Brominated Flame Retardants in Settled Dust of a Commercial Aircraft

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Introduction

Brominated flame retardants (BFRs) are a diverse class of chemicals that are added to materials such as plastic products and textiles in order to reduce their flammability (Bromine Science and Environmental Forum (BSEF), 2006). However, certain BFRs are suspected to cause negative health effects in humans and wildlife (Birnbaum and Staskal, 2004). To minimize risks resulting from the use of BFRs, exposure of human and wildlife to BFRs should be kept as low as possible.

In order to prevent fires, fire safety regulations exist for many products and applications (e.g. electronic equipment, upholstery furniture). It is obvious that strict regulations are essential for materials used in the interior of commercial aircrafts (National Materials Advisory Board, 1995), because fires on board of an aircraft are likely to cause disastrous accidents. These fire safety regulations regulate the flammability of materials, but they do not specify specific chemicals to be used. Therefore it is not known to which extent BFRs are used in the interiors of commercial aircrafts. However, it appears likely that BFRs are used to some extent.

While numerous brominated compounds have been suggested as BFRs, only a small list of compounds is used today in quantities exceeding 1'000 tons per year (Örn and Bergman, 2004). Tetrabromobisphenol A (TBBPA), decabromodiphenyl ether (DecaBDE) and hexabromocyclododecanes (HBCDs) are the most widely used BFRs today. In the past, also large quantities of polybrominated biphenyls (PBBs) and pentabromodiphenyl ethers (PentaBDE) were used. The use of these two BFRs has been banned in many countries and major producers also voluntarily ceased their production.

Human exposure to PentaBDE and DecaBDE has recently been reviewed (Hites, 2004). Hites pointed out that in most studies a minority of people exhibited much higher PentaBDE residues than the average. On the basis of these findings, Hites suggested that indoor exposure at the workplace or at home could be a relevant exposure pathway. This suggestion is supported by a number of studies, which report elevated concentrations of PentaBDE, DecaBDE and other BFRs in settled house dust or indoor air (Sjödin et al., 2001; Knoth et al., 2003; Pettersson-Julander et al., 2004; Stapleton et al., 2005; Wilford et al., 2005; Fischer et al., 2006; Gevao et al., 2006; Harrad et al., 2006). Uptake of BFRs present indoor air or dust may take place via inhalation, swallowing of inhaled particles or oral uptake of dust. Oral uptake of dust is especially likely for toddlers. USEPA estimates that a toddler takes up 50-100 mg of indoor dust (USEPA, 1997).

Herein, we present data on the concentration of various BFRs in settled dust of a commercial aircraft. The aim of this preliminary study was to address the question whether dust and air in airplanes are a potential route of exposure and whether more research is warranted to assess the exposure of people working in airplanes (pilots, cabin crew etc...).

Materials and Methods

Chemicals. Standards were purchased from Cambridge Isotope Laboratories (Andover, USA): $^{13}C_{12}$-BDE-28, $^{13}C_{12}$-BDE-47, $^{13}C_{12}$-BDE-99, $^{13}C_{12}$-BDE-100, $^{13}C_{12}$-BDE-126, $^{13}C_{12}$-BDE-153 and $^{13}C_{12}$-BDE-183; from Wellington Laboratories (Guelph, Canada): $^{13}C_{12}$-BDE-197, $^{13}C_{12}$-BDE-206,

$^{13}C_{12}$-BDE-209, $^{2}H_{18}$-gamma-HBCD, 1,2-bis($^{13}C_{6}$-2,4,6-tribromophenoxy)ethane, BDE-17, BDE-28, BDE-47, BDE-49, BDE-66, BDE-85, BDE-99, BDE-100, BDE-119, BDE-126, BDE-138, BDE-153, BDE154, BDE-155, BDE-156, BDE-183 BDE-197, BDE-206, BDE-207, and BDE-208; from AccuStandard (New Haven, USA): BDE-198, BDE-203, BDE-204 and BDE-205.

Sampling. Dust sample was collected manually in the front pocket of a commercial aircraft (flight SK 841 on August 25, 2006). Details on the interior materials of the aircraft are not known.

