

Global Atmospheric Transport of Persistent Organic Pollutants to the Russian Arctic

M. A. Zapevalov^{a*}, D. P. Samsonov^a, A. I. Kochetkov^a, E. M. Pasynkova^a,
and E. G. Bogacheva^a

^aTaifun Research and Production Association, pr. Lenina 82, Obninsk, Kaluga oblast,
249020 Russia

*e-mail: zap@rpatyphoon.ru

Received March 25, 2019

Revised October 23, 2019

Accepted December 17, 2019

Abstract—The experimental results of evaluating levels of air pollution with persistent organic pollutants (POPs) listed in the Stockholm Convention at Amderma and Tiksi stations in 2015–2017 are presented. The list of POPs includes polychlorinated biphenyls, organochlorine pesticides, and polybrominated diphenyl ethers. The ranges of the POP concentration are revealed and the statistical characteristics (mean, median) over the observation period are calculated. Based on the analysis of diagnostic ratios and temperature dependences, the features of global transport sources are considered. A wide range of variations in the concentration of POPs is shown that depends on environmental factors and the source type (local sources or global transport).

DOI: 10.3103/S1068373920090071

Keywords: Persistent organic pollutants, Stockholm Convention, Arctic region, polychlorinated biphenyls, organochlorine pesticides, toxaphenes, polybrominated diphenyl ethers, ambient air

INTRODUCTION

The urgency of the problem of the Arctic region pollution is determined by the fact that ecosystems of the northern regions are very sensitive to anthropogenic impacts. One of the most unpredictable and poorly explored phenomena is the impact on the Arctic ecosystem of persistent organic pollutants (POPs), which have exclusively anthropogenic origin. Due to the features of the global atmospheric circulation, POPs that arrive to the atmosphere are concentrated exactly in the polar regions of the globe [8, 14]. In the Northern Hemisphere, where most of population lives, the main portion of industrial and agricultural products are produced, and the anthropogenic impact of POPs on the Arctic ecosystem puts under great risks favorable living conditions on the whole Earth.

The majority of long-term series of POPs observations in the atmosphere (>20 years) were obtained for the Arctic regions of North America and Western Europe (AMAP stations: Alert (Canada), Zeppelin (Norway), Pallas (Finland)). There is an acute lack of regular data for the Arctic zone of Eastern Europe and Asia, which leads to great uncertainties in modeling and estimating the global transport of POPs.

Besides the scientific and practical value, the monitoring of POPs in the Russian Arctic is one of the elements of international obligations of the Russian Federation in the framework of the Stockholm Convention on POPs (2001) [4].

The given paper presents and summarizes experimental results of studying the concentration of several groups of the most common organochlorine compounds: hexachlorobenzene (HCB), HCH isomers, DDT, DDD, DDE, polychlorinated biphenyls (PCBs), as well as polybrominated diphenyl ethers (PBDEs) included to the list of the Stockholm Convention at Amderma and Tiksi stations in 2015–2017.



Fig. 1. The scheme of location of Arctic stations for monitoring persistent organic pollutants (Amderma and Tiksi) and AMAP stations.

METHODS

The regular observations of POPs in ambient air were organized at Amderma (69°45' 22" N, 61°40' 15" E) and Tiksi (71°35' 10" N, 128°55' 78" E) stations to study their global atmospheric transport in the Russian Arctic during the period from September 2015 to March 2017 (Fig. 1). At Amderma and Tiksi stations, 41 and 24 samples, respectively, were taken. The sampling points were situated in the open areas: close to Amderma weather station, towards the east on the outskirts of the village at a distance of about 500 m from the residential area; in Tiksi, at Polyarka weather station 14 km south of the residential area of the village (the economic activity is not carried out). The observations of POPs content were conducted by the continuous weekly sampling of ambient air with a volume of about 10000 m³, with the concentration of analytes to aerosol filters and special sorbents by the method adopted in international practice [4, 17].

All laboratory studies of POPs were performed by the modern isotope dilution analysis methods (high-resolution chromatography-mass spectrometry) using the last-generation instruments (DFS HR and Agilent 7200 Q-TOF) in the accredited laboratory of Taifun Research and Production Association (Obninsk) using the method described in [7]. The utilized analytic method allowed the maximum reliable identification of analytes (in total, more than 150 individual compounds), including POPs, and the determination of their concentration at the levels of 0.01–0.1 pg/m³.

RESULTS AND DISCUSSION

The air transport of POPs from the middle and southern latitudes to the Arctic region is directed from west to east and has a pronounced seasonal pattern [8]. Due to the prevalent tropospheric west-to-east transport, the northern regions of Russia are the zone of the global fallout of pollutants accumulated as a result of atmospheric emissions from industrially developed countries of Western and Eastern Europe, North America, and Asia [1, 6]; the Russian Arctic mainly acts as a recipient of transboundary pollution (including POPs).

Seasonal variations. To reveal seasonal variations, observational data were divided into two groups: data obtained at the negative and positive values of surface air temperature. Hereinafter, these periods are named “cold” and “warm.”

