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PASSIVE AIR SAMPLING SURVEY OF POLYBROMINATED DIPHENYL ETHER IN PRIVATE CARS: IMPLICATIONS FOR SOURCES AND HUMAN EXPOSURE

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ABSTRACT

In order to characterize polybrominated diphenyl ether (PBDE) contamination in vehicle interiors, airborne concentrations of polybrominated diphenyl ethers were investigated using PUF disk passive air samplers in 25 private cars. Passive air samplers were fixed inside the selected cars for a period of 4 to 6 weeks. ΣPBDE concentrations (sum of the 10 congeners) ranged between 0.01 and 8.2 ng/m^3 with respective arithmetic and geometric mean concentrations of 0.71 and 0.091 ng/m^3. High concentrations of polybrominated diphenyl ethers found in cars might provide an important source of human exposure to PBDEs either via inhalation or dust ingestion. A driver spending 8 hours a day inside a contaminated car (the worst scenario) would receive a daily inhalation intake of 54 ng. Age of the vehicles was found to be the most influential factor affecting polybrominated diphenyl ether emission in car interiors ($R=0.47$, $r<0.01$). Furthermore, significant variations were observed in polybrominated diphenyl ether concentrations between cars from same manufacturer with similar ages. The median ratio of BDE 47:99 for air samples was 1.7 comparing with the respective values of ~1 and ~0.7 reported for BK 70-5DE and DE-71, suggesting these commercial formulations to be likely sources of polybrominated diphenyl ethers in the car indoor environments.

Key words: Polybrominated diphenyl ether, Car, Indoor air, Passive sampler, Inhalation exposure

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a class of organic compounds widely detected in all environmental compartments as a result of their intense industrial and commercial applications (Abraham *et al*., 1994; Koopmanesseboom *et al*., 1994; Bencko *et al*., 2004; Jones-Otazo *et al*., 2005; Harrad *et al*., 2006). While generally their ambient concentrations in air and water are not considered to exert severe direct hazards via inhalation and ingestion, respectively, their hydrophobicity, combined with their resistance to degradation via mechanisms like photolysis, hydroxyl radical attack and biological action has resulted in global dispersion of PBDEs and subsequently biomagnification in terrestrial, freshwater, aquatic, and pelagic food chains.

Whereas the legacy persistent organic pollutants (POPs) (e.g Dioxins) pose much sever toxic effects on human health (Ebtekar, 2004) than the PBDEs, their widely reported presence and rapidly rising levels in wildlife and human tissue (i.e. doubling concentration time of ~3-7 years) has raised concerns over PBDEs potential health effects (Meironyte *et al*., 1999, Hites, 2004).

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Such concerns have led to bans or voluntarily restriction on use of lower brominated technical formulations in Europe and North America (EU, 2003; Tullo, 2003; NICNAS, 2007). PBDEs are halogenated hydrocarbons in which 1-10 brome atoms are attached to

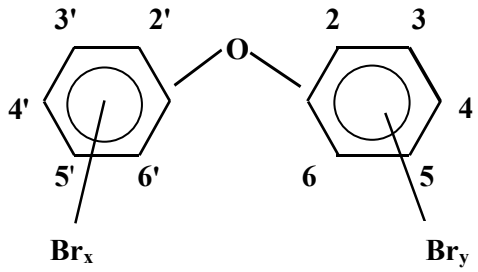

Fig. 1: Generic formulae for PBDE

a biphenyl nucleus (Fig. 1). Based on the number of halogen substituents there are 10 homologue groups containing 209 discrete congeners.

PBDEs have been produced commercially as mixtures under a variety of trade names (e.g. Bromkal 70, Bromkal 70 5DE, Great Lakes DE-60F, and Saytex 115) since the early 1970s (de Boer and Cofino, 2002). Three major commercial mixtures of the PBDEs are produced, which vary in the degree of bromine substitution on the aromatic rings. They are decabromodiphenylether, which contains about 97-98% deca-BDE congener, octabromodiphenyl ether (31-35% octa-BDE and 44% hepta-BDE), and pentabromodiphenyl ether, which is comprised of roughly 24-38% tetra-BDE, 50-60% penta-BDE and 4-8% hexa-BDE congeners (de Wit, 2002).

Owing to their thermal stability, high bromine content (good flame retardant properties), and relatively low costs, PBDEs are used as flame-retardant additives (i.e. they are only dissolved in the material) in order to reduce fire hazards by interfering with the combustion of the polymeric materials (Rahman *et al*., 2001). They are also added to wires and cables, textiles, polyurethane foam, carpets and upholstery used in household and business furnishings, cars, buses, trucks, and aircraft (WHO, 1994; de Wit, 2002; Hardy, 2002; Branchi *et al*., 2003).

