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Brominated flame retardant exposure of aircraft personnel

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HIGHLIGHTS

- High concentrations of several BFRs were present in aircraft air and dust.
- Maintenance workers had serum PBDE levels three-fold as high as pilots/cabin crew.
- Pilots/cabin crew had similar serum levels of most PBDEs as control subjects.

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ABSTRACT

The use of brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) in aircraft is the result of high fire safety demands. Personnel working in or with aircraft might therefore be exposed to several BFRs. Previous studies have reported PBDE exposure in flight attendants and in passengers. One other group that may be subjected to significant BFR exposure via inhalation, are the aircraft maintenance workers. Personnel exposure both during flights and maintenance of aircraft, are investigated in the present study. Several BFRs were present in air and dust sampled during both the exposure scenarios; PBDEs, hexabromocyclododecane (HBCDD), decabromodiphenyl ethane (DBDPE) and 1,2-bis (2,4,6-tribromophenoxy) ethane. PBDEs were also analyzed in serum from pilots/cabin crew, maintenance workers and from a control group of individuals without any occupational aircraft exposure. Significantly higher concentrations of PBDEs were found in maintenance workers compared to pilots/cabin crew and control subjects with median total PBDE concentrations of 19, 6.8 and 6.6 pmol g^{-1} lipids, respectively. Pilots and cabin crew had similar concentrations of most PBDEs as the control group, except for BDE-153 and BDE-154 which were significantly higher. Results indicate higher concentrations among some of the pilots compared to the cabin crew. It is however, evident that the cabin personnel have lower BFR exposures compared to maintenance workers that are exposed to such a degree that their blood levels are significantly different from the control group.

1. Introduction

Brominated flame retardants (BFRs) are added to plastics, textiles, furniture and electronics to prevent the outbreak of fires or to slow down the rate of the initial stages of a fire. The polybrominated diphenyl ethers (PBDEs) have been extensively used for this purpose and are the most well-studied BFRs today. The use of technical PentaBDE and OctaBDE mixtures, in new products are now banned within the EU (Cox and Efthymiou, 2003) and restricted in other parts of the world. The use of the third mixture, DecaBDE is restricted within the EU (Cox and Drys, 2003) but still in use for certain applications. However, PBDEs that are already in use still remain in the materials and goods to which they were once added, and there are numerous other BFRs in current use (Bergman et al., 2012; EFSA, 2012). Examples of currently used BFRs are, hexabromocyclododecane (HBCDD), decabromodiphenyl ethane (DBDPE) and bis(2,4,6-tribromophenoxy) ethane (BTBPE). DBDPE and BTBPE are used to replace Deca- and OctaBDE mixtures, respectively (EFSA, 2012).

Occupational exposure to BFRs, especially the PBDEs, came early into focus revealing elevated serum concentrations in electronic dismantlers (Sjödin et al., 2001; Thomsen et al., 2001), computer technicians (Jakobsson et al., 2002) and rubber workers (Thuresson et al., 2005). More recent studies include carpet

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installers (Stapleton et al., 2008) and Californian fire fighters (Shaw et al., 2013), also showing elevated serum concentrations of PBDEs. An additional group of special interest is personnel working in and with aircraft. The use of BFRs in materials such as carpets, seats, plastics and electronics is quite evident due to high fire safety demands in aircraft; as a result, high concentrations of PBDEs in aircraft dust have been reported (Gerecke, 2007; Christiansson et al., 2008; Allen et al., 2013a). Likewise, high air concentrations of PBDEs in aircraft, levels exceeding the levels reported for homes, e.g. from the UK and USA, have been reported (Allen et al., 2013b). BTBPE and HBCDD have also been reported in aircraft dust (Gerecke, 2007; Allen et al., 2013a), as well as several other brominated, chlorinated and phosphorous containing flame retardants (Allen et al., 2013a).

Serum concentrations in humans possibly exposed to PBDEs via air and dust during flights have been reported in a few studies. In a small study on Swedish passengers on transcontinental flights, post-travel serum levels of certain PBDE congeners were significantly higher than pre-travel levels, possibly due to PBDE exposure during the flights (Christiansson et al., 2008). However, in a study of flight attendants at a North American airline company total concentrations of PBDEs were not elevated compared to the general US population and it was not possible to correlate concentrations of PBDEs to time spent in aircraft (Schecter et al., 2010). Concentrations of a few congeners were however elevated in some individuals, but were most likely the result of non-occupational exposure (Schecter et al., 2010). Another group with potentially high PBDE exposure is aircraft maintenance workers performing work that includes removal of seats and interior panels prior to inspection, and repair of the mechanical and electrical construction parts. These working tasks can generate dust and hence constitute a potential significant risk of exposure for the workers. The present study aims to investigate the occupational exposure to BFRs during flights and maintenance work.