The seasonal pattern of variations in the POPs concentration is manifested in the fact that during the warm season POPs concentrations are much higher than in the cold one (Tables 1, 2). For example, at Amderma station during the warm season as compared to the cold season, the concentration of the DDE,

Table 1. The concentration (pg/m³) of organochlorine POPs in air over Amderma station (2015–2017)

Analyte, ratio	Cold season ($T < 0^{\circ}\text{C}$)			Warm season ($T > 0^{\circ}\text{C}$)			Year		
	Range	Mean/ median	, %	Range	Mean/ median	, %	Range	Mean/ median	, %
Hexachloro- benzene	6.4–30.1	17.6/18.2	100	6.9–23.5	14.7/14.3	100	6.4–30.1	16.3/16.6	100
HCH isomers									
-HCH	3.4–15.1	7.1/6.8	72	3.5–26.5	11.1/9.3	69	3.5–26.5	8.8/7.8	70
-HCH	0–3.6	1.0/0.9	10	0.2–3.2	1.3/1.1	8	0–3.6	1.1/0.9	9
-HCH	0–4.5	1.8/1.8	18	0.6–18.7	3.8/2.9	23	0–18.7	2.6/2.3	21
Total -, -, -HCH	3.6–20.1	9.8/9.5	100	8.3–46.8	16.1/11.4	100	3.6–46.8	12.6/10.3	100
-HCH/ -HCH	1–19.2	4.9/2.6	–	1.4–39.5	9.2/4.6	–	1–39.5	7.3/3.4	–
Organochlorine pesticides									
2,4 -DDE	0–2.0	0.5/0.4	8	0.4–5.2	1.1/0.9	6	0–5.2	0.8/0.6	7
4,4 -DDE	0.3–4.4	1.5/1.2	27	0.9–25.9	5.4/4.3	30	0.3–25.9	3.2/1.9	29
2,4 -DDD	0–2.4	0.5/0.2	9	0.2–3.5	1.4/1.2	7	0–3.5	0.9/0.7	8
4,4 -DDD	0–4.4	0.7/0.5	13	0.3–2.9	1.6/1.5	9	0–4.4	1.1/0.9	9
2,4 -DDT	0.3–2.8	0.9/0.8	16	2.1–6.1	3.7/3.4	20	0.3–6.0	2.1/1.4	19
4,4 -DDT	0.3–5.8	1.5/1.2	27	2.4–8.6	5.1/4.9	28	0.3–8.6	3.1/2.3	28
Total DDE, DDD, DDT	2.6–19.7	5.6/4.4	100	7.8–49.9	17.8/15.8	100	2.6–19.7	11.0/7.1	100
4,4 -DDT/ 4,4 -DDE	0.23–6.23	1.18/0.96	–	0.33–4.18	1.42/1.16	–	0.23–6.23	1.28/1.12	–
2,4 -DDT/ 2,4 -DDE	0.51–5.52	2.17/1.88	–	0.96–12.9	4.47/4.03	–	0.51–12.9	3.23/2.52	–
4,4 -DDT/ 2,4 -DDT	0.41–4.10	1.80/1.53	–	0.93–2.13	1.40/1.44	–	0.41–4.10	1.62/1.47	–
Polychlorinated biphenyls									
PCB-28 + PCB-31	0–8.14	2.02/1.41	–	1.17–7.80	2.89/2.38	–	0–8.14	2.40/1.89	–
PCB-52	0.15–5.47	1.78/1.17	–	1.10–23.6	4.51/3.23	–	0.15–23.6	2.98/2.18	–
PCB-101	0–5.89	1.54/0.63	–	1.77–13.1	4.62/3.38	–	0–13.1	2.89/1.93	–
PCB-105	0–4.02	1.05/0.56	–	0.86–10.9	3.40/2.31	–	0–10.9	2.08/1.43	–
PCB-118	0–9.71	1.85/0.84	–	0–17.3	4.72/2.99	–	0–17.3	3.11/1.74	–
PCB-138	0–7.56	1.38/0.46	–	0.47–11.2	3.13/2.35	–	0–11.2	2.15/1.30	–
PCB-153	0–3.12	0.83/0.28	–	0.43–5.59	2.13/1.80	–	0–5.59	1.40/0.90	–
PCB-156	0–0.75	0.12/0	–	0–0.38	0.11/0.06	–	0–0.75	0.12/0	–
PCB-180	0–0.74	0.12/0	–	0–1.62	0.27/0.11	–	0–1.62	0.18/0	–
Total trichloro-PCB	0.1–8.5	2.2/1.4	11	1.2–8.4	3.7/2.7	7	0.1–8.5	2.9/2.3	9
Total tetrachloro-PCB	0.1–16.3	4.8/3.8	25	3.1–47.8	12.9/8.7	26	0.1–47.8	8.4/5.4	25
Total pentachloro- PCB	0–34.1	9.0/5.2	46	9.6–65.4	25.4/17.0	51	0–65.4	16.2/10.7	49
Total hexachloro-PCB	0–17.3	3.6/0.8	18	1.2–26.1	8.2/6.7	16	0–26.5	5.6/3.7	17
Total PCB	1.5–67.9	19.7/11.5	100	16.3–146	50.3/38.3	100	1.5–146	33.1/22.0	100

Note: Here and in Table 2, is the fraction in mixture calculated using the mean values of concentrations.

Table 2. The concentration (pg/m³) of organochlorine POPs in air over Tiksi station (2015–2017)

