

SURVEY FOR LOWER BROMINATED PBDE CONGENERS IN AUTOMOBILE COMPARTMENTS IN EASTERN POLAND

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of synthetic organobromine compounds, which has been used as additive flame retardants in combustible materials to increase their fire resistance. There are 209 possible PBDE congeners, but commercial PBDE products used widely in the past have been marketed as three technical mixtures of several congeners, labelled as Penta-BDE, Octa-BDE and Deca-BDE. The Penta mixture contains mainly BDE 47, 99, 100 with smaller contributions from BDE 28, 153 and 154; the Octa mixture contains BDE 153, 154, 183 while the Deca mixture consists mainly of BDE 209. Penta-congeners were added to the Stockholm list in 2009 and forbidden in many countries. At present Deca-BDE (BDE 209) is the only permitted compound in the EU and the USA. But due to its fotolability, and debromination processes lower brominated congeners are still present in indoor environments.

PBDEs are in high-impact plastics, electronics and textiles, as well as polyurethane foams, polyesters and phenolic and epoxy resins, so they might be found in domestic and industrial appliances and equipment, e.g. computers, printers, TV sets, mobile phones, mattresses and insulation boards. Therefore, the highest PBDE levels were detected in indoor samples, namely in dust, at concentrations which were often 50-fold higher than the one reported for the outdoors¹.

By indoor air we understand all closed environments, which are not under regulation related to occupational safety. With increasing time spend indoor, the indoor air became a significant parameter, affecting people's health and well-being. Studies on indoor air have been focused mainly on the places of residence, offices, schools and education premises.

But in the modern societies, the automobile cabin is an important part of the leaving environment. In many countries, time spend on commuting to a workplace is growing and easily exceeds one hour. Statistics on the USA citizens' way of living show that they spend 87% of their time indoors, 8% outdoors and 5% in transportation (by car, bus, train or plane), and in Europe similar tendencies are observed: 90% indoors, 6% outdoors and 4% transportation for French people². There is not such an evaluation for Poland, but due to the increased traffic, time spend in either private car or public transport vehicle increased last years significantly.

Therefore, the exposure in transport vehicles is of growing importance. For a person whose occupation required longer periods to be spent inside a vehicle (policemen, taxi, bus and truck drives, servicemen, sales representatives), the relative contribution of in-vehicle exposures to overall is greater than 30%.

Research on indoor air quality in car compartments was rather scarce until very recently. Toxic substances originate from interior materials, gasoline loss, infiltration of outdoor air pollutants. Yoshida and Matsunaga³ identified over 160 substances in the cabin of the new car. Some of published in-vehicles studies have identified elevated levels of many unleaded and diesel fuel related pollutants, such as volatile organic compounds (VOCs), carbon monoxide, and particulate matters compare to other indoor environments.⁴ Particulate matter collected in automobile compartments may contain elevated levels of semivolatile compounds (SVOCs), such as polyaromatic hydrocarbons (PAHs) or brominated flame retardants (BFRs), including PBDE (polybrominated diphenyl ethers). Dust analysis from vehicles is complicated due to the fact that dust may originate not from the automobile interior components but from outdoor aerosols, soil from users' shoes or cigarette smoke.

First attempt to measure PBDE in the dust samples collected from cars were made by Harrad et al⁵ and Lagalante et al⁶. Both research groups continued measurements, studying degradation of BDE-209 in dust from personal automobiles^{7,8}.

Due to the evaluation of the exposure to different pollutants in public and private cars in Lublin, Poland in 2011 and 2012, some measurements of VOC and SVOC were performed, with special respect to car model, producer, kilometrage and air condition system. Special attention, according to Stockholm convention, was focused on banned lower brominated PBDEs.

Materials and methods

Dust samples were collected by vacuum cleaner with HEPA filter from a number of private cars in Lublin, south-eastern Poland. Lublin, the city of 400 thousand inhabitants suffers from traffic problems and a lot of cars and bus users complain about growing amount of time spent in vehicles. Lublin is situated in south-eastern, less developed, part of Poland and one of the poorest regions of the EU. A lot of cars used by private owners are second hand cars, older than 10 years.