Based on available toxicity data, toxicological endpoints likely to be the most sensitive for the PBDEs are: thyroid hormone disruption (Legler and Brouwer, 2003), neurobehavioral effects and, for some congeners possibly cancer (de Wit, 2002). PBDE levels in humans and biota have been shown to increase with a doubling time of ~5 years (Meironyte *et al*., 1999). Although PBDEs are ubiquitous environmental contaminant, however, less is known about it's concentrations in car indoor microenvironments. In order to characterize airborne concentrations of PBDE in indoor microenvironments, their possible sources, and implications for human exposure, this study monitored PBDEs levels in 25 private cars in the West Midlands, UK using passive air sampling technique.

MATERIALS AND METHODS

Sample collection

PUF disk passive samplers were used to collect air samples. The procedure for sampler conFig. uration has been fully described elsewhere (Hazrati and Harrad, 2006). A total of 25 private cars from variety of marques and makes were selected and PUF disk passive samplers were located on the cradle and fixed inside car boots (Fig. 2) for a period of 4-6 weeks. Sampling rate (SR) of PUF disk samplers obtained employing a calibration campaign using a low

Fig. 2: Illustration of passive samplers in a car boot

volume active air sampler (Hazrati and Harrad, 2006). Congener based sampling rates were applied to estimate ambient concentrations of 7 BDE congeners. Passive sampling rates for the 7 PBDE congeners monitored showed relatively low variability (RSD = 17.6%) varying from 1.12 (BDE 99) to 1.94 m^3/day (BDE 47), therefore, a sampling rate of 1.64 m^3/day based on average of SR values determined for PBDEs 17, 28, 47, 49, 66, 99, and 100 was applied to estimate airborne concentrations for other PBDEs.

Sample preparation and analysis: PUF disks were treated with 10 ng of PBDE surrogate standards (ISs including PBDE #s: 28, 47, 99, and 153) prior to extraction in a pre-cleaned 200 ml soxhlet apparatus for 8 h using HPLC grade hexane. The crude extract was concentrated to approximately 2 mL, treated with 2 mL concentrated sulphuric acid, prior to elution through a column containing one gram Florisil (Aldrich Chemicals, 60–120 mesh, pesticide grade). Analyses were conducted on a Fisons' MD-800 GC/MS system fitted with a 60 m VF5 MS column.

Table 1: Specifications of sampling locations and BDE concentrations (pg/m^3) in car microenvironments

Sample ID	Made	BDE 17	BDE 28	BDE 49	BDE 47	BDE 66	BDE 100	BDE 99	BDE 85	BDE 154	BDE 153	ΣPBDE
C1	2001	5	16	7	137	4	32	179	4	15	12	411
C2	1991	0	1	0	5	0	1	4	0	0	0	12
C3	1991	0	6	0	7	0	0	4	0	0	0	17
C4	1984	1	2	1	10	0	1	4	0	0	0	18
C5	1989	135	293	225	1297	134	67	414	0	4	4	2571
C6	2000	0	1	2	8	2	4	8	5	5	8	42
C7	1988	1	2	0	19	0	3	12	0	0	0	37
C8	2003	127	365	368	2468	236	89	977	8	5	5	4648
C9	1999	0	0	0	3	0	1	6	0	1	3	15
C10	2001	0	2	3	7	4	9	20	13	13	19	89
C11	1993	90	215	141	4702	53	615	2281	19	48	20	8184
C12	1990	0	1	0	15	0	3	11	0	0	0	30
C13	2001	0	1	0	7	0	2	13	0	0	0	23
C22	1991	0	2	2	23	0	4	11	0	0	0	41
C14	1991	0	6	0	5	0	0	0	0	0	0	11
C16	1992	1	5	4	102	0	13	52	0	0	0	177
C15	2000	1	3	2	38	0	4	17	0	0	0	64
C17	1991	0	11	3	29	0	3	11	0	0	0	58
C18	1998	10	25	10	192	0	16	68	0	0	0	322
C19	2000	27	48	20	419	6	44	179	0	5	4	752
C20	1996	0	1	0	7	0	0	12	0	0	0	20
C21	1990	0	2	1	14	0	3	13	0	0	0	34
C23	1994	0	1	1	13	0	4	21	0	0	1	41
C24	1996	4	10	2	43	0	3	12	0	0	0	74
C25	1992	0	1	2	11	1	3	8	3	3	5	36
Average	1994	16	41	32	383	18	37	173	2	4	3	709
SD	5	39	97	87	1050	54	122	485	5	10	6	1866

QA and QC measures

The precision of passive sampling and analytical procedures combined was evaluated by simultaneously deploying 5 passive samplers in a temporarily vacant domestic microenvironment for 6 weeks. They were extracted and analysed separately and the concentrations of all quantifiable PBDE congeners determined. Average relative standard deviations (RSD) between the 5 replicate analyses for the PBDE congeners was 17%. The low RSD observed for PBDE congeners in this exercise demonstrate good repeatability for the sampling and analytical method employed in this study.

