Bolshoe Goloustnoe is located within the Lake Baikal Natural Territory. The application of organochlorine pesticides was banned in the Lake Baikal Natural Territory in the past.

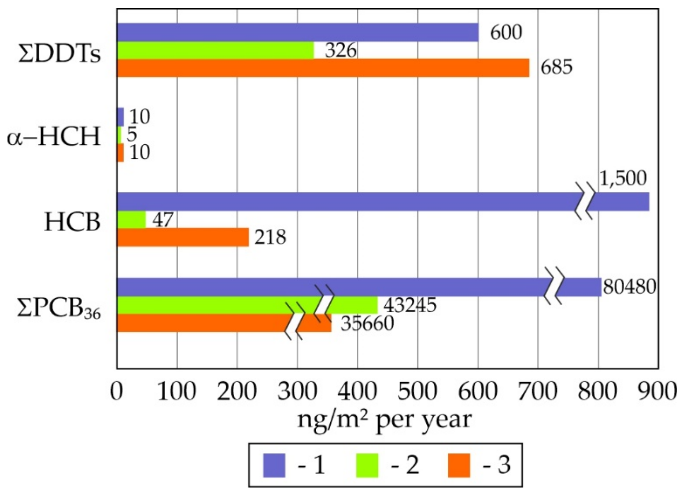

Figure 9. The annual deposition fluxes of organochlorines in Usol'e-Sibirskoe (1), Bolshoe Goloustnoe (2), and Irkutsk (3) (ng/m^2 per year).

If the highest HCB level at St. 31 is excluded from the calculation, the annual HCB deposition in Usol'e-Sibirskoe is 1500 ng/m^2 per year, which is one and two orders of magnitude higher than those in Irkutsk and Bolshoe Goloustnoe, respectively. The highest PCB annual deposition flux was found in Usol'e-Sibirskoe (80 $\mu g/m^2$ per year), followed by the deposition fluxes in Bolshoe Goloustnoe and Irkutsk. It should be noted that the PCB deposition flux in Bolshoe Goloustnoe is higher than that in Irkutsk due to the triCB abundance in the snow from Bolshoe Goloustnoe compared to the Irkutsk and Usol'e-Sibirskoe sites (Figures 10 and S8), whereas the total PCB deposition flux in Usol'e-Sibirskoe is mainly determined by pentaCB and hexaCB.

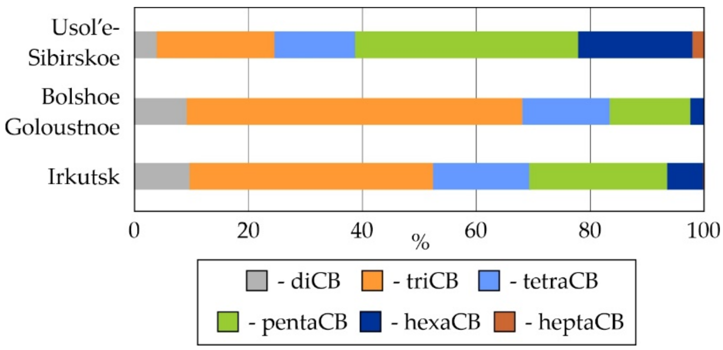

Figure 10. The contribution of PCB homologues in total PCB annual deposition flux (%).

The deposition with wet precipitation in the wintertime provides a 3–8% annual deposition flux. During the year, the first massive POP deposition with wet precipitation occurs in May (about 12–18%). July, August and September are the rainiest months in a year. The deposition fluxes in this period contribute about 60–65% of the total annual deposition fluxes.

The annual organochlorines deposition fluxes obtained from the settlements in the southern part of Irkutsk Region (Figure 9) are significantly higher than those found in high-mountain areas of Switzerland, Austria, Spain, and Slovakia [40,42,43].

There are some uncertainties in the calculation of annual deposition fluxes with all types of wet precipitations. The scavenging abilities of the snow and rain for POPs contained in gas and particle phases from the atmosphere are different [4,10]. Snow is a more effective "scavenger" of POPs associated with particles, whereas the rain is also an effective "scavenger" of low-molecular-weight compounds [10]. Thus, it is possible that the values of the annual deposition flux of heavier chlorinated PCBs are overestimated more than those of the lighter chlorinated PCB congeners. The permanent snow cover in the winter is another factor in the uncertainty. Due to the constant snow cover during the winter, the POP levels found in snow are likely the sum of the POP concentrations from both the wet and dry deposition fluxes of these compounds during the winter. Thus, the use of the POP levels determined in snow for the annual wet deposition flux results in an overestimation of values, especially for warm periods of the year. Thus, we suppose that, in regions where there is a strong temperature gradient between cold and warm seasons, the application of POP concentrations in both rain and freshly fallen snow would be more appropriate for calculating annual POP wet deposition fluxes.

