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

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Supplement materials.

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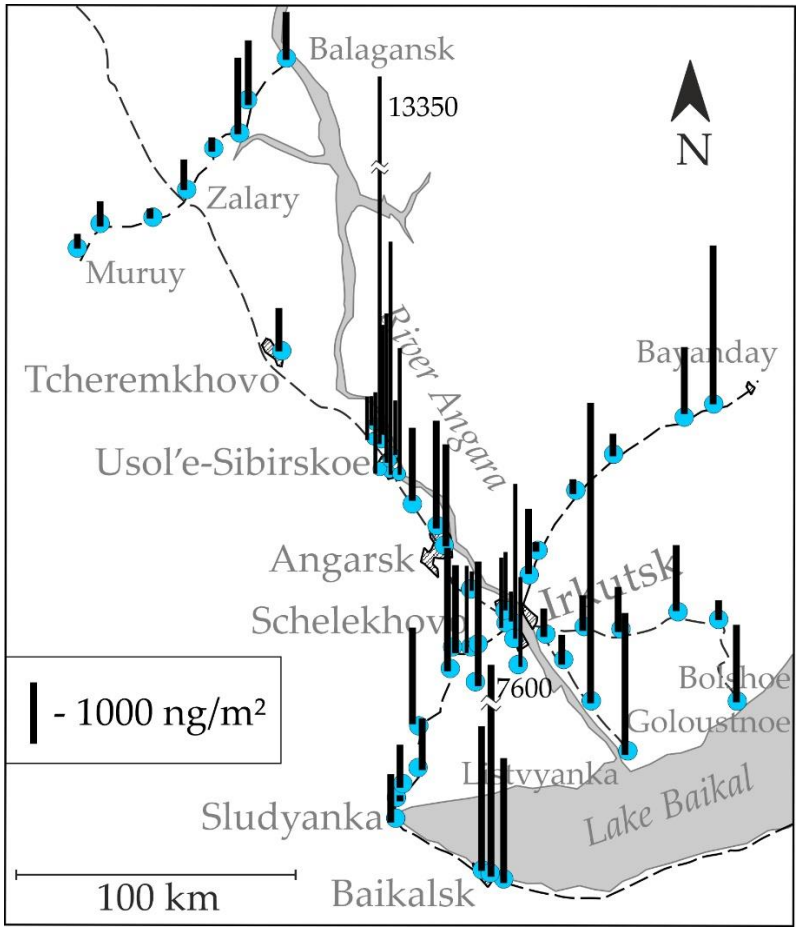

Figure S1. The sum of six indicator PCB congeners (PCB-28, 52, 101, 138, 153, and 180) in snow of the southern part of Irkutsk Region in 2021 (ng/m^2).

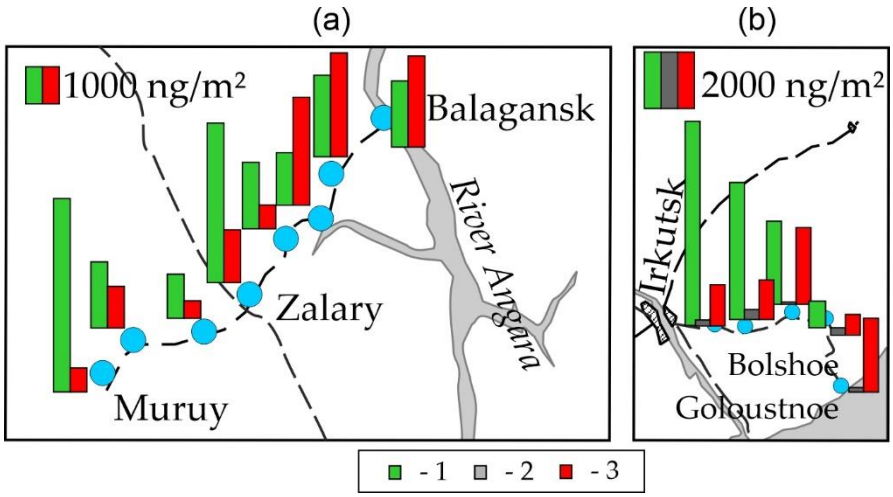

Figure S2. The total PCB levels in snow sampled along the road from Muruy to Balagansk (**a**) and from Irkutsk to Bolshoe Goloustnoe (**b**) in 1994 (1) [1,2], 2009 (2) [3], and 2021 (3) (ng/m²).