Private automobiles varied in the model, producer, kilometrage and air condition system. Owners have been asked not to vacuum clean them for one week before sampling.

Dust was collected from all interior surfaces of the cars (excluding trunks). Rigorist cleaning procedure of all not disposable parts of vacuum cleaner was followed to eliminate the contamination of samples.

Dust samples were sieved and only fractions up to 125 μm were analyzed.

All chemicals used for PBDE analysis were of high purity. Toluene and dichloromethane (Ultra-Resi Analysed) were purchased from T.J. Baker (Germany). PBDE analytical mixture standards series BDE-CVS-F containing BDE 28, 47, 85, 99, 100, 153, 154, 183 congeners, as well as mass labeled (^{13}C) PBDE recovery solution BDE-MFX containing BDE 77L and 138L were obtained from Wellington Laboratories (Ontario, Canada). Additional standard solutions of native PBDE (BDE-MXF) containing BDE 28, 47, 85, 99, 100, 153 congeners at a concentration 2000 ng/cm^3 were obtained from Wellington Laboratories and from Accustandards (mixture BDE-527). All glass equipment applied for the PBDE analysis was amber type glass.

Dust samples were extracted with toluene in a Soxhlet apparatus for 16 hours in a dark room. The extract was evaporated under a gentle nitrogen stream and then the solvent was changed to dichloromethane. Further purification was performed using size exclusion chromatography (SEC) Brezee 1525, (Waters) system equipped with a double pump system, 2000 μL loop, combined 19x150 mm and 19x300 mm Envirogel-GPC[®] cleanup columns (Waters, USA), tunable UV-VIS detector Waters M2487 working @ 254 nm, FC III fraction collector (Waters, USA); system control and data acquisition Breeze 3.30SPA software. Dichloromethane was used as a mobile phase with the flow rate 5 cm^3/min . Purified extracts were collected at the window from 11 to 17 minutes. Typically, this method is used to clean-up samples for PAHs analysis⁹ but it has also been applied for other compounds e.g. pharmaceuticals¹⁰, chlorinated and brominated compounds¹¹, and also for PBDE^{12,13}. Final chromatographic analysis was done on the Trace Ultra – Polaris Q GC-MS system. The GC-MS technique which is cheaper and is more suitable for analyses of low substituted PBDE congeners than LC-MS, which has been used for PBDE analyses by many researchers^{14,15}. The parameters of the GC-MS system were published by Dudzinska and Czerwinski¹³.

Our research was focused on the Penta mixture, which has been banned in the EU since 2009, therefore 2,4,4'-TriBDE (BDE 28), 2,2',4,4'-TeBDE (BDE 47), 2,2',4,4',6-PeBDE (BDE 99), 2,2',4,4',5-PeBDE (BDE 100), 2,2',3,4,4',5'-HxBDE (BDE 138), and 2,2',4,4',5,5'-HxBDE (BDE 153) were measured. The detection limit for this method was evaluated on 0.5 ng/dm^3 ($S/N \geq 3$) in extracts for PBDE 28 and PBDE 100, and 1.2 ng/dm^3 for PBDE 153. The quantification limit was evaluated on the level 10 pg / injection ($S/N \geq 5$). Linearity was better than 10-250 for all congeners except for BDE-153 (better then 10-200). 74 to 91% recovery was obtained in triplicate analysis while the relative standard deviation for triplicate analysis of real samples ranged from 12% for PBDE 28 to 27% for PBDE 153.

Results and discussion

Lower brominated congeners have been detected in all the examined vehicles, although in some of them some congeners were found below the detection limits. In Table 1 the results for BDE-28, 47, 66, 99, 100, 101, 138, 153, 154 183 congeners (minimum, maximum, mean and median) are presented. The highest concentrations among targeted congeners were found for BDE-99 and for Tetra-BDE. Other Penta-BDE have been present at considerably high levels, but showed bigger discrepancies.

