

PBDEs, HBCD AND OTHER NON-PBDEs FLAME RETARDANTS IN CAR DUST SAMPLED IN THE CZECH REPUBLIC IN 2009

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Introduction

Brominated Flame Retardants (BFRs) are used in various commercial and industrial applications to delay ignition and reduce the rate of combustion. They are commonly present in daily used products such as carpets, mattresses, armchair padding, soft furnishings, household appliances, computers, TVs, pipes, wires, cables, products of aircraft, automotive industries, etc. Most of the BFRs are not covalently bound to polymeric materials and they are therefore over time released from the product into the environment, namely as vapour or dust. Due to their lipophilicity and persistence, they can be found in many environmental compartments, both biotic and abiotic^{1,2,5,6}.

In the Czech Republic BFRs are monitored within the national project BIOBROM. The aim of our group was to investigate BFRs levels in the Czech ecosystem between 2006 and 2010 in various matrices including river sediments, wastewater treatment plants sludge, human adipose tissue collected during the liposuction procedure, human breast milk, indoor household dust and car dust. The monitoring included PBDEs (polybrominated diphenyl ethers congeners 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203, 206 and 209), HBCD (hexabromocyclodecane – isomers α , β , γ) and six non-PBDE BFRs including DBDPE (decabromodiphenyl ethane), BTBPE (bis-2,4,6-tribromophenoxy ethane), PBT (pentabromotoluene), PBEB (pentabromoethylbenzene), HBB (hexabromobenzene) and Br Indane (octabromo-1-phenyl-1,3,3-trimethylindane). The data from car dust analysis were selected for the presentation at “Dioxin 2010”.

Material and Methods

Sampling – in 2009 dust from 27 cars used in the Czech Republic for personal transport was sampled by scumming of indoor car dust with cotton duster (30 cm \times 30 cm). Car dust was sampled from the dashboard, windows and leather areas.

Extraction and clean up – the dusters with dust were extracted in a Soxhlet extractor over 8 hours by dichloromethane and then cleaned up using florisil SPE columns.

Instrumental analysis

- PBDEs and non-PBDE BFRs determination was performed using an Agilent 6890 gas chromatograph coupled to a mass spectrometer (Agilent 5975 MSD) operated in a negative chemical ionization mode.
- Determination of α , β , γ -HBCD was performed using an Alliance 2695 liquid chromatograph with a Quatro Premier XE tandem mass spectrometer in a negative electrospey ionisation mode

Results and discussions

Data obtained within these experiments are shown in **Table I** and on **Figure 1** and **2**. Non-PBDEs BFRs data are presented only for DBDPE and OBIND since the levels of other non-PBDE BFRs were in all samples below the limit of quantification (LOQ ranged from <1 to <2 $\mu\text{g}/\text{kg}$) and BTBPE were indentified only in two samples in low concentrations (13 $\mu\text{g}/\text{kg}$ and 14 $\mu\text{g}/\text{kg}$).

Table I: Concentrations of BFRs determined in car dust ($\mu\text{g}/\text{kg}$, $n=27$, 2009)

Car specification		PBDEs $\mu\text{g}/\text{kg}$			HBCD $\mu\text{g}/\text{kg}$	non-PBDE BFRs $\mu\text{g}/\text{kg}$		Sum BFRs $\mu\text{g}/\text{kg}$
Car type	Production year	Sum 13 PBDEs	Sum BDEs 206+207	BDE 209	Sum HBCD	OBIND	DBDPE	Sum BFRs
Skoda 120 L	1984	<1.5	17.7	0.0	27.0	67.0	591.0	702.7
Mazda 323	1990	29.3	73.9	242.9	161.2	2684.0	136.0	3327.3
Skoda 125	1993	<1.5	<2.5	<5	<0.3	<2	<20	<20
Honda Civic LSI	1994	<1.5	53.1	374.1	120.8	<2	81.0	629.0
Peugeot 106	1998	<1.5	25.8	87.5	25.0	<2	83.0	221.3
Volkswagen Sharan	1998	948.7	677.3	21593.9	241.4	150.0	112.0	23723.3
Renault Twingo	1999	<1.5	68.4	30.7	19.3	<2	219.0	337.4
Skoda Oktavia	1999	196.2	18.4	<5	30.1	<2	44.0	288.7
Skoda Fabia	2000	15.2	9.7	5.0	101.6	<2	85.0	216.5
Renault Megan sedan	2001	27.3	47.1	15.5	118.5	<2	91.0	299.4
Skoda Fabia 1	2002	36.6	54.3	310.1	52.7	35.0	297.0	785.7
Skoda Fabia 2	2002	3.6	22.4	168.5	1.6	<2	72.0	268.1
Skoda Fabia 3	2002	<1.5	17.6	96.9	26.8	34.0	288.0	463.3
Skoda Oktavia	2003	14.6	368.6	13417.7	18.5	48.0	197.0	14064.4
Ford	2004	41.2	12.2	103.8	43.3	<2	186.0	386.5
Skoda Fabia	2005	49.5	57.5	213.1	103.2	<2	61.0	484.3
Mazda 6 Wagon	2006	<1.5	1152.8	32575.2	14.2	122.0	33.0	33897.2
Skoda Fabia	2006	<1.5	101.5	1221.9	<0.3	<2	282.0	1605.4
Skoda Roomster	2006	7.5	8.4	7.6	43.7	<2	207.0	274.2
Mercedes A	2007	<1.5	39.5	79.8	47.7	13.0	69.0	249.0
Peugeot 206	2007	19.6	279.1	3737.4	14.5	56.0	45.0	4151.6
Skoda Fabia	2007	3.6	15.5	74.7	2.7	<2	99.0	195.5
Skoda Roomster	2007	<1.5	39.0	229.7	19.6	16.0	61.0	365.3
Subaru Outback	2008	70.2	577.8	18532.5	6.1	561.0	139.0	19886.6
Skoda Oktavia	2008	<1.5	97.3	1529.5	124.5	27.0	98.0	1876.3
Volkswagen Transporter	2008	10.0	10.4	157.9	71.5	<2	114.0	363.8
Nisan Navaro	2009	7.1	74.3	321.1	35.4	<2	3567.0	4004.9