Analyte, ratio	Cold season ($T < 0^{\circ}\text{C}$)			Warm season ($T > 0^{\circ}\text{C}$)			Year		
	Range	Mean/ median	, %	Range	Mean/ median	, %	Range	Mean/ median	, %
Hexachloro- benzene	5.9–39.1	18.9/19.3	100	4.7–21.7	13.3/12.1	100	4.7–39.1	16.8/18.0	100
HCH isomers									
-HCH	2.7–13.4	6.8/5.8	80	6.9–29.0	15.1/12.1	78	2.7–29.0	9.9/8.1	80
-HCH	0–1.9	0.4/0.2	5	0.1–2.6	1.3/1.2	7	0–2.6	0.7/0.4	5
-HCH	0–2.9	1.4/1.5	15	1.0–7.7	3.2/2.7	15	0.0–7.7	2.0/1.6	15
Total -, -, -HCH	3.1–15.5	8.4/7.8	100	9.0–38.2	19.6/16.9	100	3.1–38.2	12.6/9.1	100
-HCH/ -HCH	1.7–23.8	7.6/5.1	–	3.8–9.1	5.4/5.0	–	1.7–23.8	6.8/5.0	–
Organochlorine pesticides									
2,4 -DDE	0.01–0.57	0.15/0.09	8	0.02–0.83	0.46/0.55	5	0.01–0.83	0.26/0.14	7
4,4 -DDE	0.19–2.05	0.76/0.57	42	0.16–4.73	2.93/3.63	33	0.16–4.73	1.57/0.92	39
2,4 -DDD	0–0.14	0.04/0.02	3	0.03–0.45	0.27/0.29	4	0–0.45	0.13/0.04	3
4,4 -DDD	0.01–0.42	0.15/0.09	8	0.04–0.75	0.44/0.53	6	0.01–0.75	0.26/0.14	7
2,4 -DDT	0.04–1.10	0.24/0.15	15	0.08–4.28	2.16/2.31	21	0.04–4.28	0.96/0.26	17
4,4 -DDT	0.13–1.58	0.40/0.29	24	0.06–6.21	3.37/3.72	31	0.06–6.21	1.51/0.46	27
Total DDE, DDD, DDT	0.58–5.22	1.72/1.58	100	0.38–17.1	9.63/11.5	100	0.38–17.1	4.69/1.99	100
4,4 -DDT/ 4,4 -DDE	0.19–1.07	0.63/0.63	–	0.39–1.36	1.00/1.08	–	0.2–1.4	0.8/0.7	–
2,4 -DDT/ 2,4 -DDE	0.08–8.65	2.89/2.24	–	3.02–6.02	4.63/5.20	–	0.08–8.65	3.54/3.62	–
4,4 -DDT/ 2,4 -DDT	0.87–4.19	2.24/1.71	–	0.83–2.27	1.50/1.45	–	0.8–4.2	2.0/1.6	–
Polychlorinated biphenyls									
PCB-28 +	0–8.03	2.40/1.20	–	1.07–7.40	2.90/1.66	–	0.00–8.03	2.59/1.59	–
PCB-31	0.23–2.84	1.15/0.94	–	0.78–7.28	2.15/1.40	–	0.23–7.28	1.52/1.14	–
PCB-52	0.35–1.88	0.88/0.77	–	0.81–9.67	2.93/2.03	–	0.35–9.67	1.65/1.09	–
PCB-101	0–1.43	0.53/0.29	–	0.18–4.89	1.70/1.11	–	0.00–4.89	0.96/0.84	–
PCB-105	0.37–2.26	0.96/0.63	–	0.41–6.86	2.54/2.33	–	0.37–6.86	1.55/1.28	–
PCB-118	0.12–1.31	0.54/0.43	–	0.34–3.75	1.36/1.02	–	0.12–3.75	0.85/0.53	–
PCB-138	0.14–1.43	0.43/0.37	–	0.30–3.20	1.09/0.79	–	0.14–3.2	0.68/0.53	–
PCB-153	0–0.13	0.02/0	–	0.00–0.29	0.06/0.00	–	0.00–0.29	0.03/0.00	–
PCB-156	0–0.35	0.04/0	–	0.00–0.35	0.14/0.14	–	0.00–0.35	0.08/0.00	–
PCB-180	0.10–8.50	3.60/2.48	25	1.19–7.89	3.10/1.77	11	0.10–8.50	3.41/2.39	21
Total	1.44–6.58	3.25/2.40	26	2.93–20.4	6.24/4.02	23	1.44–20.4	4.37/3.16	25
trichloro-PCB									
Total	1.86–10.3	4.72/4.16	38	3.93–43.4	14.0/10.4	52	1.86–43.4	8.21/5.79	43
tetrachloro-PCB									
Total	0.47–4.33	1.33/0.80	10	0.89–11.0	3.72/2.63	13	0.47–11.0	2.22/1.46	11
pentachloro- PCB									
Total	5.9–27.2	12.9/10.4	100	8.9–82.7	27.1/20.3	100	8.9–82.7	18.2/14.8	100
hexachloro-PCB									
Total PCB									