Analysis: The dust sample (206 mg) was transferred into a soxhlet thimble. Extraction was performed with a 1:1 mixture of hexane and acetone for 6 hours in a soxhlet apparatus. The extract was concentrated and the solvent exchanged to cyclohexane/ethylacetate. After extraction, isotope labeled standards were added. Subsequently, large molecules originating from partially dissolved polymers were removed by gel permeation chromatography. Extracts were further purified on a silica gel column. The first fraction (40 ml hexane) containing all PBDEs was further purified on an aluminum oxide column. The second fraction of the silica gel column (40 ml hexane/dichloromethane, 1:1 (v/v) contained HBCDs and 1,2-bis(2,4,6-tribromophenoxy)ethane. Volumes were reduced to 100 µl and $^{13}C_{12}$-BDE-126 was added as a syringe standard for calculation of recoveries. Recoveries varied between 40% and 95%. GC analysis was carried out using a DB-1 equivalent stationary phase (10 m × 0.28 mm, film 0.1 µm). Samples were injected on-column (1 µl). Positive ion EI-MS spectra were acquired on a MAT 95 high resolution mass spectrometer (Thermo Finnigan MAT) in single ion monitoring mode at an ionization energy of 70 eV and a mass resolution of 8,000.

	Laboratory blank	**Settled aircraft dust**
	ng/sample	ng/g dw
1,2-bis(2,4,6-tribromophenoxy)-ethan	n.d.	2.1×10^{1}
ΣHBCDs	n.d.	2.8×10^{2}
BDE-17	n.d.	9.5×10^{1}
BDE-28	0.01	1.3×10^{2}
BDE-47	0.26	$\mathbf{2.5 \times 10^{4}}$
BDE-49/71	n.d.	3.5×10^{2}
BDE-66	n.d.	9.0×10^{2}
BDE-85	n.d.	1.8×10^{2}
BDE-99	0.14	$\mathbf{5.7 \times 10^{4}}$
BDE-100	0.03	8.3×10^{3}
BDE-119	n.d.	1.3×10^{2}
BDE-155	n.d.	3.0×10^{1}
BDE-138	0.02	2.1×10^{2}
BDE-153	0.02	6.3×10^{3}
BDE-154	n.d.	3.0×10^{3}
BDE-156	0.11	6.0×10^{0}
BDE-183	n.d.	3.5×10^{2}
ΣOctaBDEs	0.14	3.9×10^{2}
BDE-206	0.06	1.6×10^{3}
BDE-207	0.05	2.2×10^{2}
BDE-208	0.04	9.2×10^{1}
BDE-209	3.06	$\mathbf{5.1 \times 10^{4}}$

Table 1 Concentration of brominated flame retardants in settled airplane dust and in a laboratory blank sample, processed at the same time.

For all PBDEs individual response factors to a isotope labeled standard containing the same number of bromines was measured and used for quantification. The mean of the response factors of BDE-194, -196, -197, -198, -200, 201, -202, -203, -204 and -205 versus $^{13}C_{12}$-BDE-197 was used for quantification of the total (partially co-eluting) octabromodiphenyl ethers (ΣOctaBDEs). Response factors for 1,2-bis(2,4,6-tribromophenoxy)ethane and HBCDs were not measured. An estimated response factor of one was used for quantification of these comounds.

Compounds were identified by comparison of retention times in chromatograms of the analyzed samples to retention times in chromatograms of pure standards. As co-elution of other congeners can not be excluded, identification and quantification, especially of congeners present is small amounts remains to be confirmed.

Results and Discussion

Table 1 lists concentration in settled airplane dust and a laboratory blank, processed simultaneously. All BFRs analysed were detected in aircraft dust and concentrations were always higher than in the laboratory blank sample.

The total concentration of PBDEs found in this sample was 160'000 ng/g dust. This concentration is among the highest concentrations ever reported for dust samples. Wilford et al. (2006) reported an even higher maximum concentration of 170'000 ng/g in house dust. Maximum PBDE concentration found in other studies on house dust were approximately one or even two orders of magnitude lower (Knoth et al., 2003; Stapleton et al., 2005; Harrad et al., 2006). Thus, this single sample of settled airplane dust indicates that BFRs are present at elevated concentrations in the interior of airplanes. Data on the uptake of airplane dust and data on the concentration of BFR in airplane air do not exist. Therefore, the uptake of BFRs during the stay in an airplane can not be estimated at present.