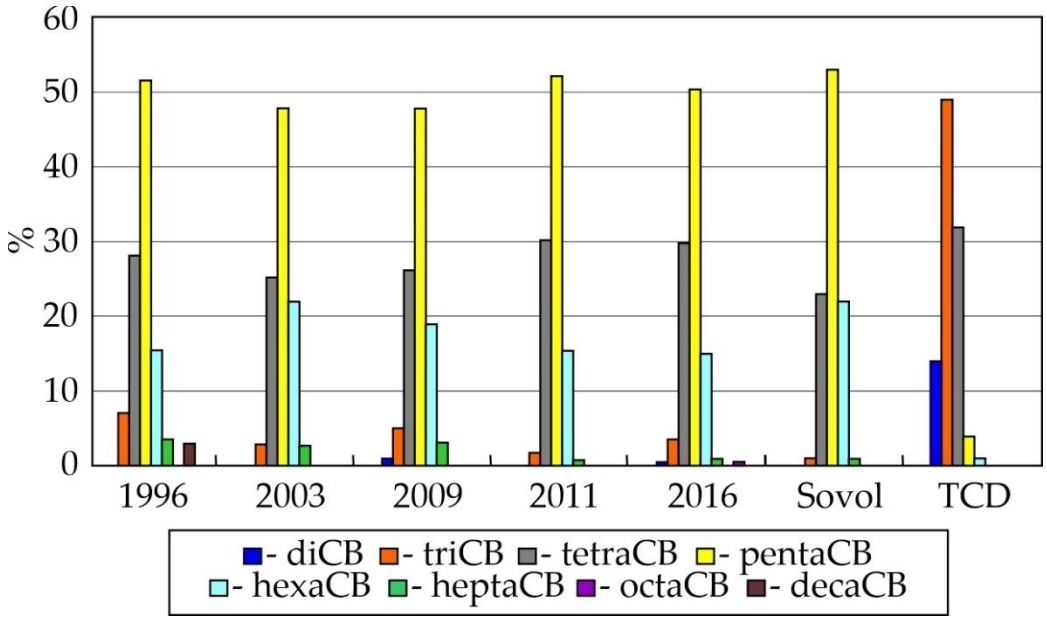

Figure S3. The relative PCB homological patterns (%) in snow from 1996 to 2016 [1-6] compared to Sovol and Trichlorodiphenyl (TCD) [7].

