# SPATIAL AND TEMPORAL DISTRIBUTION OF PERSISTENT ORGANIC POLLUTANTS IN THE AMBIENT AIR OF THE RUSSIAN ARCTIC

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## Introduction

Concerns of the international community about the consequences of POPs pollution main a driving force behind the adoption in May 2001 the Stockholm Convention on POPs - a global international agreement, which aims to protect human health and the environment from POPs. The aim of the Stockholm Convention is to regulate the treatment of POPs, which should be prohibited for usage, their production should be stopped, and all stocks have been destroyed. The Stockholm Convention entered into the force in May 2004, Russia signed the Convention in May 2002, and in June 2011, ratified it, on becoming a Part to the Convention, and taking on their respective responsibilities.

In Russia, the problem of waste, which may contain POPs, is very crucial. In most enterprises a lack of a modern technology for the disposal of such wastes has resulted in the fact that the total amount of waste completely neutralized only a small part.

In Russia, environmental monitoring has been traditionally conducted on the Roshydromet network. Data are presented in annual reviews of the environmental pollution (air, surface and sea water, soils) in Russian Federation (up to 10 annual reports).

Transport of POPs occurs mainly in the ambient air. That is why, monitoring of POPs in the ambient air and their deposition is of paramount importance. Roshydromet focuses its efforts on establishing stations for monitoring POPs in the ambient air, special emphasis is placed on the Russian Arctic, which is the region exposed to particular risk of POPs pollution.

## Materials and methods

In Russia air monitoring have been conducted at 4 places: the station Dunai in the vicinity of Tixi (1993 - 1995), the settlement of Amderma (1999-2001), Valkarkai at the coast of the East Siberian Sea, Chukotka Peninsula (2002 – 2003 and 2008 – 2010) and in Tixi region at the coast of Laptev Sea in the mouth of the Lena river (2010 – 2011). The location of POPs monitoring stations in the Russian Arctic is shown in Figure 1.


Fig.1 Location of POPs monitoring stations in the Russian Arctic (A – Amderma, T – Tixi, V - Valkarkai)

Air samples were collected at all stations by high-volume air sampler with one glass fiber filter (GFF) and two layers of polyurethane foam plugs (PUF)[1]. At Valkarkai and Tixi samples representing about 10000 $m^3$ of air were taken each week. Then air samples were packed in glass jars, labeled and transport to RPA Typhoon for further analysis. Extraction of samples was carried out by Soxlet apparatus during about 24 hours. Then the extract was divided in the ratio 2:1[2]. In each part the surrogate standard was added which is the mixture of isotope-labeled PCBs, OCPs. Defined compounds are polychlorinated biphenils (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenil ethers (PBDEs). Instrumental analysis was performed by gas chromatography-mass spectrometry.

**Results and discussions**

*Spatial trends*

*PCBs.*

Total mass concentration of PCB mixture (57 congeners) in the ambient air of Valkarkai (2008 - 2010) was in the range of 12.9 - 579 pg/$m^3$ (mean - 124 pg/$m^3$ ) . This is well above the levels seen on Tixi, where the total concentration of these compounds was 6.0 - 55.2 pg/$m^3$ (mean - 20.2 pg/$m^3$ ) . The total mass concentration of 10 PCB congeners AMAP ( 28, 31 , 52, 101 , 105, 118 , 138, 153, 156 and 180 according to the nomenclature IUPAC) equals 5 and 51 pg/m3 for Valkarkai and Tixi, respectively.

*OCPs.*

Air samples were analyzed on the content of 22 OCPs. Table 1 shows the values of OCP mass concentrations detected in air samples.

Table 1 – Average OCPs concentrations in the ambient air of Valkarkai and Tixi

| Compound | Mass concentration, pg/$m^3$ | | | | |
|---|---|---|---|---|---|
| | Valkarkai | | | Tixi | |
| | 2008 | 2009 | 2010 | 2010 | 2011 |
| HCB | 17,3 | 14,6 | 17,7 | 4,50 | 4,09 |
| α-HCH | 42,8 | 8,22 | 8,68 | 9,78 | 2,32 |
| β-HCH | 1,89 | 1,01 | 0,11 | 0,18 | 0,04 |
| γ-HCH | 1,88 | 1,90 | 0,40 | 0,24 | 0,11 |
| ∑HCH | 46,6 | 11,1 | 9,19 | 10,2 | 2,47 |
| 2,4'-DDD | 0,31 | 0,08 | 0,39 | 0,11 | 0,15 |
| 4,4'-DDD | 0,04 | 0,22 | 0,73 | 0,40 | 0,02 |
| 2,4'-DDE | 0,35 | 0,99 | 0,08 | 0,25 | 0,04 |
| 4,4'-DDE | 2,29 | 1,38 | 3,33 | 0,86 | 0,19 |
| 2,4'-DDT | nd** | 0,70 | 1,26 | 1,86 | 0,11 |
| 4,4'-DDT | 1,22 | 0,89 | 2,21 | 3,94 | 0,54 |
| ΣDDT | 4,21 | 4,26 | 8,00 | 7,42 | 1,05 |
| c-chlordane | nd | 0,12 | 0,26 | 0,51 | 0,09 |
| t-chlordane | nd | 0,11 | 0,07 | 0,18 | nd |
| oxychlordane* | 1,09 | 0,31 | 0,20 | 0,28 | 0,06 |
| transnonachlore | 0,19 | 0,25 | 0,23 | 0,29 | 0,08 |
| endosuphane (α+β) | 0,27 | nd | 0,17 | 0,16 | nd |
| *sum oxychlordane and heptachloroepoxide<br>** no detection | | | | | |