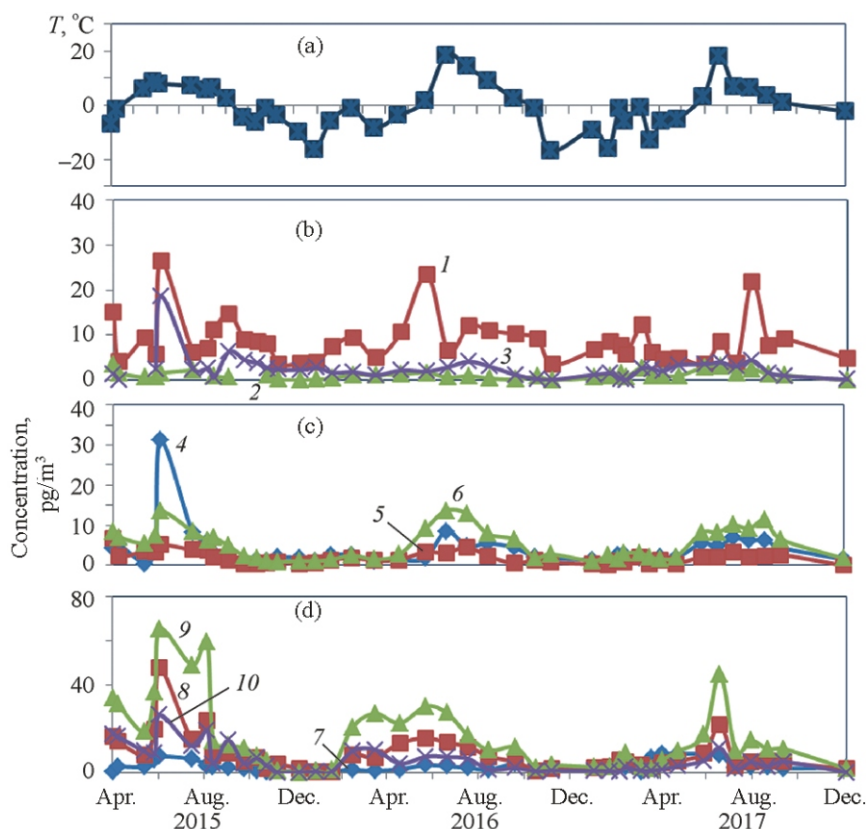


Fig. 2. Temporal variations in (a) surface temperature and (b–d) concentration of organochlorine POPs at Amderma station. The HCH isomers: (1) γ -HCH; (2) β -HCH; (3) α -HCH; (4) total DDE; (5) total DDD; (6) total DDT; the PCB isomers: (7) total trichloro-PCB; (8) total tetrachloro-PCB; (9) total pentachloro-PCB; (10) total hexachloro-PCB.

DDD, and DDT isomers is higher by 2.3–4 times, the content of HCH isomers is higher by 1.3–2.1 times, the sums of trichloro-PCB isomers are higher by 1.7 times, and the sums of tetrachloro-, pentachloro-, and hexachloro-PCB isomers are higher by 2.3–2.8 times. At Tiksi station, the concentrations of POPs in ambient air during the warm season are also higher than in the cold season: by 2.1–3.3 times for the HCH isomers, by 3.3–8 times for the DDE, DDD, and DDT isomers, and by 1.9–2.8 times for the sums of tetrachloro-, pentachloro-, and hexachloro-PCB isomers. The curves in Fig. 2 demonstrate temporal variations in the concentration of HCH isomers, DDE, DDD, and DDT isomers, and the sum of PCB isomers in air over Amderma station. The seasonal course of HCB concentrations is not observed at both stations.

The concentration of PBDEs in air over Amderma and Tiksi stations is low, and the concentrations of the identified isomers PBDE-47, -99, -100, -183, -209 were above the detection limits only for 50% of samples. The arithmetic mean values of concentration for the PBDE isomers during the warm and cold seasons were (pg/m^3):

—at Amderma station:

PBDE isomer	-47	-99	-100	-183	-209
Warm season	0.89	0.41	0.54	0.37	0.46
Cold season	0.38	0.12	0.25	0.31	0.31

—at Tiksi station:

PBDE isomer	-47	-99	-100	-183	-209
Warm season	0.15	0	0.047	0.013	1.0
Cold season	0.067	0.011	0.019	0.025	1.2

Thus, the lighter isomers PBDE-47, -99, -100 are characterized by the higher concentrations in air in the warm season, and no such regularity is observed for the heavier PBDE-183, -209. As well as in case of

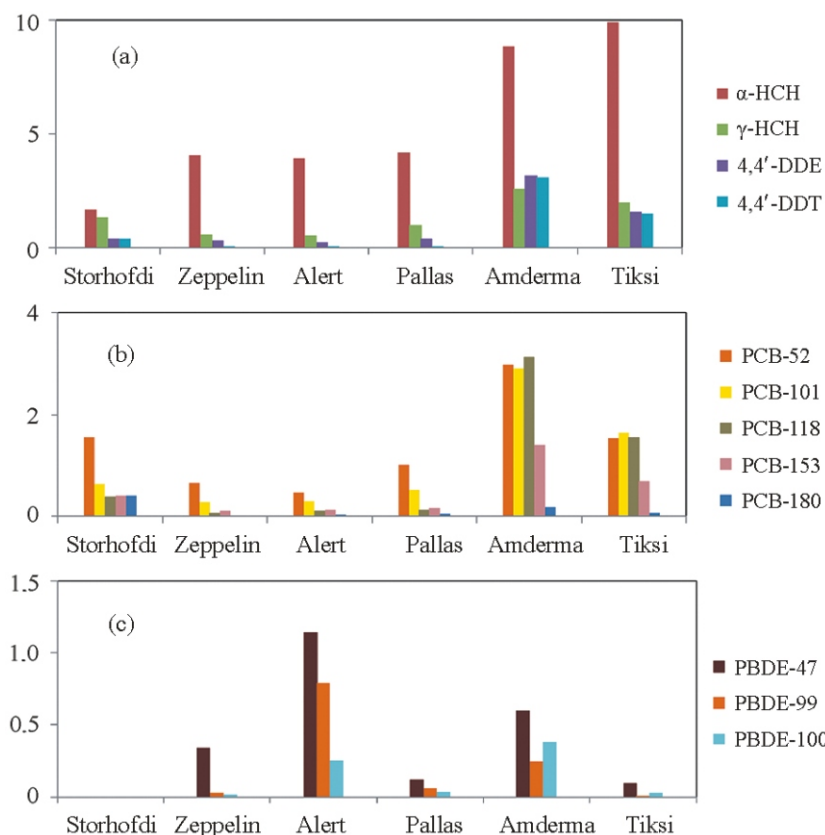


Fig. 3. The average concentrations of POPs at the Arctic stations over the observation period: (a) HCH, DDE, DDT isomers; (b) PCB isomers; (c) PBDE isomers.

organochlorine POPs, the mean concentrations of PBDE at Tiksi station are 2–10 times smaller than at Amderma station.

In terms of the absolute values, the average annual concentrations of POPs at Amderma and Tiksi stations in 2015–2017 were comparable to similar data from the foreign Arctic stations. The comparison of the mean values of concentrations (Fig. 3, Table 1) shows that the concentrations of α - and γ -HCH on the Russian Arctic coast observed in 2015–2017 are 2–4 times higher than the concentrations observed in that period at the Arctic stations Alert, Zeppelin, Pallas, Storhofdi, data for which were obtained from the EBAS database (NILU).

