

PBDES IN AMBIENT AND INDOOR AIR IN FOUR LOCATIONS IN THE RUSSIAN FEDERATION

Chernyak Sergej,¹ Konoplev Alexey,² Batterman Stuart,¹ Kochetkov Alexandr,²
Pasyukova Elena,² Samsonov Dmitry,² and Jia Chunrong¹

¹Environmental Health Sciences, University of Michigan, Ann Arbor, MI 48109-2029, USA.

²Centre for Environmental Chemistry SPA "Typhoon", Obninsk, Kaluga region, 249039, Russia

Introduction

Brominated flame retardants (BFRs) have been and continue to be widely used in residential, commercial and industrial applications in the Russian Federation in construction materials, foam, insulation, furniture, and household and office equipment, e.g., TVs, VCRs, computers, and other appliances.¹⁻³ The major BFRs include several commercial mixtures of polybrominated diphenyl ethers (PBDEs; penta, octa and deca), tetrabromobisphenol-a (TBBPa), tribromophenol (TBP), hexabromocyclododecane (HBCD), 1,2-bis(2,4,6-tribromophenoxy)ethane (HBCB), and 2,3,4,5,6-pentabromoethylbenzene (PEB).^{4,5} In this paper, we report on PBDE concentrations in indoor and outdoor air and household dust in four cities of the European part of the Russian Federation. This is the first study to examine the distribution of BFRs in this large region.

Materials and methods

High-volume "Vihir" samplers developed at the SPA "Typhoon" laboratory and equipped with glass fiber aerosol filters and quartz fiber adsorbents were used to sample up to 3000 m³ of air for outdoor measurements. Low-volume samplers using quartz wool elements were used indoors to collect 100 m³ samples. Quartz wool was used since a set of other chemicals were also analyzed in this project. It was shown previously that quartz fiber is an efficient adsorbent for a number of POPs.⁶ The indoor samplers have been described earlier.^{7,8}

Samples were taken at four locations (Figure 1): The capital city of Moscow (downtown and the city's most industrialized districts); the mid-sized town of Obninsk (pop. 100,000, about 100 km southwest of Moscow); the industrial metropolitan area of Archangelsk (pop. 350,000, a major lumber port on the White Sea); and the remote polar meteorological station of Amderma (pop. 1,000, about 2,000 km northeast of Moscow and 300 km from the nearest town). Amderma is one of the most remote settlements inside the Polar Circle.

Figure 1: Air sample locations in the Russian Federation



Outdoor samples were taken at meteorological stations to ensure their representativeness, quality control and security. Indoor samples were collected in apartments and scientific facilities not involved with the PBDE analyses. Nine private residences were selected to represent different conditions. These included Soviet-style blocks of apartments furnished with Soviet-made furniture, the same buildings with so called “euro-improvement” renovations and furnishings, and newly-constructed individual homes furnished with mostly imported furniture, modern appliances, etc.

After sampling, filters and adsorbents were extracted with dichloromethane in a Soxhlet apparatus. Extracts were cleaned by column chromatography, and analyzed for 18 BDE congeners (BDE-17, 28, 47, 49, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 206, 207, 208 and 209) using a SATURN 1200/Varian GC/MS, chemical ionization mode, and negative ion detection. In this paper, “total BDE” refers to the sum of these 18 congeners. Data collected in the Russian Federation were compared with recent samples from North America.

Results and discussion:

PBDE concentrations in indoor air

The 18 target congeners were detected in each air and dust sample, including samples collected at the remote site in Amderma. Concentrations of selected congeners and the total abundance are presented in Table 1.

Table 1. Average BDE levels (pg/m³) in indoor and outdoor air in vapor and particulate phases

PBDEs	Indoors				Outdoors							
	Obininsk (n= 9)		Amderma (n= 1)		Obininsk (n= 9)		Moscow (n= 5)		Arkhangelsk (n= 2)		Amderma (n= 2)	
	Vapor	Parti	Vapor	Parti	Vapor	Parti	Vapor	Parti	Vapor	Parti	Vapor	Parti
BDE47	28.46	11.85	14.57	5.46	0.92	0.35	0.83	1.18	0.54	0.25	0.21	0.09
BDE99	51.52	49.50	3.54	6.21	0.33	0.21	0.20	0.80	0.15	0.15	0.08	0.04
BDE100	11.28	9.70	1.71	1.82	0.15	0.12	0.07	0.20	0.06	0.06	0.03	0.02
BDE138	0.23	0.38	0.00	0.00	0.00	0.22	0.01	0.03	0.01	0.01	0.01	0.01
BDE183	0.85	13.20	0.33	0.74	0.07	1.24	0.06	0.24	0.04	0.06	0.03	0.01
BDE209	9.28	6.35	0.00	0.00	0.56	3.30	1.88	12.11	0.15	0.13	0.03	0.11
Total BDE	124.22	113.40	24.25	16.51	3.13	10.22	4.24	19.55	1.21	0.83	0.51	0.35