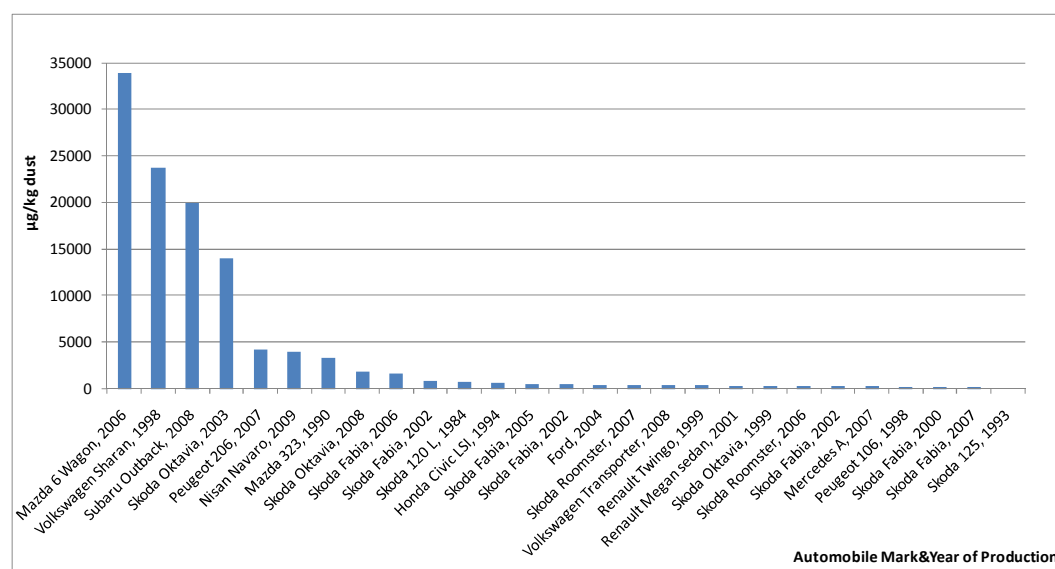


Figure 1: Levels of BFRs expressed as sum of all target analytes determined in car dust ($\mu\text{g}/\text{kg}$, $n=27$, 2009)