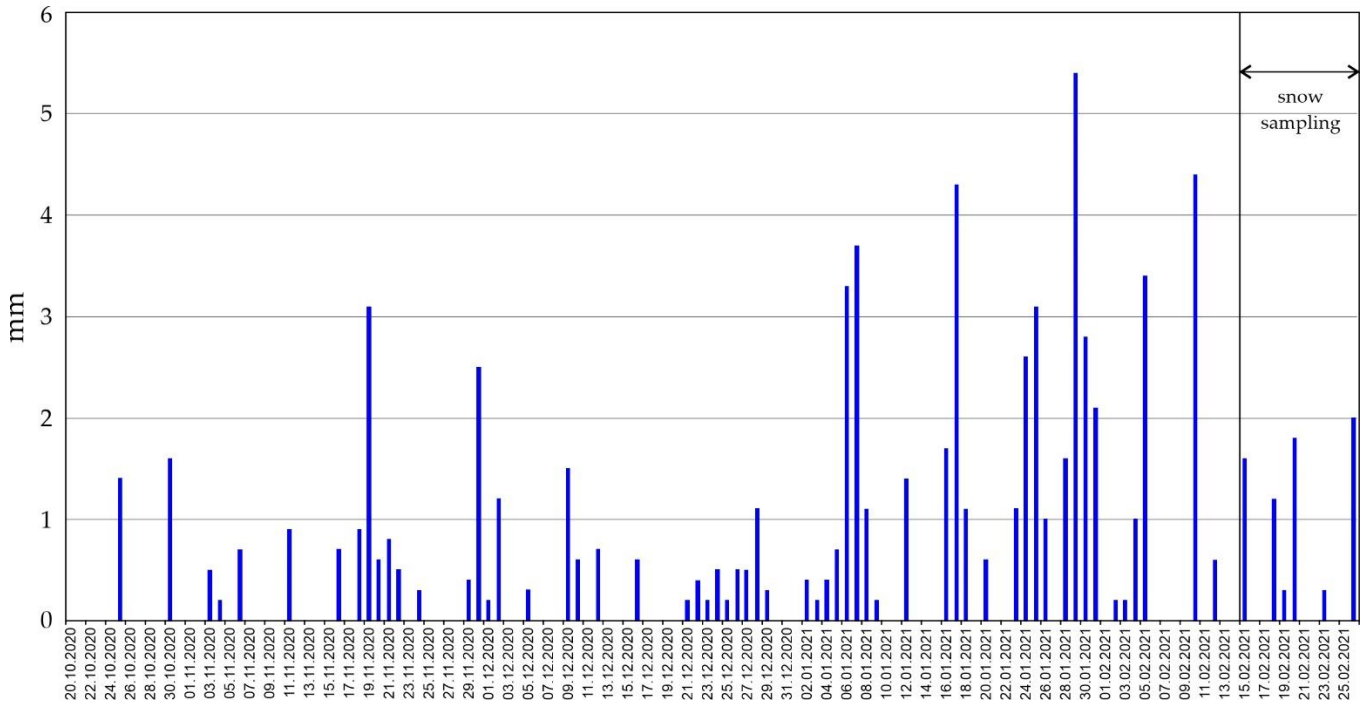

Figure S4. The precipitation volume during the period of snow pack formation prior to snow sampling in February, 2021 (mm) [8].

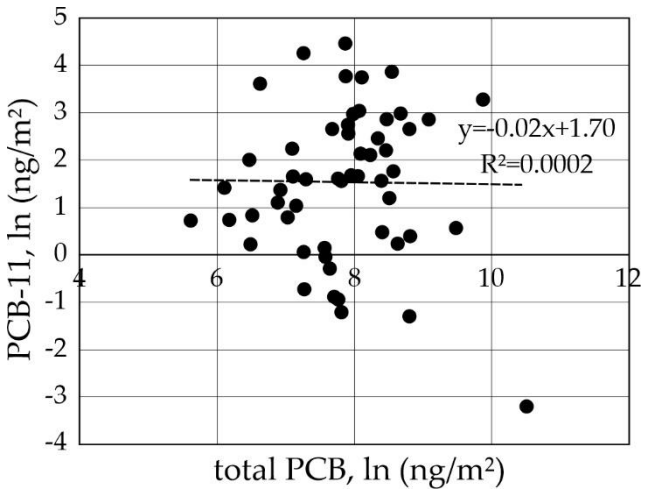

Figure S5. The relationship between ln-transformed levels of total PCBs and PCB-11 in snow in the southern part of Irkutsk Region in 2021.

