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Seasonal variations of polybrominated flame retardants bound to car dust under Mediterranean climate

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are commercial flame retardants that have been commonly used in vehicle interior to reduce fire-related hazards. Due to high temperatures and intense insolation that can be attained inside cars parked in the sun, additive PBDEs are prone to leach out and attach to in-vehicle dust, as well as to photo-debrominate. This study examines seasonal variations of concentrations of three common PBDE congeners (BDE-47, BDE-99 and BDE-209) in car dust in Israel. The overall concentrations of these BDEs ranged from 1 to 29 μg/g, and were higher in the summer than in the winter (average of 10.2 and 5.3 μg/g, respectively). Congener-specific concentrations showed distinct seasonal pattern, representing the interplay between leaching, evaporation and photodebromination. Photolysis of the three congeners, while adsorbed on glass filters and exposed to solar radiation, revealed first order kinetics with debromination rates on the order of 10^{-2}/min. Hence, seasonal variations of the meteorological conditions were found to affect the in-vehicle PBDE concentrations, and are therefore expected also to affect the exposure of passengers to PBDEs.

Introduction

Flame retardants (FRs) are chemical compounds used to reduce fire hazards by interfering with the combustion of polymeric materials. Whereas reactive FRs are covalently bonded with the polymeric materials, additive FRs are only dissolved in the polymer. Hence, additive FRs tend to leach out from the matrix into the environment more easily than reactive FRs (Besis and Samara, 2012; Rahman et al., 2001). To inhibit leaching and ensure improved fire retarding capabilities, high molecular weight FR products, such as polybrominated diphenyl ethers (PBDEs) were developed. PBDEs were produced mainly as three homologs: penta-BDE, octa-BDE and deca-BDE, and used in different synthetic building materials, consumer products, textiles, upholstery and in cars' interior (Besis and Samara, 2012; Birnbaum and Staskal, 2004). The outstanding flame-retarding capabilities of PBDEs ensure compliance with the most stringent fire safety requirements. However, the prevalent use of flame retardants resulted in inevitable exposure to PBDEs, including in utero, due to their ubiquity in all environmental media: air, water and food. Like polychlorinated biphenyls, PBDEs are lipophilic compounds that can accumulate in living organisms and biomagnify (Birnbaum and Staskal, 2004; Söderström et al., 2004). In general, our understanding about health outcomes in people due to exposure to PBDEs is limited, but adverse health effects have been reported in animals (Birnbaum and Staskal, 2004; EPA, 2010; Eriksson et al., 2004). While highly brominated PBDEs (in particular deca-PBDE) are considered to be less toxic, under real-world conditions people are exposed to mixtures of PBDEs rather than to only one congener. Due to the accumulated evidence on PBDE toxicity, restrictions on PBDEs production and use were applied in the EU and the USA since the late 1990s (Birnbaum and Staskal, 2004). Specifically, a ban on the use and marketing of penta- and

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octa-PBDE in EU is in effect since 2004, and of deca-PBDE since 2008. In the US, a ban on penta- and octa-PBDEs manufacturing is in effect since 2005, and deca-BDE production, import and sale was phased out in 2012/2013 following a 2009 legislation. As a result of these regulations, the concentrations of PBDEs in breast milk of Swedish women, which doubled every five years between 1980 and 2004 (Eriksson et al., 2004), decreased modestly since the ban has been enacted (Bramwell et al., 2014). The ban is expected to lower the exposure to PBDEs also in vehicles, yet as the average vehicle lifetime is ≥15 years (Lagalante et al., 2009), in-vehicle exposure to PBDEs may still be significant. Indeed, high PBDE levels in human adipose tissue were recently reported and attributed to continued exposures (Antignac et al., 2009; Bramwell et al., 2014).