Odometer readings, air condition system (AC) and years in service have been considered as possible parameters influencing PBDE concentrations in the indoor dust. The mean concentrations of BDE-28, 47, 66, 99 100, 101, 138, 153 and 154 in the cars older than 5 years compared with cars younger than 5 years are presented in Figure 1. For most of the examined congeners, higher mean concentrations were found in the older cars, despite BDE-99 and BDE-153. BDE-99 was present on the highest levels in the most of the examined vehicles, rising up to 14 447 ng/g as maxim found. The second congener, according to concentration, was BDE 47 with the maximum

value of 5476 ng/g of dust. The most significant differences between 'old' and 'new' cars were noticed for BDE-66 and BDE-100.

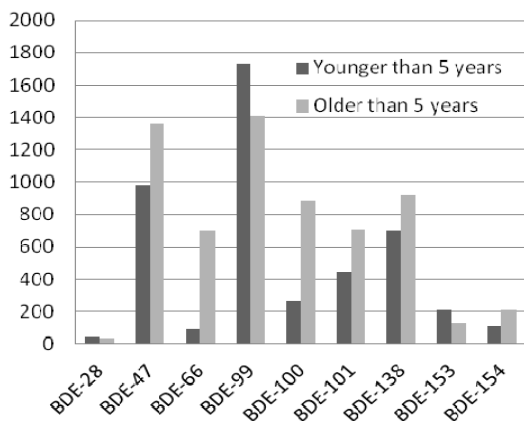


Fig.1. Mean concentrations of BDE congeners for 'old' and 'new' vehicles (ng/g).

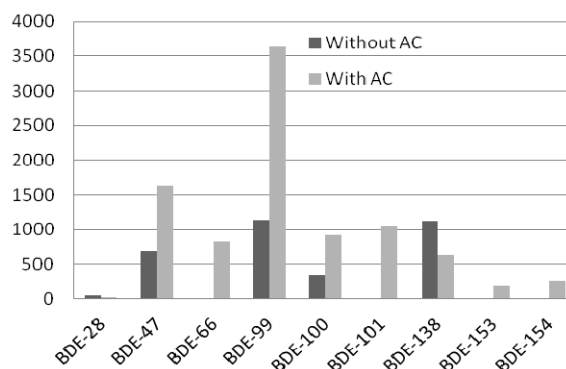


Fig.2. Mean concentrations of BDE congeners (ng/g of dust) in the cars equipped with AC system and without AC system.

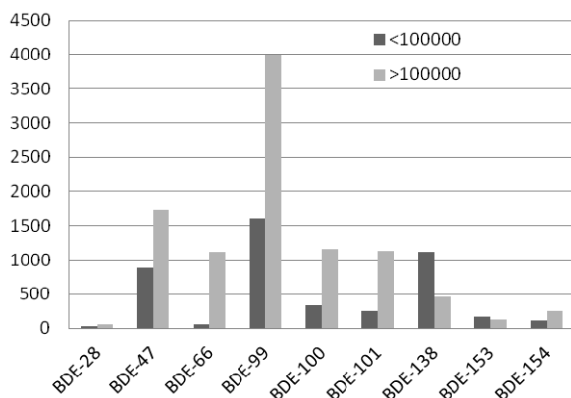


Fig.3. Mean concentrations of BDE congeners (ng/g of dust) in relation to odometer reading (below and above 100 000 km).