Mass concentration of α- HCH in the air at Valkarkay dropped significantly in 2009 – 2010 (about 9 pg/$m^3$) compared to value observed in 2008 (43 pg/$m^3$). The maximum value of the total concentration of HCH isomers is also celebrated in 2008 (more than 46 pg/$m^3$), it was significantly decreased in 2009 (to 9.2 pg/$m^3$). Atmospheric levels of HCB were approximately the same for all years of observations. A similar trend is noted in the case of Tixi, i.e. the concentration of α- HCH reduced from 9.78 pg/$m^3$ in 2010 to 2.32 pg/$m^3$ in 2011. Stable levels HCB shows throughout the observation period (4 pg/$m^3$). 4,4 ' - DDE concentrations declined in 2009 compared with levels observed in 2008 (1.38 pg/$m^3$ and 2.3 pg/$m^3$ , respectively).

Levels of chlordane isomers found in the ambient air were negligible. Average mass concentrations of cis-chlordane were almost similar at Valkarkai in 2009 (0.12 pg/m3 ) and Tixi in 2011 (0.09 pg/m3 ) . However, in 2010, atmospheric levels of this compound at Tixi rose slightly to 0.51 pg/m3 , which is also higher than at

Valkarkai (0.26 pg/m3 in 2010). Mass concentration of trans - chlordane at Valkarkai totaled 0.11 and 0.07 pg/m$^3$ in 2009 and 2010, respectively. This is somewhat lower than at Tixi where this value is equal to 0.18 pg/m$^3$ in 2010. The highest levels of oxychlordane were observed at Valkarkai in 2008 (1.09 pg/m$^3$). In subsequent years, it has decreased and amounted to 0.31 and 0.20 pg/m$^3$ in 2009 and 2010, respectively.
The total concentration of PBDEs (18 individual compounds) at Tixi was 1.2 pg/m$^3$. This value is lower than in the Canadian Arctic (8.4 pg/m$^3$) and comparable with the levels in Greenland and Finland (approximately 1.1 pg/m$^3$). PBDE congeners with the highest levels are BDE-47 and BDE-99 but their levels are lower than in Canada and USA[3] (Fig. 2).

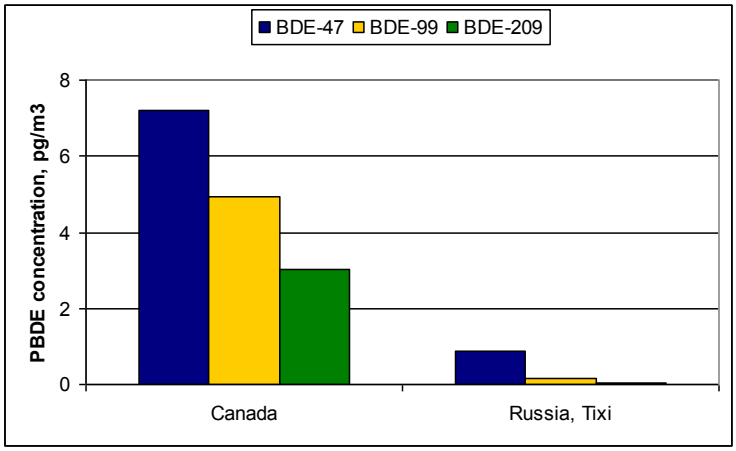


Fig. 2. Mass concentration of PBDE congeners in the Canadian and Russian Arctic

*Temporal trends*
For studying temporal trends of POPs data obtained at Valkarkai (2002 - 2003) and at the station of Dunai (1993 - 1994) were used.
The total mass concentration of PCB congeners in the period from 2010 to 2011 at the Tixi region was slightly lower values determined at the station of Dunai (300 km north-west from Tixi) in 1993 -1994 which was about 40 pg/m$^3$. In turn concentration of 10 PCB congeners controlled by AMAP was similar in 1993, 1994 and 2010 (about 7 pg/m$^3$)[3], and 2011 has significantly decreased (to 1 pg/m$^3$).
The lowest levels of PCB congeners at Valkarkai were observed in 2003. They were somewhat higher in 2002 (approximately 42 and 20 pg/m$^3$ for the sum of PCB congeners and 10 congeners AMAP, respectively). In 2008, significant growth of PCB levels was revealed, when the average annual concentration of PCB congeners mixture was approximately 125 pg/m$^3$, a gradual decrease revealed in 2009 and 2010 (to 90pg/m$^3$).
Mass concentration of α-HCH increased significantly both in the Tiksi region and Valkarkai at considerably lower levels of γ-isomer. Airborne levels of 4,4 '-DDT increased slightly with a slight increase of concentration of 4,4'-DDE. The above trends can talk about lack of fresh sources of HCH isomers, as well as on the availability of sources of DDT. HCB shown relatively stable levels (about 23 pg/m$^3$ in 2002-2003 and 18 pg/m$^3$ in 2008-2010).
The remaining OCPs included in the list of POPs show reduced levels, in some cases even below the detection limit.

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