BIOMONITORING OF BROMINATED FLAME RETARDANTS IN RUSSIA

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Introduction

Brominated Flame Retardants (BFRs) have attracted increasing attention from scientists, government agencies, and the general public in recent years. These chemicals are produced in high volumes and are used in a variety of manufactured products (e.g., foam padding used in furniture, textiles, building insulation materials, plastics and printed circuit boards used in televisions and computers, etc.). BFRs are found to be widely distributed in the environment; they are also found in humans at levels that have been increasing. These findings have raised concerns about the potential risks to human and environmental health from exposure to BFRs[1].

Since 2004 BFRs have not been produced in the Russian Federation, yet a total of 200 tonnes were produced over 4 years from 2000 to 2003, of which 93 tonnes were hexabromocyclododecane and 107 tonnes – tetrabromoparaxylene. Furthermore, about 1900 tons of different BFRs were imported to Russia during 5 years from 2000 to 2004 to be mainly used in production of foam heat insulation materials and foam rubber products. Most likely, most of them were subsequently (re)exported from the Russian Federation.

Levels of PBDEs in human milk from North America exhibited rapid increases over time, reflecting use. Until recently, data on BFR levels such as PBDE in the environment and biota in the Russian Federation have not been available. The present work aimed to study the PBDE levels in blood serum and breast milk in the population of selected areas of Russia, including indigenous peoples of the North

Materials and Methods

This paper discusses the study of the samples of blood serum from adults living in four regions of the Russian Arctic (indigenous people)[2,3] and breast milk from women living in the Moscow region, St. Petersburg and Chukotka for polybrominated diphenyl ethers. The study areas in the Russian Arctic include the Kola Peninsula (Krasnoshchelie and Lovozero), Nenets AO (Nel'min Nos), Taimyr (Khatanga) and Chukotka (Kanchalan and Uelen). The compounds determined in blood serum and breast milk were those PBDE congeners most frequently used in products, namely: 2,4,4'- tribromodiphenyl ether (BDE-28); 2,2',4,4'-tetrabromodiphenyl ether (BDE-47); 2,2',4,4',5 - pentabromodiphenyl ether (BDE-99); 2,2',4,4',6-pentabromodiphenyl ether (BDE-100); 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153); 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154); 2,2',3, 4,4',5',6-heptabromodiphenyl ether (BDE-183).

Serum samples were extracted by a mixture of Hexane/MTBE in ratio 1:1 with subsequent cleanup on Bio-beads and Silica-gel columns. Breast milk samples were extracted by a mixture of Acetone/Hexane in ratio 9:1 with the same cleanup. The analysis was performed by GC/MS using SATURN 1200 MS/MS (VARIAN) in the mode of chemical ionization with detection of negative ions (NCI) and the selective ion monitoring (SIM). Identification of analytes was based on the presence of characteristic ions and coincidence of chromatographic retention times. For calculations, data of calibration solutions PBDE of the mixture of EO-4149 standards manufactured by Cambridge Isotope Labs containing all determined compounds was used. The detection limit of individual congeners of PBDE was in the range from 100 to 250 pg/L for serum samples, and from 300 to 1200 pg/L for breast milk.

A total of 38 samples of blood serum from indigenous people of the North, 17 samples of breast milk from Chukotka (Chukotsky and Anadyrsky districts), 35 samples of breast milk from the Moscow region (Serpukhov, Sergiev Posad,, Shchelkovo and Solnechnogorsk) and 2 samples of breast milk from St Petersburg have been analyzed.

Results and Discussion

Fig. 1 presents the geographic distribution of geometric means of concentrations determined in the samples of serum of indigenous adults from Russian Arctic.