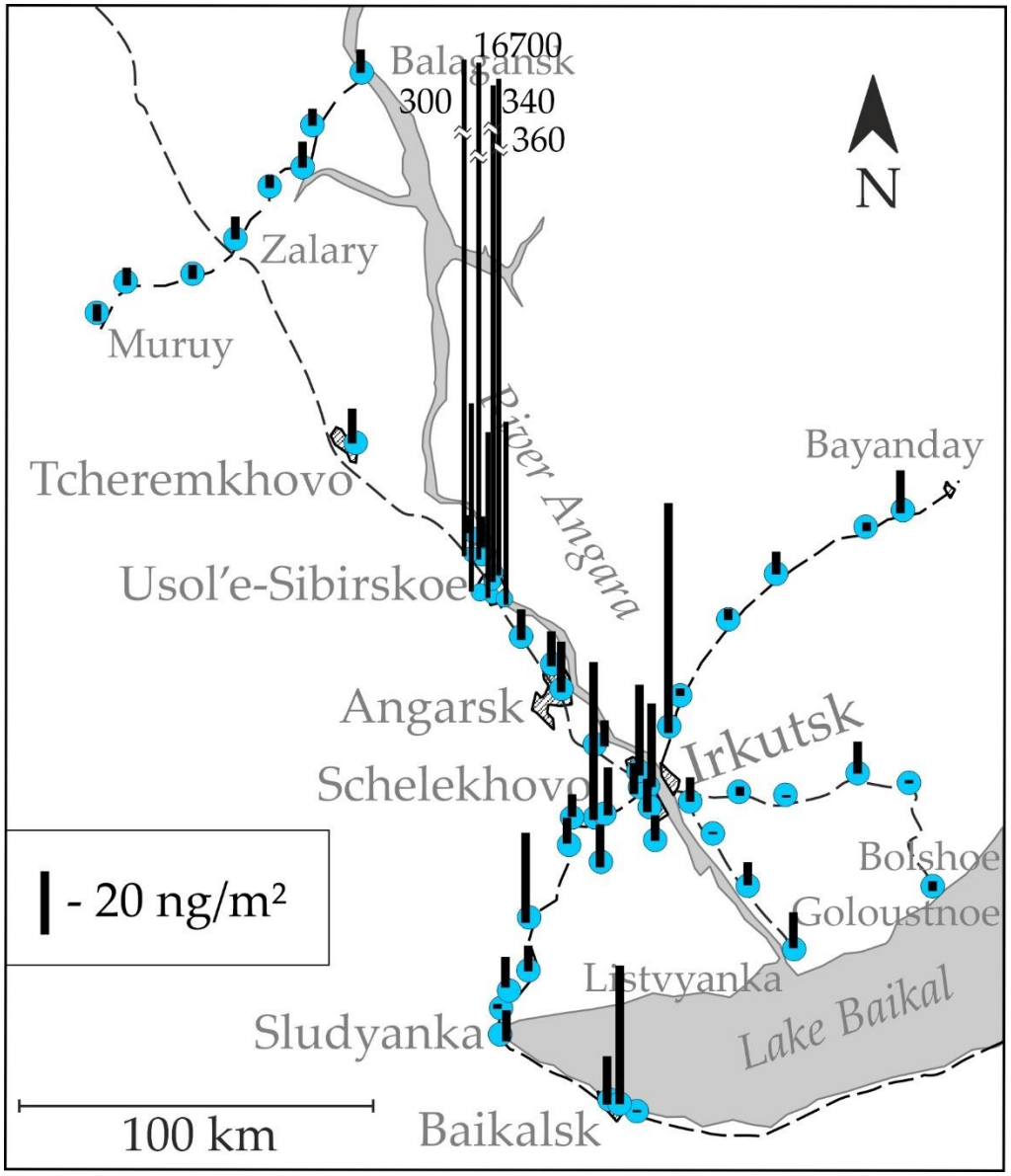

Figure S6. HCB in snow of the southern part of Irkutsk Region in 2021 (ng/m²).

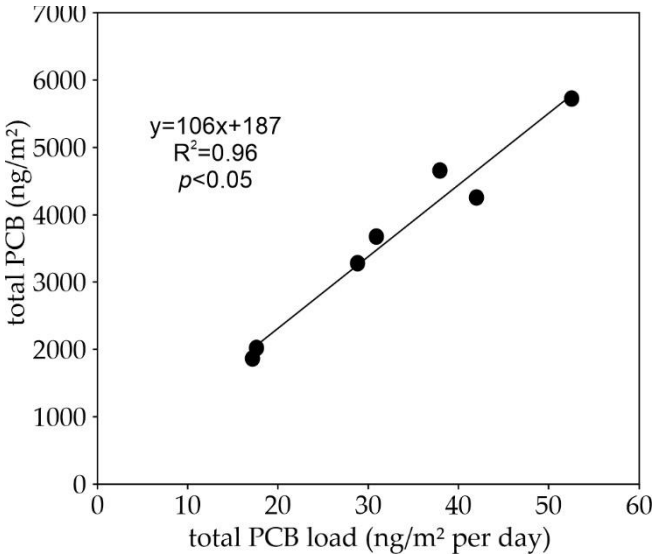

Figure S7. The relationship of mean annual values of total PCB load (ng/m² per day) and total PCB concentration (ng/m²) from 1994 to 2021.