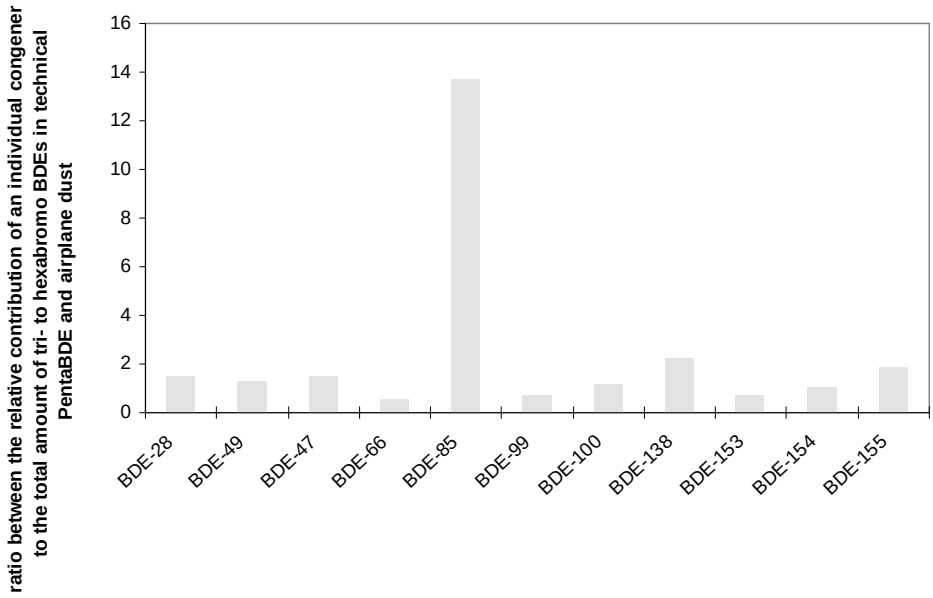

Figure 1. Ratio between the relative contribution of individual congeners to the total amount of tri- to hexabromo BDEs in technical PentaBDE and residues in airplane dust. A ratio of one signifies a similar contribution in technical PentaBDE and in airplane dust. Ratios above one signify a much higher contribution in technical PentaBDE than in airplane dust.

Highest concentrations of individual congeners were found for BDE-47 and BDE-99 as well as for BDE-209. These three congeners are the principal components of technical PentaBDE and technical DecaBDE, respectively. Obviously, these two products were used as flame retardants in this airplane. In Figure 1, the relative contribution of individual congeners to the total amount of tri- to hexabromo BDEs are compared between technical PentaBDE (LaGuardia, 2006) and residues found in airplane dust. For most congeners the ratio of the relative contribution is approximately one. Thus, the composition of airplane dust and technical PentaBDE are very similar. One congener is an exception. BDE-85 (2,2',3,4,4'-pentabromodiphenyl ether) is more present in technical PentaBDE than in airplane dust. Explanations for this finding are not immediately evident. Future research, however, should study, whether BDE-85 may be used as a marker for specific processes or products.

Hexabromocyclododecanes and 1,2-bis(2,4,6-tribromophenoxy)-ethane were also found in this airplane dust sample. However, concentrations were much lower (see Table 1) than concentration of PBDEs.

In conclusion, PBDEs were found in very high concentration in a sample of settled airplane dust, concentrations of HBCDs and 1,2-bis(2,4,6-tribromophenoxy)-ethane were much lower. Due to lack of uptake data for settled dust in airplanes, the exposure caused by the measured elevated concentrations of PBDEs can not be estimated at present. We recommend that future research studies the exposure of airplane professionals (pilots, cabin crew, cleaners).

Acknowledgements

We acknowledge the Swiss National Science Foundation for financial support (Project ENDAIR, National Research Program 50).

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