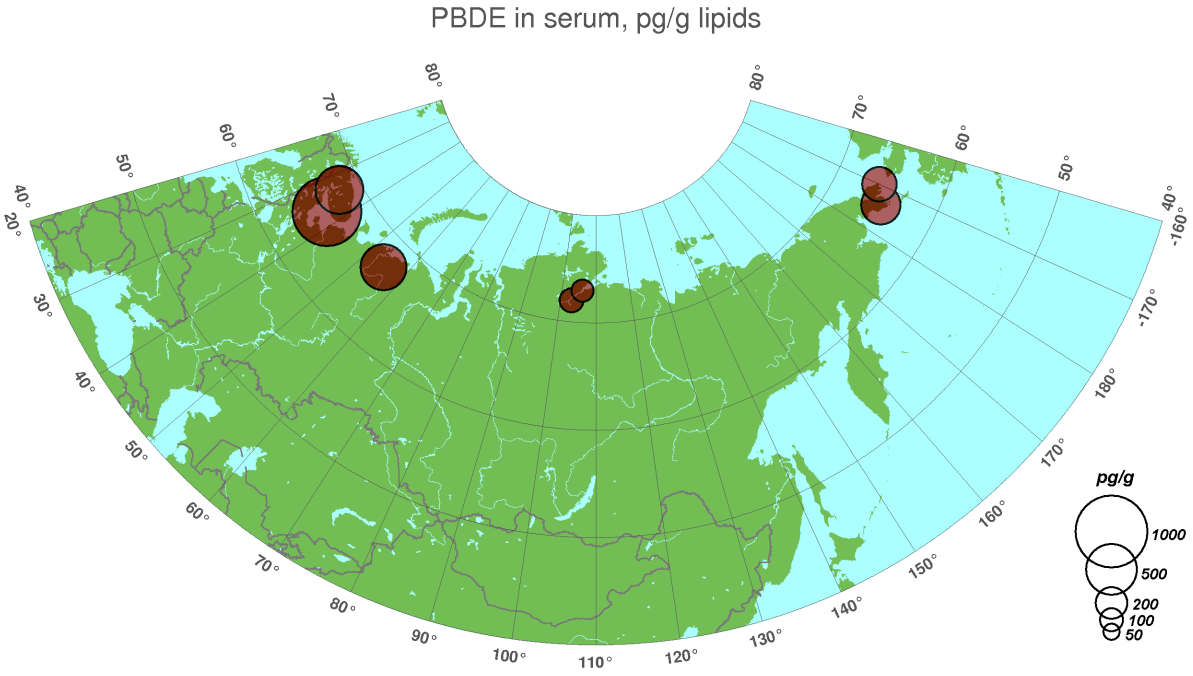

Fig. 1. Levels of total PBDE (sum of concentrations of seven congeners) in serum of indigenous adults in Russian Arctic

The highest mean concentrations of PBDE were found in serum samples from adults of Krasnoshchelie, Kola Peninsula (mean 930 pg/g of lipids and the range 375-1750 pg/g of lipids). The lowest concentrations were indicated in blood samples from population of Taimyr AO. The geographical distribution of PBDE in the Russian Arctic suggests 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 are either below, or close to the detection limit.

Table 1 shows the breast milk concentrations of seven individual congeners of PBDE and their sum in indigenous females from Chukotka.

Table 1. Concentrations (pg/g lipids) of PBDE in breast milk from Chukotka (n.d. – not detected)

PBDE	Chukotsky district	Anadyrsky district
BDE#28	14.8 (n.d. - 42.3)	7.0 (n.d.-16.9)
BDE#47	223 (n.d. – 697)	83 (31 – 268)
BDE#99	16.1 (n.d. – 77.9)	19 (n.d. – 41.9)
BDE#100	17.2 (n.d. – 86.6)	8.6 (n.d. – 19.2)
BDE#153	22.4 (n.d. – 189)	n.d.
BDE#154	n.d.	n.d.
BDE#183	n.d.	n.d.
Total PBDE	307 (48.5 – 823)	112 (30.7 – 268)
Lipids, %	2.96 (0.67 – 4.58)	2.52 (0.62 – 4.86)

The analysis of breast milk samples from towns of the Moscow region (Fig. 2) indicates that the mean total concentrations of polybrominated diphenyl ethers (seven PBDE congeners) in breast milk from Sergiev Posad (1430 pg/g lipids) are higher than those from three other towns. Thereafter, in order of decreasing concentrations in breast milk, Schelkovo (730 pg/g lipids), Serpukhov (480 ng/g lipids) and Solnechnogorsk (340 pg/g lipids). Similar levels of PBDE were found in breast milk from St Petersburg: from 350 to 3200 pg/g lipids, with the mean geometric value of 1060 pg/g.
In all studied samples the dominant congener was BDE#47, its concentrations being generally 10 times higher the concentration of any other congener.