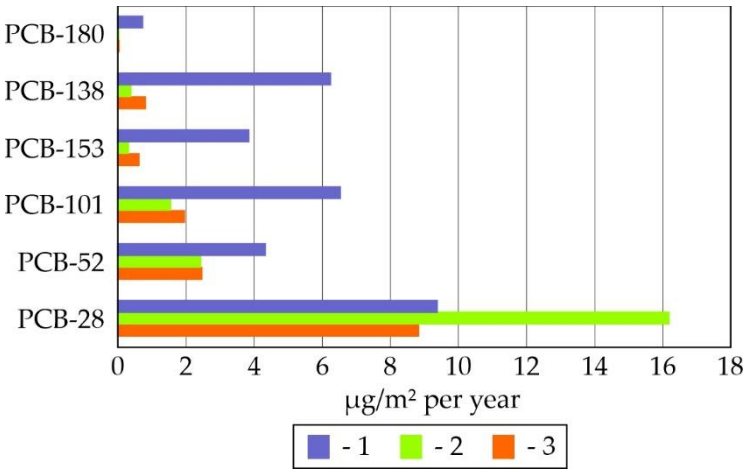

Figure S8. The annual deposition fluxes of indicator PCB congeners in Usol'e-Sibirskoe (1), Bolshoe Goloustnoe (2), and Irkutsk (3) (μg/m² per year).

Table S1. The list of individual organochlorine analytes, characteristic ions, and MDL.

№№	Compounds	Retention time (min)	Quantification ion m/z	Confirmation ions m/z	MDL
1	α-HCH	19.94	181	219, 183	0.015
2	hexachlorobenzene (HCB)	20.65	284	286, 249	0.003
3	β-HCH	21.82	181	183, 219	0.030
4	γ-HCH	22.39	181	183, 219	0.011
5	δ-HCH	24.19	181	183, 219	0.014
6	heptachlor	28.77	272	100, 274	0.006
7	aldrin	32.24	66	263, 261	0.068
8	*o,p`*-DDE	39.69	246	248, 176, 318	0.003
9	*p,p`*-DDE	43.36	246	318, 248, 176	0.011
10	dieldrin	43.43	79	263, 277, 237	0.069
11	*o,p`*-DDD	44.31	235	165, 176, 237	0.003
12	Endrin	45.91	263	81, 245, 82	0.062
13	*p,p`*-DDD	48.31	235	165, 237	0.008
14	*o,p`*-DDT	48.73	235	237, 165	0.004
15	*p,p`*-DDT	52.90	235	165, 199, 237	0.014
16	PCB-8	19.91	222	152, 224	0.304
17	PCB-11	22.39	222	152, 224	0.002
18	PCB-31	27.11	256	258, 186	1.021
19	PCB-28	27.26	256	258, 186	1.172
20	PCB-52	30.57	292	220, 290	0.314
21	PCB-49	31.02	292	220, 290	0.199
22	PCB-47	31.33	292	220, 290	0.012
23	PCB-44	32.68	292	220, 290	0.261
24	PCB-74	36.51	292	220, 290	0.096
25	PCB-66	37.34	292	220, 290	0.015
26	PCB-91	38.11	326	328, 324, 254	0.004
27	PCB-56	39.21	292	220, 290	0.001
28	PCB-101	39.98	326	328, 324, 254	0.181
29	PCB-99	40.60	326	328, 324, 254	0.728
30	PCB-97	42.46	326	328, 324, 254	0.023
31	PCB-87	43.08	326	328, 324, 254	0.004
32	PCB-85	43.56	326	328, 324, 254	0.013
33	PCB-77	44.20	292	220, 290	0.004
34	PCB-110	44.22	326	328, 324, 254	0.197
35	PCB-149	47.11	360	362, 358	0.008
36	PCB-118	47.32	326	328, 324, 254	0.132
37	PCB-153	50.07	360	362, 358	0.045
38	PCB-132	50.36	360	362, 358	0.004
39	PCB-105	50.48	326	328, 324, 254	0.044
40	PCB-141	51.61	360	362, 358	0.004
41	PCB-138	53.42	360	362, 358	0.010
42	PCB-126	54.48	326	328, 324, 254	0.002
43	PCB-187	55.54	394	396, 324	0.003
44	PCB-183	56.16	394	396, 324	0.009
45	PCB-128	56.74	360	362, 358	0.011
46	PCB-177	59.04	394	396, 324	0.001
47	PCB-156	59.70	360	362, 358	0.005