At the Russian stations Amderma and Tiksi, the concentrations of 4,4-DDT, 4,4-DDE, 2,4-DDT, 2,4-DDE were equal to 3.1, 2.1, 3.2, 0.8 pg/m^3 and 1.5, 0.96, 1.6, 0.26 pg/m^3 , respectively; the concentrations of PCB-52, -101, -118, -153, -180 were equal to 2.3, 2.9, 3.1, 1.4, 0.18 and 1.5, 1.7, 1.6, 0.68, 0.08 pg/m^3 , respectively, which is 5–20 times higher than at Alert, Zeppelin, Pallas, and Storhofdi stations. The concentrations of PBDE-47, -99, -100 at Amderma station were 0.60, 0.25, and 0.38 pg/m^3 , respectively. This is approximately twice smaller than at Alert station and close to the values at Zeppelin station, but it is ~4 times higher than at Pallas station. At Tiksi station, the concentrations of PBDE-47, -99, -100 were 0.092, 0.007, and 0.029 pg/m^3 and were close to the values obtained in the analyzed period for Zeppelin and Pallas stations.

The pattern of seasonal variations in the POPs concentrations in ambient air is significantly determined by the geographic conditions and physical and chemical properties of POPs. For example, Alert station is in ice all year round, and the concentrations of POPs in air are determined by the global transport alone; at the same time, the summer peak of α -HCH at Storhofdi station is caused by evaporation from the nearby ocean [9]. An increase in the concentration of POPs observed at Amderma and Tiksi stations in the warm season is also typical of the stations located in Greenland [11] and cannot be explained by the global transport alone.

Diagnostic ratios. The diagnostic ratios of the isomers γ -HCH/ δ -HCH, DDT/DDE and PCB congeners with various degree of chlorination are widely used to identify the sources of POPs inflow to the environment. The closeness of the values of diagnostic ratios in the environment to the ratios in the supposed sources of inflow to the environment (as a rule, these are technical products of producing PCB-based pesticides or insulating fluids) provides a basis for judging about the most probable sources of inflow and about the “age” of POPs in the environment.

The possible sources of HCH isomers are the technical mix of HCHs (it contains about 60–70% of δ -HCH, 5–12% of γ -HCH, and 10–15% of α -HCH [18], the theoretical ratio δ -HCH/ γ -HCH is about 8) or lindane (99% of δ -HCH).

The ratios δ -HCH/ γ -HCH calculated from observational data for the cold and warm seasons and for the whole year are 2.6, 4.6, and 3.4 at Amderma station and 5.1, 5.5, and 5.0 at Tiksi station, respectively (Tables 1 and 2; the medians of concentrations for different seasons and for the entire year are used for calculations hereinafter). These values are lower than the theoretical ratio in the technical mix of HCH, which may indicate the use of pure lindane and long-range transport of δ -HCH. At Amderma station, a clear increase in the ratio δ -HCH/ γ -HCH is observed for the warm season; unlike this, seasonal variations are almost not observed at Tiksi station (Tables 1 and 2). Thus, proceeding from the ratios δ -HCH/ γ -HCH, it is possible to conclude that the sources of HCH isomers at Amderma and Tiksi stations are different. The values of the ratios δ -HCH/ γ -HCH obtained in the present study are close to similar data from Zeppelin and Alert polar stations in 1993–2005, that varied from 3 to 7 and from 5 to 8 and did not exhibit any clear trends [10].

The diagnostic ratios 4,4-DDT/4,4-DDE, 2,4-DDT/2,4-DDE, and 4,4-DDT/2,4-DDT are widely used for organochlorine pesticides. The ratios DDT/DDE allow assessing the “age” of DDT in the environment: the increased concentrations of DDT as compared to DDE indicate the presence of the new inflow of DDT to the environment. The ratio 4,4-DDT/2,4-DDT allows judging about the sources of DDT inflow to the environment. In technical DDT, that is the mixture of 85% of 4,4-DDT and 15% of 2,4-DDT, the ratio 4,4-DDT/2,4-DDT is equal to ~ 5 [19]. One more source of DDT inflow to the environment is the pesticide dicofol widely used in China and containing DDT as an impurity. The commercial product of dicofol mainly contains the isomer 2,4-DDT, the ratio 4,4-DDT/2,4-DDT is much smaller than in the technical DDT and is equal to ~ 0.15 [15].

The ratios 4,4-DDT/4,4-DDE calculated using measurement data for the cold and warm seasons and for the year are equal to 0.96, 1.16, and 1.12, respectively, at Amderma station and 0.63, 1.08, and 0.7 at Tiksi station. The ratios 2,4-DDT/2,4-DDE are equal to 1.88, 4.03, and 2.52 at Amderma station and 2.24, 5.20, and 3.62 at Tiksi station (Tables 1 and 2).

The insignificant seasonal variations in diagnostic ratios may be noted for both stations. Their values indicate that DDT at Amderma station is “fresher” than in Tiksi. The ratios 4,4-DDT/2,4-DDT in the cold and warm seasons and for the year are 1.53, 1.44, and 1.47, respectively, for Amderma station and 1.71, 1.45, and 1.60 for Tiksi station (Tables 1 and 2). Based on these data, it may be concluded that the possible contribution of the “dicofol” source of DDT does not exceed 15–20%. The presence of such source in Southeast Asia is confirmed in some papers [19, 20].