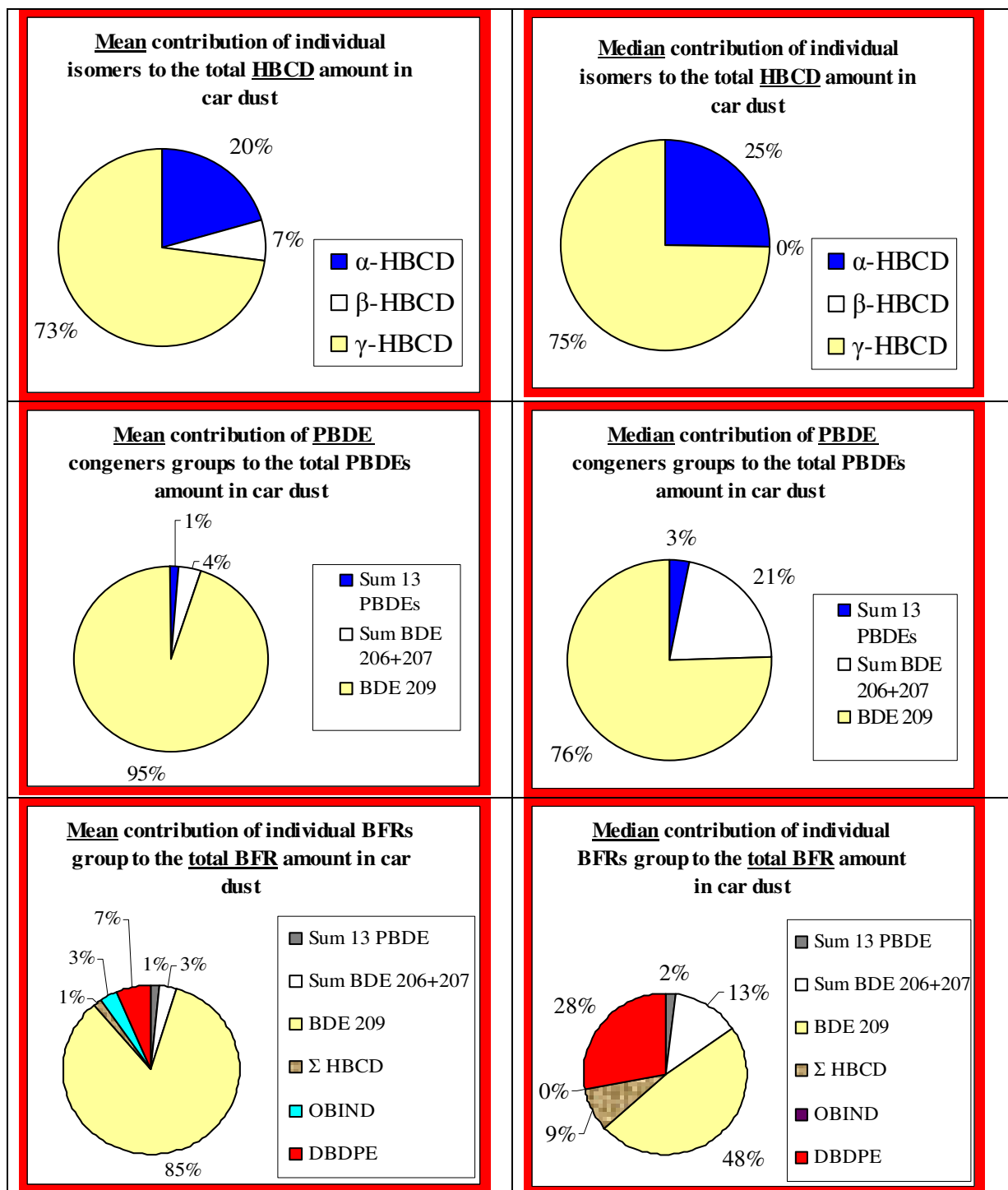


Figure 2: Mean and median contribution of various BFRs representatives to the total BFR contamination of car dust ($\mu\text{g}/\text{kg}$), $n=27$, 2009

The contents of individual groups of BFRs in car dust were very variable for each examined car dust sample. Dominant BFRs in all samples were PBDEs congeners, especially BDE 209, BDE 206 and BDE 207 (median 63%, average 89%). HBCD ranged from 1 to 9% of total BFRs content. Isomer γ presented $\frac{3}{4}$ of sum of HBCD isomers, more than 20% correspond to α -isomer and the rest was β -isomer. DPDPPE was the only important compound from investigated group of non-PBDE BFRs, which was identified in 26 of all analyzed samples but its presence was not necessarily related to car production, e. g. the highest amount of DBDPPE from all tested samples of the dust was determined in the sample "Skoda 120L" even though this chemical was not available in 1984 when this car was produced. This car was not also additionally improved with any new/er technology. Hence, the presence of BFRs in sampled car dust is not only related to the car production process but also to goods and materials transported in it as well as to the ubiquitous ambient dust. No relationship was found, within the Skoda cars group, between the year of cars' production (52% of analyzed samples belong to Skoda brand) and BFRs content. Altogether 62% of sampled cars had lower than 1000 $\mu\text{g}/\text{kg}$ dust BFRs content. Three highest concentrations of total BFRs were determined in samples from Mazda 6 Wagon (production year 2006), Volkswagen Sharan (production year 1998) and Subaru Outback (production year 2008) with 34 000, 24 000 and 20 000 $\mu\text{g}/\text{kg}$ dust.

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References

1. Pulkrabova J., Hradkova P., Hajslova J., Poustka J., Napravnikova M., Polacek V. (2009); *Environment International*, 35:63-68, doi:10.1016/j.envint.2008.08.001.
2. Kazda R., Hajslova J., Poustka J., Cajka T. (2004); *Anal Chim Acta*; 520:237.
3. Cunha S.C., Kalachova K., Pulkrabova J., Fernandes J.O., Oliveira M.B.P.P., Alves A., Hajslova J. (2010); *Chemosphere* 78: 1263–1271
4. Kalachova K. (2009), Annual report of Biobrom project 2009 (available only in Czech), an article in English is prepared for publishing
5. de Boer J.D., Wester P.G., van der Horst A., Leonards P.E.G. (2003); *Environ Pollut*; 122; 63
6. Dufton P.W. (2008); *Flame Retardants for Plastics, Market Report*, Rapra Technology Limited, UK, July 2008, ISBN 1-85957-385-1
7. Hamm S. (2004); *Organohalogen Compounds*, Vol.66,
8. Hale R.C., Alae M., Manchester-Neesvig J.B., Stapleton H.M., Ikonou M.G. (2003); *Environment International* 29; 771
9. Stavelova M., Brenner V., Polacek V., Pulkrabova J., Hajslova J. (2008); 6.th International Conference Remediation of Chlorinated and Recalcitrant Compounds, May 19-22, Monterey, USA, Abstract G-009, ISBN 1-57477-163-9