PBDE homologs with fewer bromine atoms tend to partition into the gas phase more readily than higher-brominated homologs. Hence, lower-brominated PBDEs are expected to be found primarily in the vapor phase while higher-brominated homologs are expected to be primarily adsorbed onto atmospheric particles. Dust is an ideal matrix for PBDE adsorption due to its omnipresence in the environment and large surface area (Harrad et al., 2006, 2008; Harrad and Abdallah, 2011). Particle-bound PBDEs contribute to human exposure through all three main exposure routes: ingestion, inhalation and dermal contact. For example, inhalation of resuspended dust can occur after dusting and vacuuming both at home and in vehicles (Cunha et al., 2010). Due to their hydrophobicity and lipophilicity, exposure to dust-bound PBDE was suggested to represent an important exposure pathway (Rahman et al., 2001), with a growing base of evidence suggesting that occupancy in vehicles is associated with increased exposure to PBDEs (Harrad and Abdallah, 2011; Lagalante et al., 2009; Mandalakis et al., 2008). Specifically, while the time spent in vehicles is usually much shorter than in other microenvironments (*e.g.*, home, work, school) (Shafran-Nathan et al., 2017), median PBDE levels in car dust were reported to be ~20 times higher than in household dust (Harrad et al., 2008; Harrad and Abdallah, 2011; Lagalante et al., 2009). Table 1 summarizes previously reported concentrations of different PBDE congeners in cars' dust, showing that in-vehicle PBDEs are present globally, and that BDE-209 is the most abundant congener.

Due to their carbon-bromine bonds, PBDEs degrade faster than other persistent chemicals following exposure to ultra-violet (UV) radiation (Söderström et al., 2004). Yet, whereas photochemical debromination is an important removal process of the heavier PBDEs (Kajiwara et al., 2013; Stapleton and Dodder, 2008), its products are lower-brominated PBDEs (EPA, 2010; Schenker et al., 2008). The latter may be more bioaccumulative and toxic than higher brominated PBDEs (Birnbaum and Staskal, 2004), and can leach out faster from the car interior. Quantitative PBDE photolysis rates under real environmental conditions are scarce, and available data mainly account for PBDE dissolved in liquid matrices such as organic solvents or aqueous solutions (Fang et al., 2008; Santos et al., 2016; Shih and Wang, 2009). Only

Table 1 – Concentrations of polybrominated diphenyl ethers (PBDEs) in car dust (ordered by study period).

Country	BDE congeners detected	Mean of ΣPBDE (range) (ng/g_{dust})	Study period	BDE-209 out of total BDE (%)	References
Sweden[a]	28, 47, 99, 153, 183, 197, 206, 207, 208, 209	8324 (54–30,000)	2006	~97	Thuresson et al. (2012)
UK[b]	28, 47, 49, 66, 99, 100, 153, 154, 183, 196, 197, 203, 209	340,000 (140–2,600,000)	July 2006–June 2007	~100	Harrad et al. (2008)
USA	28, 47, 99, 100, 153, 154, 183, 209	276,800, (5237–3,571,961)	October 2007–February 2008	~95	Lagalante et al. (2009)
Portugal	28, 47, 49, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, 209	4660 (193–22,955)	December 2008	~53	Cunha et al. (2010)
USA	7, 15, 17, 28, 47, 49, 66, 99, 100, 138, 153, 154, 181, 183, 196, 197, 203, 206, 207, 208, 209	30,337 (912–345,540)	–	~82	Lagalante et al. (2011)
Czech Republic[c]	28, 47, 49, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, 209	3723 (20–33,728)	June–July, 2009	~84	Kalachova et al. (2012)
Kuwait	28, 47,66,85,99, 100, 138,153,154, 183, 208, 207, 206, 209	2065 (68–17,200)	April 2011	~89	Gevao et al. (2016)
Egypt	17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 209	6943 (171–37,440)	2013	~98	Hassan and Shoeib (2015)
Nigeria	47, 99, 100, 118, 128, 153, 154, 183, 209	722 (159–3182)	April–June, 2014	~47	Olukunle et al. (2015)
Nigeria	47, 49, 99, 154, 197	14,951 (70–65,874)	September–October, 2014	~67	Harrad et al. (2016)
Israel	47, 99, 209	Summer: 10,211 (3290–28,284) Winter: 5333 (943–21,619)	July, 2014–March, 2015	Summer: ~1.3 Winter: ~14	This study

[a] Dust samples collected using vacuum cleaner bag.
[b] Samples collected using nylon socks (25 mm pore size) mounted on the vacuum cleaner hose.
[c] Samples collected using previously weighed cotton dusters (30 cm × 30 cm).

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