Persistent organic pollutants (POPs) in blood of indigenous people from Russian Arctic

Alexey Konoplev[1], Valery P Chaschin[2], Galina V Chernik[1], Alexey A Dudarev[2], Elena M Pasynkova[1], Rimma I Pervunina[1], Dmitry P Samsonov[1]

[1]TYPHOON
[2]NPHRC

Introduction

Long-range atmospheric transport of POPs causes pollution of remote areas including Arctic regions. Low temperatures and short daylight during the winter season promote POP accumulation in Arctic ecosystems[1]. The highest levels of POPs have been detected for sea birds and marine mammals[1]. Peculiarities of the traditional diet of indigenous people in Northern Russia (higher ratio of fish, meat and fat of marine mammals etc.) bring POP intake to humans. Up to now the data on POP concentrations in human tissues of indigenous people of Russian Arctic was insufficient and noncomplete[1,2].

The aim of this work was to study the levels of POP in blood of indigenous population of Russian Arctic and their geographical distribution.

Methods and Materials

Human blood sampling covered two types of respondents: pregnant women/cord blood sampling at the delivery departments of local hospitals and general adult indigenous population in the selected indigenous settlements of the following areas of Northern Russia:

1) Kola Peninsula (Murmansk Oblast): populated by Saami people; relying heavily on reindeer and freshwater fish as components of the traditional diet; the area covered Lovozero, the main settlement with compact Saami population and its vicinities, as well as the village Krasnoshchelye.
2) Lower basin of the Pechora River: Nenets people; traditional diet includes reindeer and freshwater fish.
3) Taimyr Peninsula, including lower reaches of the Yenisey River: Dolgan and Nenets peoples; traditional diet includes reindeer, freshwater fish and game; the area included Dudinka (Nenets people) and Khatanga (Dolgan people).
4) Chukotka Peninsula: Chukchi and Yupik peoples; traditional diet includes marine mammals and fish, and reindeer; the area included Chukotsky and Anadyrsky districts.

Blood was collected from mother's *vena ulnaris* and from fetus' umbilical cord step by step, one after another. Blood sampling have been performed using vacutainers, i.e: plungerless vacuum fiberglass test-tubes with a needle screwed on a holder for dosed intravenous blood sampling. A 3000 rpm centrifuge was used for separation of serum. Blood samples were kept in a freezing chamber at – 20^0C. Blood collection from mother's vein was carried out on the 1st – 3rd day after delivery. Cord blood collection was done immediately after umbilical cord legation and cutting off. Blood sampling and treatment technique from mother's vein is identical to that of umbilical cord.

The following pollutants were determined in all samples of serum.

Organochlorine pesticides and their metabolites:

Hexachlorobenzene, α-HCH, β-HCH, γ-HCH, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT, 2,4'-DDE, 2,4'-DDD, 2,4'-DDT, toxaphene (Parlar-26, Parlar-50, Parlar-62), heptachlor, cis-chlordane, trans-chlordane, oxychlordane, dieldrin and mirex.

Polychlorinated biphenyls (PCBs):

Congeners #28, #31, #52, #99, #101, #105, #118, #128, #138, #153, #156, #170, #180, #183, #187.

Some samples have been analyzed for *PCDD/F* (17 2,3,7,8-substituted congeners) and *PBDE* (congeners #28, #47, #99, #100, #153, #154, #183.

Overall more than 600 samples of serum have been analyzed for listed POP. Prior to extraction the blood serum samples were defrozen at room temperature. A serum sample was weighed to an accuracy of 0.01 g and put in an Erlenmeer flask. Then the solution of isotope-labeled surrogate standards was added and mixed during 30 minutes, after which methanol (MeOH) was added in volume equal to the sample and shaken during 1 minute.

The analytes were extracted with the mixture 1:1 hexane-MTBE (methyl-tret-butyl ether). The extraction was repeated twice using 20-35 ml of extracting agent. After separation of the organic and aqueous layers the extracting agent was transferred to an Erlenmeer flask using the Paster pipette. The extracts were combined, and the remaining water was removed by anhydrous sodium sulfate during 30 minutes. The extract was filtrated through a fiberglass filter and concentrated on a rotor evaporator to the volume 10 ml. The extract aliquot of 2 ml volume was used to determine the level of lipids in blood serum. The remaining amount of extract was concentrated to the volume 1 ml, cleaned from lipids using gel-filtration on the Bio-Bead SX-3 column and impurities were separated using activated aluminum oxide by column chromatography using columns of silica gel, Florisil and carbon AX-21.