Data on the PCB levels at Amderma and Tiksi stations presented in Tables 1 and 2 coincide with monitoring data from the foreign polar stations, although there are some essential peculiarities. They consist in the fact that the ratio of tri-, tetra-, and pentachlorinated isomers at the foreign polar stations is more similar to the distribution of congeners in the foreign brands of production of PCB mixtures [12]. The mass fractions of tri-, tetra-, penta-, and hexachlorinated PCB congeners consecutively decrease; in addition, as the latitude increases, the enrichment with lighter tri- and tetra-chlorinated PCB congeners occurs in ambient air [16]. On the contrary, at Amderma and Tiksi stations, there are increased concentrations of tetra- and pentachlorinated congeners. These data are consistent with the composition of PCB mixtures of sovol and sovtol brands, that were produced before on the territory of the former USSR. These mixtures mainly included the heavier tetra-, penta-, and hexachlorinated congeners, the ratio of mass concentrations for which is 19–21, 53–58, and 19–23%, respectively [2]. It should be noted that such distribution of PCB congeners in air was registered over the Russian polar stations in the 2000s [5].

Over the whole period of observations at Amderma and Tiksi stations, the relative contributions to the sum of congeners were: 21 and 9% for trichloro-PCB, 25 and 25% for tetrachloro-PCB, 43 and 49% for pentachloro-PCB, and 11 and 17% for hexachloro-PCB, respectively (Tables 1 and 2). The revealed differences in the ratios of PCB congeners indicate different sources of their inflow; in any case, the contribution of secondary PCB sources at Tiksi station is higher than at Amderma station.

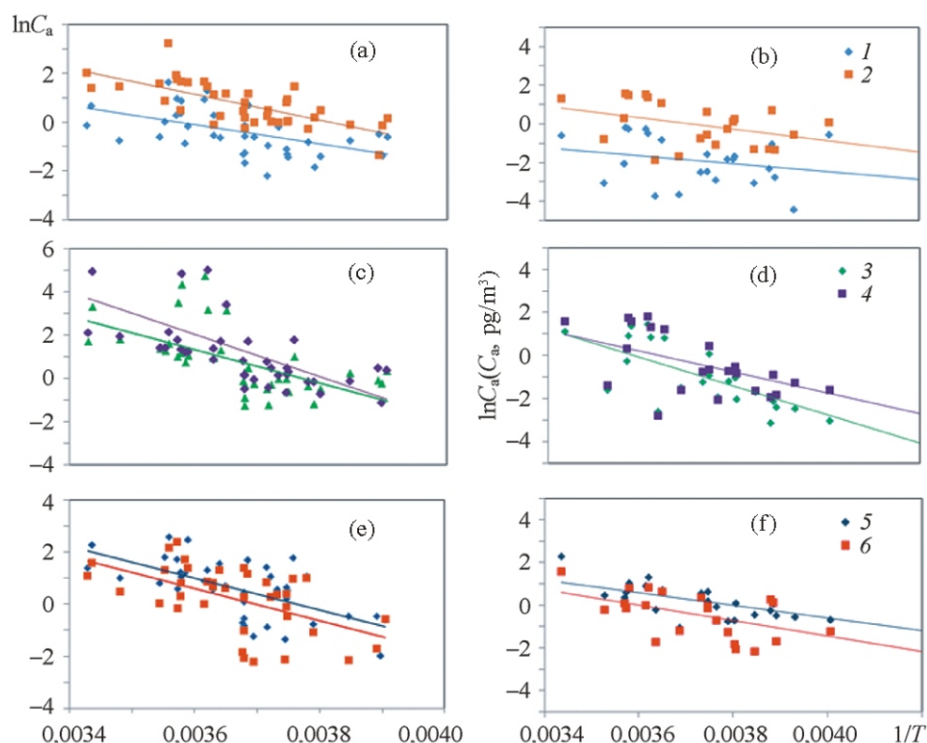


Fig. 4. The dependences of logarithms of POPs concentration (pg/m^3) (gas + aerosol) versus inverse temperature (K) $\ln C_a = m/T + b$ over the observation period of 2015–2017 for (a, c, e) Amderma and (b, d, f) Tiksi stations. (a, b; 1) 2,4-DDE and (2) 4,4-DDE; (c, d; 3) 2,4-DDT and (4) 4,4-DDT; (e, f; 5) PCB-101 and (6) PCB-105.

The comparison of the obtained ratios of PCB congeners in the Russian Arctic and at the foreign Arctic stations demonstrates that over the analyzed observation period (2015–2017) the contribution of tri-, tetra-, penta-, and hexachlorinated PCB congeners, for example, at Zeppelin station makes up 68, 22, 6, and 5% against 19, 24, 45, 12% and 9, 25, 49, 17% at Amderma and Tiksi stations, respectively.

The seasonal variations in the composition of PCB congeners was manifested only at Tiksi station, where the contribution of trichlorinated PCB congeners considerably increases in winter (from 11 to 28%), the tetrachlorinated congeners remain at the same level, and the contribution of penta- and hexachlorinated ones drops from 46 to 37% and from 18 to 10%, respectively (Tables 1 and 2, Fig. 4). The absence of seasonal variations in the ratios of PCB congeners at Amderma station indicates the presence of local sources of this group of POPs.

Air temperature effects. Temperature is one of the most important factors that determine the concentration of POPs in air. The dependence of POPs concentrations on temperature is used to estimate the contribution of primary and secondary sources of their inflow. The approach is common that is based on the revelation of statistically significant dependences of logarithm of POPs partial pressure or concentration (gas) in ambient air versus inverse temperature described by the equation [13]:

$$\ln C_a = m/T + b$$

where C_a is the concentration of POPs in air; T is temperature (K); m , b are the coefficients of linear regression. If such dependence is statistically confirmed, it is assumed that the remission of POPs due to the air temperature rise (for example, evaporation from the surface) is quite significant.

The results of processing experimental data on the evaluation of parameters of the linear regression $\ln C_a - 1/T$ (the examples are given in Fig. 4 and Table 3) demonstrate that the dependences of observational data on temperature are significant for the whole observation period, including the warm and cold seasons (the calculated level of significance of the acceptor hypothesis rejection $p < 0.05$ [3]).