To determine the accuracy and precision of the analytical protocol, 5 replicate aliquots of SRM 1944 (New York/ New Jersey Waterway Sediment) were analysed for PBDEs throughout the study.

RESULTS

ΣPBDE in this study refers to the sum of the BDE #s 17, 28, 47, 49, 66, 85, 99, 100, 153, and 154. Specifications of sampling locations and BDE concentrations quantified in car microenvironments from 12 different manufacturers are provided in Table 1. ΣPBDE concentrations in private cars varied from 0.01 to 8.2 ng/m^3 with respective arithmetic and geometric mean concentrations of 0.71 and 0.091 ng/m^3. The age of the cars varied from 2 to 21 years.

Table 2: Summary of indoor air concentrations of PBDEs (pg/m3) worldwide

Indoor microenvironment	average	Min	Max	
Offices		80	2100	Shoeib *et al*., 2004
Homes and offices	1800	60	15500	Harrad *et al*., 2004
Homes	260	2	3600	Wilford *et al*., 2004
Homes	15			Gevao *et al*., 2006
Offices	30			
Offices	205*			Mandalakis *et al* 2008 a
Homes	8*			
Cars		0.4	2644	Mandalakis *et al* 2008b
Windscreen Film		280000	1772000	Gearhart and Posselt (2006)
Cars	709	11	8184	This study

DISCUSSION

Concentrations of PBDE in indoor air

The summary of ΣPBDE concentrations in private cars in this study along with the PBDE levels reported by other researchers are provided in Table 2.

ΣPBDE concentrations found in air in car interior are comparable to those studies monitoring contaminant levels in office microenvironments in which PBDE concentrations were in a range of 0.06-15.5 ng/m^3 (Shoeib *et al*., 2004, Harrad *et al*., 2004). PBDE levels detected in air in automobile cabins (Mandalakis *et al* 2008b**)** demonstrated similar contamination levels as for this study, although higher brominated

Deca–BDE congener was included in ΣPBDE concentrations. Similarly, higher concentrations of PBDE were quantified in windshield film and dust sampled from the interior of US cars (Gearhart and Posselt, 2006). However, our findings are much higher than the concentrations reported by the studies in which PUF disk passive air samplers were employed to monitor indoor air concentrations of PBDEs in residential homes (Wilford *et al*., 2004, Gevao *et al*., 2006). Similar