For determination of lipids in blood serum the aliquot of primary extract prepared for POP analysis was used. Determination of lipids was done by the gravimetric method.

For PCBs and OCPs extracts have been analyzed using GC/MS (SATURN-2200T by Varian in the mode of electron impact ionization). For PCDD/Fs, PBDEs and Toxaphenes - GC/MS (GC/MS SATURN 1200MS/MS using chemical ionization with detection of negative ions (NCI) characteristic of these compounds). As part of QA/QC program the samples were analyzed in series. Each series included not more than 12 samples, a procedural blank and a control sample, containing known amounts of analytes. The validity and accuracy of measurements was ensured by using isotope-labeled surrogate standards: analogues of analytes introduced to the samples prior to extraction.

Results and Discussion

The highest HCB concentrations of 1.6 μg/L and 0.8 μg/L have been found in maternal and cord blood (respectively) from the Chukotsky, the most North-Eastern coastal district of Chukchi AO. Samples from other areas of Chukchi AO (Anadyrsky, Iul'tinsky districts, town of Anadyr) contain HCBs in the amounts 2-3 times lower and comparable to the samples from other regions. The concentrations of HCB in cord blood are 1.6-3 times lower than in maternal blood. This leads us to conclude that the placenta barrier at the border of the mother's body and fetus prevents transfer of this toxicant from mother to child, even though this barrier is not always very effective. This is observed for all regions. The exception is the Kola Peninsula where the difference in maternal and cord blood concentrations is not statistically significant. In the control blood samples (from Aral Sea) the mean HCB concentrations are 6-8 times lower than in other regions and 20 times lower than in blood samples in the Chukotsky district. The comparison with results presented earlier[3] suggests that, on a whole, the HCB concentrations in maternal blood from the Russian Arctic are close to those detected in the coastal areas of Greenland and Canada (mean 1.5 and 1 μg/L of plasma, respectively). With this in mind, the maximum concentrations of HCB in blood of the coastal Chukotka area are causing a concern.

High concentrations of total DDT in maternal blood samples ranging from 1.4 μg/L (Anadyrsky district, Chukchi AO) to 3.3 μg/L (Norilsk) occur in all four regions, with the concentration in maternal blood higher than in cord blood by 1.5-3 times. Among the areas of Chukchi AO the highest concentrations of total DDT in cord blood (1.1 μg/L) were found in the Chukotsky district, while in other districts they are 2-3 times lower. The levels of DDT in maternal blood from Anadyr city, however, are also high (2.7 μg/L). The samples of maternal and cord blood from the Kola Peninsula are comparable, the DDT concentrations in them being high and amounting to 2.7 and 2.4 μg/L, respectively. It should be noted that control blood groups (Aral Sea) contain DDT in significant amounts from 8.7 μg/L (mean values) in maternal blood to 2.8 μg/L in cord blood. In separate control blood samples the concentration of total DDT is as high as 18.2 μg/L in maternal and 5.8 μg/L in cord blood. DDE is the most frequently occurring component of total DDT. The DDE/DDT concentration ratio is 3-8.

Total HCH levels in human blood are predominantly determined by β-HCH as the most stable compound of HCH group. The distribution of β-HCH in human blood in the Russian Arctic is similar to that of HCB, specifically: the highest levels (0.8-2 μg/L) are observed in blood of the Chukotka residents. The difference, however, is that the increased levels of β-HCH also occur in maternal blood from Norilsk (1.3 μg/L). In all maternal blood samples (besides the Kola Peninsula) the concentrations of β-HCH are 2-4 times higher than in cord blood. As in the case with DDT, the β-HCH concentrations in the control samples (the Aral area) are high and equal to 2.9 μg/L of serum (geometric mean). In separate samples the concentration is as high as 9.5 μg/L of serum, which is determined by long-term usage of lindane and DDT in this area.