Table 1. The concentrations of BDE-28, 47, 66, 99, 100, 101, 138, 153 and 154 in automobile dust (ng/g).

| | Min | Max | Mean | Median |
|----------------|-----|-------|--------|--------|
| BDE-28 | <dl | 269 | 35.8 | <dl |
| BDE-47 | <dl | 5476 | 1233.3 | 210 |
| BDE-66 | <dl | 5593 | 497.3 | <dl |
| BDE-99 | <dl | 14447 | 2600 | 230 |
| BDE-100 | <dl | 4042 | 680.1 | 54.5 |
| BDE-101 | <dl | 5673 | 620.5 | <dl |
| BDE-138 | <dl | 4169 | 844 | 550.5 |
| BDE-153 | <dl | 492 | 153.1 | <dl |
| BDE-154 | <dl | 1033 | 177.3 | <dl |

In Figure 2 the mean concentration of BDE in cars with and without air condition (AC) was also compared. In most cases cars with AC had higher mean concentration, despite BDE-28 and BDE-138. The highest level of mean concentration reported for BDE-99 and was 3638 ng/g. For cars without AC BDE-66, BDE-153, BDE-154 and BDE-183 were under detection level. The highest difference between mean concentration for car with and without AC noticed for BDE-99 and BDE-47. Air condition system circulates air inside the automobile compartment and causes the increase in the concentration of pollutants. Therefore also PBDE level might be elevated.

The criterion was also kilometrage. In this case the highest mean concentration was for BDE-99 3999 ng/g. All types of congeners were detected in both cases. As in the case for car with/without AC, the biggest differences noticed for BDE-99 and BDE-47. For cars of kilometrage upper then 100 000 km were found higher mean concentration of almost every congeners, except BDE-128. Although measurements were limited, odometer reading and air condition system were the most noticeable parameters influencing PBDE concentrations in the indoor dust. Car age had also impact on the level of congeners, although not so significant.

Higher concentrations of particular congeners in cars equipped with AC relate mainly to indoor sources of PBDE. Higher odometer readings might show the impact of outdoor sources, although some transformation of congeners during usage and sun light influence might be a reason. PBDEs in older cars, but with lower odometer readings due to time spent in garage (without direct sunlight), might be not so easily decayed via debromination.

Acknowledgements

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References

1. Kemmelein S, Hahn O, Jann O. (2003); *Atmos. Environ.* 37(39-40): 5485-93
2. Abadie M, Liman K, Bouilly J, Genin D. (2004); *Atmos. Environ.* 38(14): 2017-27
3. Yoshida T, Matsunaga I. (2005); *Environ Int.* 32 (1): 58-79.
4. Knibbs LD, de Dear RJ, Atkinson SE. (2009); *Indoor Air* 19(4): 303-13
5. Harrad S, Ibarra C, Abdallah MAE, Boon R, Neels H, Covaci A. (2008); *Environ Int.* 34(8): 1170-5
6. Lagalante AF, Oswald TD, Calvosa FC. (2009); *Environ Int.* 35(3): 539-44
7. Lagalante AF, Shedden CS, Greenbacker PW. (2011); *Environ Int.* 37 (5): 899-06
8. Harrad S, Abdallah MA-E. (2011); *Chemosphere* 82(9): 1240-5.
9. Gevao B., Al-Bahloul M., Al-Ghadban A.N., Al-Omair A., Ali L., Zafar J., Helaleh M. (2006); *Chemosphere* 64(4): 603-608
10. Debska J, Kot-Wasik A, Namiesnik J. (2004); *Critical Reviews in Anal. Chem.* 34(1): 51-67
11. Jansson B, Andersson R, Asplund L, Bergman A, Litzen K, Nylund K, Reutergardh L, Seelström U, Uvemo U-B, Wahlberg C, Wideqvist U. (1991); *Fresenius' Journal of Analytical Chemistry* 340: 439-445
12. Saito K, Sjödin A, Sandau CD, Davis MD, Nakazawa H, Matsuki Y, Patterson DG Jr. (2004); *Chemosphere* 57(5): 373-381
13. Dudzińska MR. Czerwiński J. (2011); *Int. J. Environmental Engineering* 3(3/4): 253-63
14. de Boer J, Cofino WP. (2002); *Chemosphere* 46(5): 625-633
15. Hyötyläinen T, Hartonen, K. (2002); *Trends in Analytical Chemistry* 21(1): 13-29