2. Material and methods

2.1. Serum samples

To study BFR exposure during service of aircraft, serum was sampled from twelve maintenance workers in 2011 and fifteen in 2010. The 2010 serum samples were analyzed separately at an earlier occasion but included in the present report. These workers include technicians, mechanics, electricians and sheet-metal workers all engaged in maintenance work that includes removal of seats and interior panels prior to inspection, and repair of the mechanical and electrical construction parts. Exposure during flight was studied in 41 serum samples collected from pilots ($n = 17$) and cabin crew ($n = 24$) in 2012. For comparison, serum was obtained from a control group ($n = 31$), also sampled in 2012. The control group included individuals working in schools or at a local environment and health administration office, persons without any known occupational exposure to brominated flame retardants. They were not frequent flyers and had not done any long-distance flights within six months prior to sampling. When donating blood, subjects answered a short questionnaire about length of present employment, work tasks during the last month, dietary habits and possible health problems. The average ages of the people included in the three study groups were 52, 45 and 45 years, for maintenance workers, pilots/cabin crew and control subjects, respectively. The average number of years working within each profession were 24, 17 and 12 years for maintenance workers, pilots/cabin crew and control subjects, respectively. Further information about the three study groups is given in the Supporting Information (SI, Tables S1–S3). Serum was stored at −20 °C prior to analysis.

2.2. Dust and air sampling

Two aircraft (model Boeing 737-800, manufacturing years 1998 and 2000) were used for sampling of air and dust during maintenance work, all sampling took place in 2012. Nine samples of settled dust were collected from different places in the aircraft by gently wiping hard surfaces with wooden sticks. Information about sampling locations is given in Table 1. For air sampling, Occupational Health and Safety Administration (OHSA) versatile samplers (OVS) were used for both personal ($n = 6$) and stationary ($n = 9$) air sampling. The OVS contained a glass fiber filter and two XAD-2 adsorbent layers (separated by polyurethane foam) to capture BFRs in both the particulate and gas phase. Air was pumped through the OVS with a flow rate of 3 mL min^{-1} for 8 h. Stationary air samplers were placed at different places within the airplane and personal samplers were worn during different assignments of the maintenance work. For further information, see Table 1. The workers carrying the personal samplers were from the same group of workers, but not the same individuals as those donating blood for the serum analysis. This type of maintenance work is performed without any ventilation except for the general ventilation system used in the hangar where the aircraft is parked.

Air and dust samples were collected during flights on three aircraft (model AVRO RJ 100), operating within Sweden. All sampling took place in 2012. Three samples of settled dust were collected from the ventilation outlets in the aircraft toilets. The air that passes through these ventilation outlets comes from the cabin. For stationary air sampling OVS ($n = 4$) samplers placed behind the pilots in the cockpit were used (3 mL min^{-1}, 8 h). The ventilation in cockpit is separate from in the cabin with higher rates in cockpit, mostly due to cooling of the instrumentation.

2.3. Chemicals

Twenty five individual PBDE congeners (BDE-28, -47, -66, -85, -99, -100, -153, -154, -183, -194, -195, -196, -197, -198, -199, -200, -201, -202, -203, -204, -205, -206, -207, -208 and -209), numbered according to (Ballschmiter et al., 1993) were used as authentic reference standards (Wellington Laboratories Inc. Guelph, ON, Canada). Other reference standards used: BTBPE and DBDPE (Wellington), and technical HBCDD (99.5%, Dead Sea Bromine Group). Compounds used as either surrogate or volumetric standards: BDE-77, BDE-128 and BDE-138 were synthesised in house (Örn et al., 1996) and BDE-139 was purchased from Wellington. Solvents and reagents used were of the highest commercial grade available. Silica gel (0.063–0.260 mm) from Merck (Darmstadt, Germany) was heated at 300 °C over night, prior to use.

2.4. Extraction

Extraction and cleanup of the serum samples followed procedures described elsewhere with minor modifications (Hovander et al., 2000). Prior to extraction, approximately 5 g of serum was spiked with BDE-138 (0.5 ng) as surrogate standard. Briefly, the serum was acidified with hydrochloric acid (6 M, 1 mL), denaturated with 2-propanol (6 mL) and extracted with cyclohexane:methyl tert-butyl ether (1:1, 6 mL). Lipids were determined gravimetrically. Neutral and phenolic compounds were separated by partitioning of the samples (dissolved in cyclohexane) with potassium hydroxide (0.5 M in 50% ethanol, 2 mL). The phenolic fraction was saved and for the neutral fraction, lipids were removed using concentrated sulfuric acid. Further cleanup included sulfuric acid/silica gel columns (0.1 g silica gel, 0.9 g silica gel:sulfuric acid (2:1, w/w)). The columns were pre-cleaned with 5 mL cyclohexane:dichloromethane (1:1, v/v), the sample was added and analytes were eluted with 15 mL of the same solvent. Prior to the