48	PCB-180	61.85	394	396, 324	0.003
49	PCB-169	64.38	360	362, 358	0.003
50	PCB-170	65.44	394	396, 324	0.004
51	PCB-196	67.28	430	358, 288, 428	0.003

Table S2. Characteristics of snow cover at the time of sampling and suspended particulate matter (SPM) levels in snow water in 2021.

	n	Mean	Median	Minimum	Maximum	Standard Deviation	Standard Error
Snow cover height, m	55	0.33	0.30	0.05	0.75	0.14	0.02
Snow density, g/sm3	55	0.18	0.17	0.12	0.31	0.04	0.01
Snow water equivalent (SWE), mm	55	59	53	8.7	215	37	5
Suspended particulate matter (SPM), mg/m^2	55	3,065	1,410	76	23,830	4,834	652
Suspended particulate matter (SPM), mg/l	55	61	27	1.4	408	92	12

Table S4. Results of the linear regression analysis between ln-transformed POP values versus ln-transformed SPM levels in 2021 (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, «-» $p > 0.05$).

Compound	b, slope	*p*-value	R^2
HCB	0.85	***	0.40
PCB-31	0.36	**	0.14
PCB-28	0.33	*	0.11
PCB-52	0.28	**	0.18
PCB-49	0.21	*	0.08
PCB-44	0.29	***	0.21
PCB-101	0.33	***	0.21
PCB-99	0.35	***	0.26
PCB-97	0.31	**	0.14
PCB-87	0.23	*	0.08
PCB-85	0.26	*	0.09
PCB-110	0.35	***	0.24
PCB-149	0.48	***	0.24
PCB-118	0.37	***	0.26
PCB-153	0.48	***	0.37
PCB-132	0.71	*	0.27
PCB-105	0.31	*	0.13
PCB-141	0.73	**	0.22
PCB-138	0.51	***	0.38
PCB-126	0.20	*	0.10
PCB-187	0.77	***	0.34
PCB-183	0.50	***	0.26
PCB-128	0.63	*	0.21
PCB-177	0.56	***	0.22
PCB-156	0.67	**	0.19

PCB-180	1.09	***	0.37
PCB-170	0.79	***	0.33
PCB-196	0.24	*	0.10
$\sum PCB_{36}$	0.36	***	0.29
$\sum PCB_{6}$	0.37	***	0.28

Text S1. Characteristics of snow cover at the time of sampling in 2021

The mean height of snow cover at 55 stations amounted to 0.33 m and changed from 0.05 to 0.75 m (Table S2). The mean snow water equivalent (SWE) was equal to 59 mm and changed from 8.6 to 206 mm. The highest snow cover and SWE were found on the south-eastern shore of Lake Baikal (the town of Baikalsk and the surrounding area) and along the road of Irkutsk–Listvyanka. The lowest heights of snow cover and SWE were found on the west shore of Lake Baikal (the settlements of Bolshoe Goloustnoe and Sludyanka and their surrounding areas). The ln-transformed means of the heights at these areas were significantly different from the ln-transformed mean heights found in towns and other road directions investigated in 2021 ($p < 0.05$). The distribution of snow cover height and the SWE on the area investigated was typical of this area [10,11].

The concentration of suspended particulate matter (SPM) changed from 1.4 to 407 mg/l or from 76 to 23,830 mg/m^2 (Table S2). The mean level of SPM amounted to 61 ng/l or 3,065 mg/m^2. The median level of SPM was 27.5 mg/l or 1410 mg/m^2. In the area under study, the lowest SPM levels were found in snow sampled along the road Muruy-Zalary-Balagansk (4.8 (1.4-11) mg/l or 255 (76-505) mg/m^2. These sites lie in a northwest, windward direction from the industrial area are include the towns of Irkutsk, Angarsk, Usol'e-Sibirskoe, Schelekhovo, and Tcheremkhovo. The current study considered this area for comparisons with other site locations in the southern part of Irkutsk Region. The highest SPM concentrations were related to towns where industrial enterprises, electro-power stations, and transport hubs are located (Usol'e-Sibirskoe: 8,510 (1,955-23,830) mg/m^2; Shelekhovo: 13,340 (5,970-20,710) mg/m^2; Angarsk: 4,255 (3,120-5,395) mg/m^2; Irkutsk: 3,910 (2,885-4,880) mg/m^2). The ln-transformed SPM means in snow samples taken around the towns of Usol'e-Sibirskoe and Schelekhovo were significantly higher than those obtained from other sites in the current study ($p < 0.05$). The ln-transformed SPM mean in snow from areas along the roads Muruy–Balagans and Irkutsk–Bolshoe Goloustnoe were significantly lower compared to those for other sites investigated ($p < 0.05$).