Maximum values of total PCB occur in maternal and cord blood samples of residents of the Chukotsky District of Chukchi AO (3.9 μg/L and 1.4 μg/L, respectively), with the PCBs levels as high as 11 μg/L in some samples from this area. Among the Taimyr areas the highest concentrations are found in Dudinka (the mean concentration is 2.2 μg/L and the maximum is 5.2 μg/L).

The concentrations of total PCBs in the maternal and cord blood sampled in the Russian Arctic, on the average, do not exceed the recommended level of 5 μg/L of blood at which no toxic effect occurs in humans[4]. Of the PCBs congeners the most frequently occurring and in largest amounts is the congener #153 (2,2',4,4',5,5' – hexachlorobiphenyl). Assessment of PCBs congeners in pair groups of maternal-cord blood from 4 regions of the Russian Arctic has shown that distributions of congeners in these pairs are similar, i.e. when PCBs are transferred to infant's blood, the ratio of congeners does not change much.

The highest levels of PCDD/F (sum of 17 2,3,7,8-substituted congeners in TEQ) were detected in the population of Uelen (Chukchi AO) and Khatanga District (Taimyr AO) (0.004-0.03 TEQ ng/L of serum). Results of PCDD/F analysis in blood samples seem to be more graphic when converted to lipid content. Dioxin concentrations (geometric means) in blood samples from adults of both genders in these regions are within the range 0.3-9.4 pg/g TEQ of lipids. The highest concentrations in separate samples are as high as 18.7-18.1 pg/g TEQ of lipids (Chukchi and Taimyr AO, respectively). The highest concentrations of PCDD/F in human blood in the northern areas of Russia are close to the minimum concentrations observed in residents of industrial regions. It should be noted that the most toxic tetra- and penta- chlorine-substituted dioxins detected, as a rule, in blood of workers at hazardous facilities have not actually been detected in people living in the north areas. The detected compounds primarily include octa- and hepta-dioxins, which normally occur in background environmental samples.

PBDE and PCDD/F were determined in the same pooled blood samples of adult population. Maximum mean concentrations of PBDE were found in blood samples from adults of Krasnoshchelie **(**Kola Peninsula) (mean 934 pg/g of lipids and the range 375-1747 pg/g of lipids). The lowest concentrations were indicated in blood samples from population of Taimyr AO.

Comparison of PBDE and PCDD/F concentrations in blood samples of the adult population showed that there is a vital difference in distribution of these contaminants in Northern Russia. It is especially important for Taimyr region, Nenets NO (Nelmin Nos) and Kola Peninsula (Krasnoshchelie). So if maximum dioxin concentrations in blood samples of population from Taimyr were detected in amount of 9.4-5.0 pg/g of lipids in Katanga district and in coastal settlements of Katanga accordingly then PBDE concentrations in those regions are minimal. And on the contrary when minimum dioxin concentration in blood samples from adult population of Krasnoshchelie (0.5 pg /g of lipids) and Nenets NO (0.3 pg/g of lipids) occurred PBDE concentrations are maximal. It is necessary to note that to PBDE as toxicant, attention was given rather recently and that why there isn't much information about their contamination in humans. Geographical distribution of PBDE in the Russian Arctic allows to suggest that their levels are determined by trans-boundary transport. Increased concentrations are observed only in the Easternmost (Chukchi AO) and Westernmost (Kola peninsula) areas of the Russian Arctic. PBDE levels in the Central part either below, or close to the detection limit.

Acknowledgements

The work was performed in frame of the Project "Persistent Toxic Substances, Food Security and Indigenous Peoples of the Russian North" funded by Global Environment Facilities and coordinated by the Secretariat of Arctic Monitoring and Assessment Program.

References

1. Arctic Pollution (2002), AMAP, Oslo, Norway.
2. Klopov V., Odland J.O. and Burkow I.C. (1998) *Int. J. Circumpolar Health*. 57: 239-243.
3. AMAP Assessment (2002): Human Health in the Arctic, AMAP, Oslo, Norway.
4. Klopov V.P. (2000) Hygienic Assessment of Environmental Pollution in the North of Russia and its Effect on Population Health (Thesis), St-Petersburg, 46.