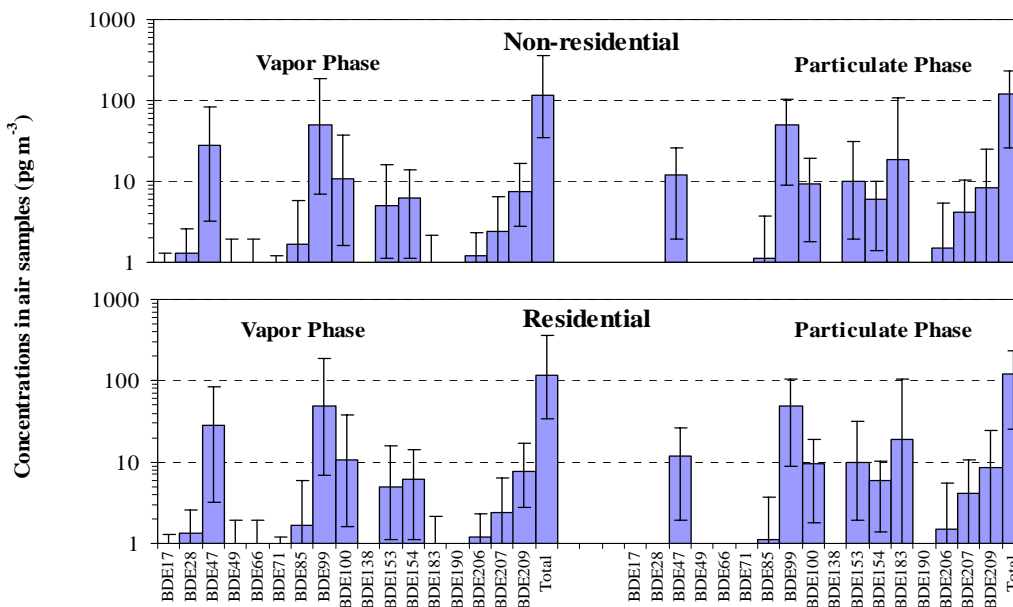
Results in Table 1 do not show the expected vapor-particulate partitioning for the deca-congener for indoor and most outdoor measurements. This may be due to breakthrough from the filter (which seems unlikely), measurement errors (deca was sometimes near the MDL), contamination in transit or use (but blanks showed very low levels), or some other factor. Given these uncertainties, we deemphasize the deca data in vapor phase in the following discussion.

These data show a strong concentration gradient from industrial centers to the remote sites. Concentrations of total-BDE were significantly higher at several sites within Moscow, especially at the downtown Balchug meteorological station. For example, the total BDE concentration at Balchug was 8 and 30 pg/m³ in vapor and particulate phases, respectively. Still, BDE concentrations in Moscow are lower than in countries that have used flame retardants in industry and household products for a decade or more.⁵

Indoors, concentrations of most congeners were elevated as compared to outdoor levels, but concentrations were low compared to most US residences.⁵ The abundance of BDE-99 in vapor (up to 50 pg/m³), followed by BDE-47 (28 pg/m³), indicates ongoing usage of the penta formula in Russian households. However, the levels of BDE-209 in settled dust (shown later), the first media where PBDEs accumulate, suggests current use is predominantly the newer deca formulation. Octa-BDE (an intermediate between the tetra and deca products)

was not widely used in the Russian Federation, and significant amounts of octa-BDEs were found in only one indoor air sample (collected in a laboratory building in Obninsk) and in dust from an apartment in the same city (remodeled prior to modern practices). The congener profiles in these samples are similar to those found in carpet in our recent measurements in a U.S. office building.⁸ BDE profiles in indoor air collected in residential and commercial buildings did not show significant differences (Figure 2), however, vapor and particulate compositions varied, as did particulate and dust samples from the same room (Figures 2 and 3).