4. Conclusions

This study discussed the current variability of PCBs and OCPs in snow cover in industrial, urban, rural, and remote areas in Eastern Siberia, which has a long-term source of PCB, dioxins, and related compounds affecting the surrounding areas as well as a historical application of OCP in agriculture and for the prevention of human vector-borne diseases. PCBs were the most abundant POPs in the snow from Irkutsk Region in Eastern Siberia, followed by HCB, DDTs, and HCHs.

The spatial distribution of organochlorines in Eastern Siberia in 2021 was similar to that found from previous studies from the 1990s to the 2010s and was determined by the presence of industrial and urban sources and atmospheric transport. The emissions from the former industrial areas of Usol'ekhimprom and the Baikalsk pulp and paper mill combined with current active sources of unintentional PCB formation in industrial towns were the main contributors to the PCB pollution of the snow in the surrounding areas. The significant relationship between PCBs, OCPs, and suspended particulate matter (SPM) in snow was found to be due both to the fact that the POPs and SPM in snow come from the same sources and to the preferred transport of POPs by air particles. The strength of the relationship between the SPM and PCB homologue concentrations increases moving from the lighter chlorinated PCBs to the heavier ones.

The long-term variation of POPs in the snow was also investigated. The HCH and DDT levels in the snow decreased significantly within the last three decades. α-HCH was the only HCH isomer sporadically determined in 2021 at levels comparable to the HCH levels in remote areas of the world. The DDT levels in 2021 were comparable to those found in other areas around the world from the 1990s to the 2000s.

The PCB and HCB temporal distributions from the 1990 to the 2020s show a V-shaped curve with a minimum from 2009 to 2011. The PCB decreasing trend of the late 2000s corresponded to the collapse of industrial production in the region and across the Russian Federation in the 1990s and to the continuous, gradual reduction of production and the cessation of individual technological processes in Usol'ekhimprom in the 2000s due to the mercury pollution as a result of chlor-alkali production via mercury electrolysis in that location. Efforts to eliminate the accumulated environmental damage in the Usol'ekhimprom industrial area that started in 2020 likely led to secondary emissions of PCB and other organic pollutants from the soil and surfaces of industrial construction, in spite of the restrictive measures taken.

The current PCB homological and congener patterns were partially shifted in direction to the abundance of lower chlorinated homologues in a part of the samples, except for in areas near the former industrial area of Usol'ekhimprom. The PCB homological and congener pattern at these stations were quite similar to those in Sovol, a technical mixture of PCBs produced in the former USSR. The spatial distribution of PCB-11, a non-Aroclor congener first determined in snow samples in 2021, is not related to that of the other PCBs.

In the area under study, the spatial distribution of the daily POP deposition fluxes during the winter was quite similar to the distribution of the POP concentrations expressed as a square. The deposition with wet precipitation in the wintertime provided a 3–8% annual deposition flux. Massive POP deposition with wet precipitation occurred in May (about 12–18%) and from July to September (60–65% total annual deposition fluxes).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atmos13122117/s1. Figure S1. The sum of six indicator PCB congeners (PCB-28, 52, 101, 138, 153, and 180) in the snow of the southern part of Irkutsk Region in 2021 (ng/m^2); Figure S2. The total PCB levels in snow sampled along the road from Muruy to Balagansk (a) and from Irkutsk to Bolshoe Goloustnoe (b) in 1994 (1) [1,2], 2009 (2) [3], and 2021 (3) (ng/m^2); Figure S3. The relative PCB homological patterns (%) in snow from 1996 to 2016 [1–6] compared to Sovol and Trichlorodiphenyl (TCD) [7]; Figure S4. The precipitation volume during the period of snowpack formation prior to snow sampling in February, 2021 (mm) [8]; Figure S5. The relationship between ln-transformed levels of total PCBs and PCB-11 in snow in the southern part of Irkutsk Region in 2021; Figure S6. HCB in snow of the southern part of Irkutsk Region in 2021 (ng/m^2); Figure S7. The relationship of mean annual values of total PCB load (ng/m^2 per day) and total PCB concentration (ng/m^2) from 1994 to 2021; Figure S8. The annual deposition fluxes of indicator PCB congeners in Usol'e-Sibirskoe (1), Bolshoe Goloustnoe (2), and Irkutsk (3) (μg/m^2 per year); Table S1. The list of individual organochlorine analytes, characteristic ions, and MDLs; Table S2. Characteristics of snow cover at the time of sampling and suspended particulate matter (SPM) levels in snow water in 2021; Table S3. The 10 most dominant PCB congeners at sites along the River Angara from Listvyanka to Usol'e-Sibirskoe; Table S4. Results of the linear regression analysis between ln-transformed POP values versus ln-transformed SPM levels in 2021 (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, «-» $p > 0.05$); Text S1. Characteristics of snow cover at the time of sampling in 2021; Text S2. Homological and congener PCB patterns in snow in Irkutsk Region from 1994 to 2021.

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