Text S2. Homological and congener PCB patterns in snow in Irkutsk Region from 1994 to 2021.

From 1996 to 2016, pentachlorobiphenyls (pentaCB) were dominant in the total PCBs (48–52%) followed by tetrachlorobyphenyls (tetraCB) (25–30%) and hexachlorobiphenyls (hexaCB) (25–22%) (Figure S3). The contributions of other PCB homologs were well below 5–7%. The PCB homological patterns in snow corresponded to those in Sovol (PCB technical mixtures produced in the former USSR [7]) with some changes in the relative increases in tetraCB content compared to hexaCB as a result of the higher ability of tetraCB to be transported through the atmosphere compared to that of hexaCB (Figure S3). In 2021, the mean contributions of pentaCB, tetraCB, and hexaCB decreased until 35%, 20%, and 9%, respectively, whereas the mean parts of triCB and diCB increased to 28% and 7%, respectively.

The sampling sites of 2021 were divided into two groups by the cluster method (Figure 4). The PCB homological pattern found in samples from the subgroup Ia was more similar to the homological pattern in Sovol (Figure 5). Sovol was also included in the subgroup Ia by the cluster analysis (Figure 4). This subgroup Ia consisted of three sites,

including one that was highly polluted with PCB, Site # 31, located near the Usol'ekhimprom industrial area. The subgroup Ib included snow samples from 30 sites. The PCB homological patterns in snow from sites of the subgroup Ib were influenced by Sovol as a PCB source and were highly similar to those found in previous studies from 1994 to 2016, except for triCB (17%) compared to 1.7–7% from 1996 to 2016 (Figure 5). The group II combined 20 snow sampling sites and was characterized by a dominance of triCB (52 (35–65)%), whereas diPCB, tetraCB, and pentaCB contributed 13% (5–21%), 14% (7.7–19%), and 16% (5.9–27%), respectively (Figures 5). The mean total PCB in the group II was twice as high as that in the subgroup Ia (1850 vs. 970 ng/m^2), mainly due to the dominant triCB. There were two sites with PCB homological patterns that were different from those at other sites. They included St. 10 in the town of Schelekhovo, where the aluminum and cable enterprises are located, and St. 33, near the pharmaceutical plant in the Usol'e-Sibirskoe area (Figure 5). We assume that these enterprises have local PCB sources as by-products influencing the environment nearby. It should be noted that Trichlorodiphenyl (TCD), a low chlorinated technical mixture of PCBs produced in the former USSR [7], remained separate from the sampling sites during the cluster analysis (Figure 4), which supports our previous conclusion about Sovol as a major potential source of PCBs in snow [1].

In 2021, the PCB congener pattern was different from those reported in previous studies [4,6]. From 2003 to 2016, pentachlorinated congeners (PCB-95, 99, 101, 105, 110, and 118) were the most abundant PCB congeners, followed by tetrachlorinated (PCB-44, 52, 66, 70, and 74) and hexachlorinated (PCB-138, 153, and 149) congeners in the majority of snow samples (Table S3). The only exceptions were snow samples from Site # 31 near the industrial area of Usol'ekhimprom where PCB-138 and PCB-153 were amongst the five most abundant PCB congeners together with PCB-101, 118, and 110, which resembles the percentage contribution of individual PCB congeners in Sovol [9]. In addition, in 2009, PCB-28 was among the five most abundant congeners, but its contribution to total PCB was below 5%. In 2016, only penta- and tetrachlorinated congeners were included in dominant PCB congeners in all locations (Table S3). The contribution of hexachlorinated congeners decreased in 2016. In 2021, PCB-28, PCB-31, and PCB-8 showed the highest concentrations in all of areas, with the exception of Site # 31 near Usol'ekhimprom's industrial area, where the abundance of PCB congeners is ordered as follows: PCB-118 (13%) > PCB-138 (12%) > PCB-110 (11%) > PCB-110 (10%) > PCB-153 (7%).

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