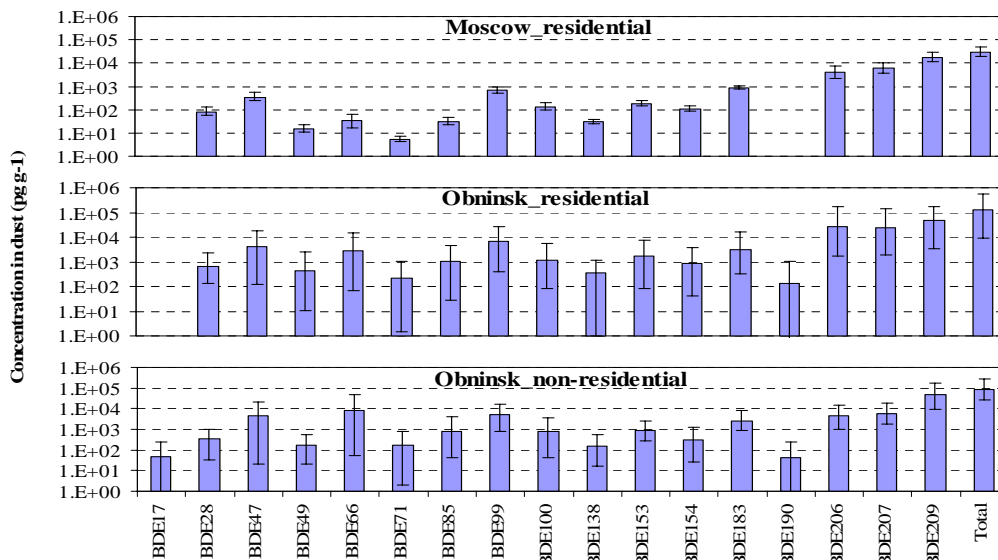
Figure 2. Profiles of BDE congeners in residential and non-residential air samples



PBDE concentrations in dust

Dust samples were collected only in Moscow and Obninsk. PBDE concentrations (18-458 ng/g) were significantly lower than levels measured in U.S. residences (160-8,800 ng/g by Stapleton⁹), and the deca-congener had the highest abundance (Figure 3). Congener profiles at commercial and residential sites were nearly identical, suggesting that BDE sources in Russia were similar, and that use was predominantly penta and deca products. However, levels of octa-congeners found at some sites in Obninsk suggest at least limited use of other BFR products in Russian households.

Figure 3. Profiles of BDE congeners in dust samples



These first measurements of BDEs in outdoor air, indoor air, and floor dust in the Russian Federation show widespread use of these persistent chemicals. Congener profiles differ from those measured elsewhere, e.g., in North America and Europe, with a notable deficiency of octa-congeners. Detection of BDEs at the very remote Arctic site shows the broad distribution of both vapor and particulate phase BDEs.

Acknowledgments

The authors acknowledge financial support by U.S. Civilian Research and Development Foundation in Project #2838 entitled “Sources, Transport and Impacts of PBDEs in the Russian Arctic.”

References:

1. Konoplev A, Chaschin V, Dudarev A, Kochetkov A, Odland JO, Pasynkova E, Pervunina R, Rakhmanova T, Reiersen L-O, Samsonov D, Wilson S *Organochlorine compounds*, v.68:2155
2. Tsydenova O., Sudaryanto A., Konisue T., Batoev V. and Tanabe S. *Environ. Pollution* 2007; 146 : 225
3. Kannan K., Moon H-B., Yun S.H., Agusa T., Thomas N., and Tanabe S. *J. Environ. Monit.*, 2008; 10: 552
4. Hites R.A., *Environ. Sci. Tech.* 2004; 38, 945
5. Allen G., McClean M., Stapleton H., Nelson J., and Webster T. *Environ. Sci. Technol.*, 2007, 41: 4574
6. Samsonov D.P., Rakhmanova T.V., Stepanova N.V., and Pervunina R.I. *Russian J. Analyt. Chem.*, 48: 1476
7. Chernyak S.M. Batterman S.A., Godwin C.C., Jia C., and Charles S.M. 2007. *Organochlorine compounds*, v.69
8. Batterman S.A., Chernyak S.M., Charles S.M., Godwin C.C. and Jia C. 2008. *Organochlorine compounds*, v.70 – this volume
9. Stapleton, H., N. Dodder, M. Schantz, and S. Wise, *Organohalogen Compounds*, 2004; 66: 3741