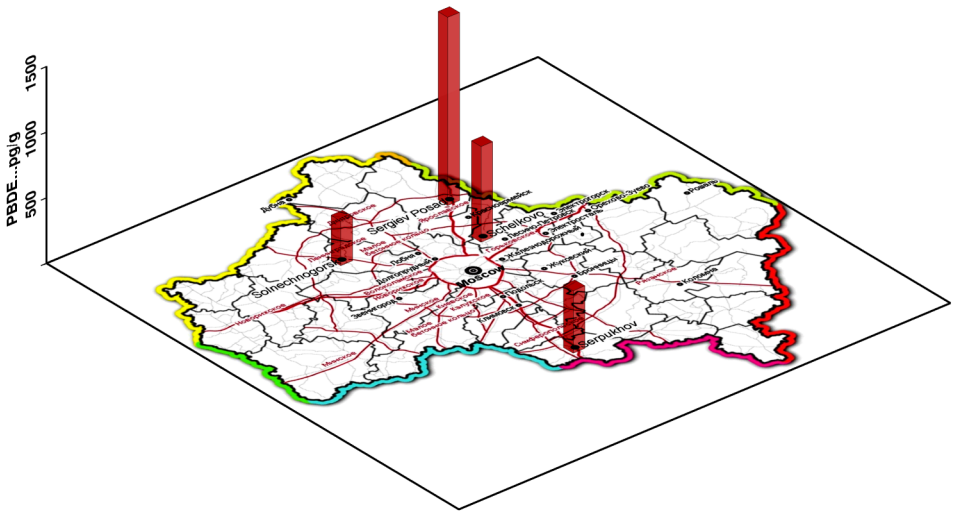

Fig. 2. Levels of total PBDE in towns of Moscow region

The higher PBDE levels in breast milk from Sergiev Posad, relative to three other towns of the Moscow region, are comparable with those from industrial cities. They are indicative of possible contamination of the environment in Sergiev Posad due to typical sources of PBDE emissions, such as the paint and varnish industry, plastic and polymers production, heat and fire protection and electric insulation materials plants, and furniture manufacturers. The detected PBDE concentrations in breast milk in Sergiev Posad and St Petersburg are close to those observed in Germany[4] and much lower the concentrations characteristic of North America[5]. The PBDE levels occurring in female breast milk from indigenous people of Chukotka are thus far much lower those found in industrial areas of Russia and Western Europe.

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References

1. Brominated Flame Retardants in the Arctic. Fact Sheet. AMAP/ACAP 2005. (http://amap.no/documents/index.cfm?action=getfile&dirsub=%2FFact%20Sheets%20%2D%20ACAP&filename=FINAL%20%2D%20brom%20post%20corrections%2D101205%20screen%2Epdf&sort=default)
2. Persistent Toxic Substances, Food Security and Indigenous Peoples of the Russian North. GEF/UNEP/AMAP/RAIPON. Final Report 2004, AMAP, Oslo, ISBN 82-7971-036-1.
3. Konoplev A, Chaschin V, Chernik G, Dudarev A, Pasynkova E, Pervunina R, Samsonov D. *Organohalogen Compounds* 2005;67:1516.
4. Fuerst P. *Organohalogen Compounds* 2001;52:185.
5. Papke O, Bathe L, Bergman A, Fuerst P, Guvenius DM, Herrmann T, Noren K. *Organohalogen Compounds* 2001;52:197.