The highest values of parameter m , that shows a degree of inclination of the regression line with changing temperature, at Amderma and Tiksi stations are observed for 4,4-DDT (−9760 and −4830) and 2,4-DDT

Table 3. The statistical parameters of the linear regression for the dependence of logarithms of POPs concentration (gas + aerosol) versus inverse temperature

POP	Amderma (<i>n</i> = 41)			Tiksi (<i>n</i> = 24)		
	<i>m</i>	<i>r</i> ²	<i>p</i>	<i>m</i>	<i>r</i> ²	<i>p</i>
HCB	890	0.07	0.090	630	0.03	0.400
-HCH	-1670	0.14	0.018	-2540	0.52	0.01
-HCH	-1720	0.06	0.148	-3180	0.15	0.064
-HCH	-3000	0.12	0.031	-2530	0.27	0.01
2,4-DDE	-3970	0.24	<0.001	-2070	0.08	0.170
4,4 -DDE	-5340	0.50	<0.001	-2970	0.21	0.025
2,4-DDT	-7820	0.36	<0.001	-6570	0.55	<0.001
4,4 -DDT	-9760	0.35	<0.001	-4830	0.35	0.002
PCB-28/PCB-31	-2230	0.07	0.091	-3380	0.24	0.019
PCB-52	-5240	0.36	<0.001	-2270	0.26	0.010
PCB-101	-6120	0.40	<0.001	-2970	0.44	<0.001
PCB-105	-6170	0.40	<0.001	-3610	0.34	0.004
PCB-118	-5620	0.32	<0.001	-2730	0.35	0.002
PCB-138	-4890	0.24	0.002	-2230	0.19	0.030
PCB-153	-5900	0.24	<0.001	-2100	0.20	0.025

Note: *m* is the coefficient of linear regression; *r*² is the coefficient of determination; *p* is calculated level of statistical significance. The values with confirmed statistical significance are bolded.

(-7820 and 6570) (Table 3). In the authors' opinion, this result demonstrates an increased role of secondary of DDT on the global scale due to the prohibition of DDT in the 1970s. At Amderma station, the temperature dependence of the concentration of PCB-52, -101, -105, -118, -138, and -153 is pronounced about two times stronger than at Tiksi station (the parameter *m* varies in the range from -6170 to -4890 and from -3610 to -2100, respectively) (Table 3). A difference in the dependences may be caused by different contributions of local and global sources of PCB inflow to air.

A number of other potentially dangerous groups of organochlorine compounds were quantified in the air samples. Toxic congeners of toxaphene (polychloropinene), that was widely used in the USSR in the 1960s–1980s, were registered at Amderma and Tiksi stations at the following levels: 0.52 and 0.1 pg/m³ for TOX-26, 0.47 and <0.01 pg/m³ for TOX-50.

The pesticides were detected that have not been used before on the territory of the USSR and Russia. The average concentrations of such substances over the observation period at Amderma and Tiksi stations were 0.57 and 0.31 pg/m³ for cis-chlordane, 0.57 and 0.29 pg/m³ for trans-chlordane, 0.26 and 0.03 pg/m³ for cis-nonachlor, 0.62 and 0.29 pg/m³ for trans-nonachlor, 0.3 and 0.19 pg/m³ for oxychlordane.

The toxic compounds whose observations have not been previously conducted in the Russian Arctic were also detected at Amderma and Tiksi stations: the concentrations of octachlorostyrene and pentachloroanisole were equal to 1.48 and 0.45 pg/m³ and 1.63 and 1.14 pg/m³, respectively.

For the above groups of organochlorine compounds, the concentrations in air over Tiksi station were 2–5 times lower than in Amderma.

CONCLUSIONS

The concentrations of persistent organic pollutants in the atmosphere over the Russian Arctic are formed under the influence of the global and regional transport and are generally comparable to monitoring data from the foreign Arctic stations. In the eastern part of the Russian Arctic (Tiksi station), the concentrations of POPs during the observation period of 2015–2017 are 2–5 times lower than in the western part (Amderma station).

All groups of organochlorine pesticides listed in the annexes to the Stockholm Convention on POPs are identified in the atmosphere over the Russian Arctic, including those that are not used or not produced in the Russian Federation or the former USSR.

The seasonal variations in the concentrations of POPs in air over the Russian Arctic are clearly observed for such groups of compounds as organochlorine pesticides and polychlorinated biphenyls. Among the most significant factors that determine the seasonal variations in POPs concentrations in air over the Russian Arctic, it is necessary to note a change in the global air mass circulation in the Northern Hemisphere in summer and winter and an increase in the emission of organochlorine pesticides due to the seasonal application of pesticides in South and South-East Asia.

The concentrations of POPs in air over the Russian Arctic are determined by the inflow from primary and secondary sources. The contribution of the secondary sources of POPs is confirmed by the statistically significant dependence of POPs concentrations on temperature.

An effect of current climate changes is the redistribution of accumulated stocks of POPs in adjacent natural environments; in view of this, the systematic monitoring of POPs in the Russian Arctic and the revelation of data relations to changing meteorological factors are required.

ACKNOWLEDGMENTS

The authors thank the specialists of Norwegian Institute for Air Research (NILU) for the opportunity of using the data on POPs concentrations contained in the public EBAS database.

FUNDING

The research was supported by the Arctic Monitoring and Assessment Program (AMAP) in the framework of the contract AMAP No. 2014/2.