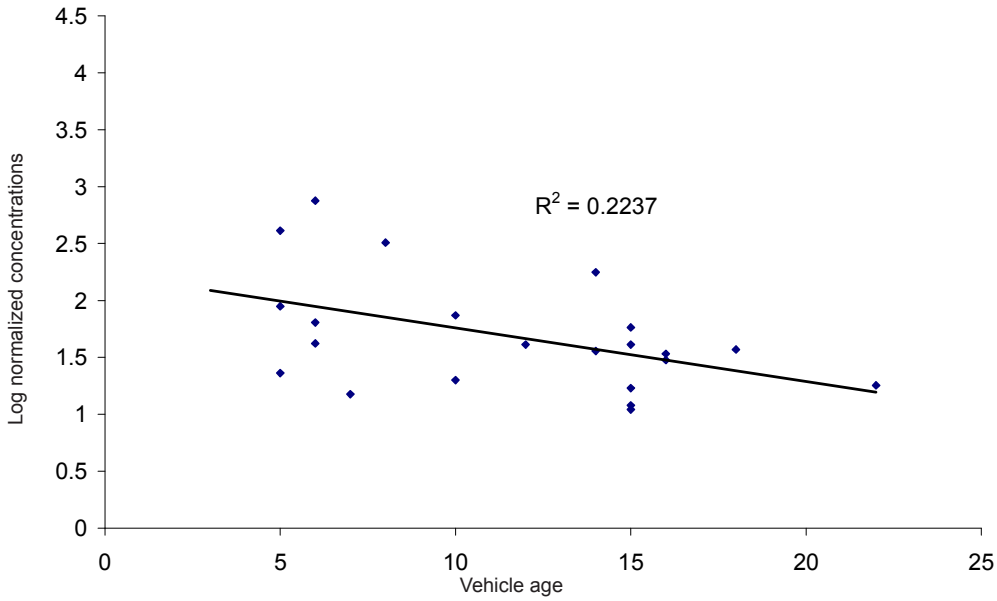

Fig. 3: Correlation between vehicle age and PBDE concent

Table 3: Ratio of BDE 47:99 in ambient air and commercial mixtures

	Mean	SD	Median	
Car	1.7	0.92	1.7	This study
Indoor air	3.8			Wilford *et al*. (2004)
Indoor air	2.4			Gevao *et al*. (2006a)
Indoor air	5.3	3.01		Harrad *et al*. (2004)
BK 70-5DE	1			Sjodin *et al*. (1998)
DE-71	0.69			Hoh and Hites (2005)

to other air pollutants (Ghasemkhani and Naseri, 2008), airborne concentrations of PBDEs in the UK cars were much higher than those of reported for outdoor (Harrad *et al*., 2004)

Inhalation exposure to ΣPBDE

Although human intakes occur principally through dust ingestion and dietary pathways (Ibarra *et al*., 2006), significant variations in concentrations

of PBDEs in ambient indoor air, means that inhalation exposure may be far more significant for some people. For instance, assuming an inhalation rate of 20 m^3/day for an adult (Currado and Harrad, 1998), a taxi driver spending 8 hours daily in a contaminated car would receive a daily inhalation exposure of 54 ng. Similar study estimated the daily inhalation intake of PBDEs during commuting to range from 0.5 to 2909 pg/day (Mandalakis *et al*., 2008b). The variations observed in PBDE concentrations (three orders of magnitude) implies that some subpopulations may receive substantially elevated intakes compared to other population sectors via inhalation and dust ingestion pathways. This finding might explain the reason for extremely high levels of PBDEs found in 5% of Swedish blood samples (both in the case and control groups) that were not attributable to intakes through the food chain or occupational exposures (Van Bavel *et al*., 2002).

Factors influencing PBDE concentrations

Indoor air temperature, vehicle age, manufacturing origins of vehicles, and the impact of other goods (e.g. hi-fi, navigation systems, cushions, and child seats) are thought to be the main factors influencing automobiles' PBDE emissions. Amongst these many potentially important factors, the age and manufacturer of cars were studied. Excluding three most contaminated cars as outliers, linear regression of log-normalised ΣPBDE concentrations with vehicle age revealed statistically significant relationship ($R=-0.47$, $p<0.01$). This is in agreement with the report of Mandalakis *et al.* (2008b) where significant outgassing of PBDEs from the interior surfaces of newer cars was observed.

The limited number of samples taken from each marque precludes the drawing of any firm conclusions as to whether cars made by different manufacturers vary in contamination levels. However, airborne concentrations of PBDEs in some cases varied by more than 2 orders of magnitude between cars from the same manufacturer (i.e. for Nissans between 11 and 2571 ng/m^3). Since the cars were similar in age, thus it does not appear to be due to variations in vehicle age, and instead may be the result of differences in the quantity and type of PBDE-containing goods such as electronic equipment. This agrees well with the significant variation in PBDE concentrations recorded for three Fords in which the concentrations varied from 126 to 2644 pg/m^3 (Manolis Mandalakis *et al*., 2008b). More data are required to characterise PBDE emission sources in cars and this area warrants further research.

PBDE sources in indoor microenvironments

Tri- to hexa-brominated diphenyl ethers were monitored in this study. These cover the majority of the congeners present in the most pertinent formulations to be produced or used in the UK (i.e. penta BDE commercial formulations). Congener profiles of PBDEs in cars were compared with the congener composition of the two penta BDE formulations principally employed in the UK, namely DE-71 and Bromkal 70-5DE (Sjodin *et al*., 1998, Hoh and Hites, 2005). For this purpose, the concentration ratios of BDE 47 relative to BDE 99 in cars along with those in commercial penta-BDE formulations are provided in Table 3.

For all air in interior car samples, the median ratio of BDE 47:99 is 1.7, which is comparable with the respective values of ~1 and ~0.7 reported for BK 70-5DE and DE-71, suggesting these commercial formulations are likely sources of PBDEs in the indoor environments studied. These relatively higher BDE 47:99 ratios in car microenvironments, supports the hypothesis that preferential volatile emissions of the lower brominated 47 c.f. 99 from household items favour higher ratios in air compared to those detected in the treated material itself (Kemmlein *et al*., 2003).

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