REFERENCES

1. A. A. Vinogradova and Yu. A. Ivanova, "Air Mass and Pollution Transport to the Russian Arctic Islands (1986–2016): Long-term, Interannual, and Seasonal Variations," *Geofizicheskie Processy i Biosfera*, No. 4, 6 (2017).
2. T. I. Gorbunova, M. G. Pervova, O. N. Zabelina, V. I. Saloutin, and O. N. Chupakhin, *Polychlorinated Biphenyls: Problems of Ecology, Analysis, and Chemical Utilization*, Ed. by V. N. Charushin (Krasand, Moscow, Yekaterinburg, 2011) [in Russian].
3. N. R. Draper and H. Smith, *Applied Regression Analysis*, Book 1 (Finansy i Statistika, Moscow, 1986) [Transl. from English].
4. M. A. Zapevalov, "Monitoring of Persistent Organic Pollutants is an Objective and Independent Tool for Evaluating Effectiveness of the Stockholm Convention on POPs," *Khimicheskaya Bezopasnost'*, No. 2, 2 (2018) [in Russian].
5. A. V. Konoplev, V. A. Nikitin, D. P. Samsonov, G. V. Chernik, and A. M. Rychkov, "Polychlorobiphenyls and Organochlorine Pesticides in the Atmosphere of the Far East Russian Arctic," *Meteorol. Gidrol.*, No. 7 (2005) [*Russ. Meteorol. Hydrol.*, No. 7, 30 (2005)].
6. A. A. Makosko and A. V. Matesheva, "Evaluation of Trends in Long-range Atmospheric Pollution in the Russian Arctic Regions in the 21st Century," *Arktika: Ekologiya i Ekonomika*, No. 4 (2017) [in Russian].
7. D. P. Samsonov, A. I. Kochetkov, E. M. Pasyukova, and M. A. Zapevalov, "Levels of Persistent Organic Pollutants in the Components of the Lake Baikal Unique Ecosystem," *Meteorol. Gidrol.*, No. 5 (2017) [*Russ. Meteorol. Hydrol.*, No. 5, 42 (2017)].
8. *AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP)*, Chapter 3: *The Influence of Physical and Chemical Processes on Contaminant Transport* (Oslo, Norway, 1998), <https://www.amap.no/documents/doc/amap-assessment-report-arctic-pollution-issues/68>.
9. *AMAP, 2012. Arctic Climate Issues 2011: Changes in Arctic Snow, Water, Ice and Permafrost. SWIPA 2011.*
10. S. Becker, C. J. Halsall, W. Tych, R. Kallenborn, Y. Su, and H. Hung, "Long-term Trends in Atmospheric Concentrations of Alpha- and Gamma-HCH in the Arctic Provide Insight into the Effects of Legislation and Climatic Fluctuations on Contaminant Levels," *Atmos. Environ.*, 42 (2008).
11. R. Bossi, H. Henrik, K. Vorkampa, J. Christensen, S. C. Rastogi, A. Egelov, and D. Petersen, "Atmospheric Concentrations of Organochlorine Pesticides, Polybrominated Diphenyl Ethers and Polychloronaphthalenes in Nuuk, South-West Greenland," *Atmos. Environ.*, 42 (2008).
12. K. Breivik, A. Sweetman, J. M. Pacyna, and K. C. Jones, "Towards a Global Historical Emission Inventory for Selected PCB Congeners—A Mass Balance Approach 3. An Update," *Sci. Total Environ.*, 377 (2007).
13. R. Hoff, D. Mur, and N. Grift, "Annual Cycle of Polychlorinated Biphenyls and Organohalogen Pesticides in Air in Southern Ontario. 2. Atmospheric Transport and Sources," *Environ. Sci. Technol.*, 26 (1992).

14. H. Hung, A. A. Katsoyiannis, E. Brorstrom-Lunden, K. Olafsdottir, W. Aas, K. Breivik, P. Bohlin-Nizzetto, A. Sigurdsson, H. Hakola, R. Bossi, H. Skov, E. Sverko, E. Barresi, P. Fellin, and S. J. Wilson, "Temporal Trends of Persistent Organic Pollutants (POPs) in Arctic Air: 20 Years of Monitoring under the Arctic Monitoring and Assessment Programme (AMAP)," *Environ. Pollut.*, **217** (2016).
15. J. S. Park, S. K. Shin, W. I. Kim, and B. H. Kim, "Residual Levels and Identify Possible Sources of Organochlorine Pesticides in Korea Atmosphere," *Atmos. Environ.*, **45** (2011).
16. L. Shen, F. Wania, Y. D. Lei, C. Teixeira, C. Derek, G. Muir, and Hang Xiao, "Polychlorinated Biphenyls and Polybrominated Diphenyl Ethers in the North American Atmosphere," *Environ. Pollut.*, **144** (2006).
17. *UNEP/POPS/COP.8/INF/38. Second Global Monitoring Report/ 2017*, <http://www.pops.int/Implementation/GlobalMonitoringPlan/MonitoringReports/tabid/525/Default.aspx> (Accessed on January 31, 2019).
18. H. Wohrnschimmel, P. Tay, H. von Waldow, H. Hung, Y.-F. Li, M. MacLeod, and K. Hungerbuhler, "Comparative Assessment of the Global Fate of α - and β -hexachlorocyclohexane before and after Phase," *Out. Environ. Sci. Technol.*, **46** (2012).
19. X. Zheng, D. Chen, X. Liu, Q. Zhou, Y. Liu, W. Yang, and G. Jiang, "Spatial and Seasonal Variations of Organochlorine Compounds in Air on an Urban–Rural Transect across Tianjin, China," *Chemosphere*, **78** (2010).
20. X.-P. Wang, T.-D. Yao, Z.-Y. Cong, X.-L. Yan., S.-C. Kang, and Y. Zhang, "Gradient Distribution of Persistent Organic Contaminants along Northern Slope of Central Himalayas," *Sci. Total Environ.*, **372** (2006).