POLYBROMINATED DIPHENYL ETHERS LEVELS IN DUST FROM CARS IN KUWAIT

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Introduction

Polybrominated diphenyl ethers have been extensively used to flame retard a whole range of consumer products such as textiles, carpets, polyurethane foams, electronic cables, television sets and computers. Although bans have been imposed on current and future use, these chemicals are present in consumer products to which they were added will continue to escape from the products to which they are added during normal use, or through wear and tear, and contaminate the indoor environment, as they are not covalently bonded into the fabric of the polymers *(1-2)*. Dust present in these indoor environments have been shown to contain significantly higher amounts of chemical additives and are considered a potential source of human exposure to chemicals including PBDEs *(1, 3-4)*. Harrad et al. *(5)*, for example, described cars as the microenvironment most contaminated with PBDEs in comparison with indoor environment of homes and offices. Their presence in vehicles is linked to their use in seat fabrics, cable insulation and other electronics present such as in-car entertainment *(6)*. As air temperatures can be as high as 90^{o}C and 120^{o}C on dash boards PBDEs can volatilize from the polymers to which they are added and condense on dust which is a sink for semivolatile organic compounds *(6)*. PBDEs are of concern because they have been found to be toxic, bioaccumulative, and persistent in the environment *(7)*. These concerns led to their inclusion in Annex A (targeted for elimination) of the Stockholm Convention, a treaty to control and phase out major persistent organic pollutants (POPs). They have been detected in the environment, animals, and humans. The goal of this study was to investigate the occurrence and concentration of PBDEs in dust from vehicles in Kuwait and to examine linkages between concentrations and vehicle manufacturers.

Materials and methods

Dust samples from 23 cars were collected using a bagless philips (FC8149) vacuum cleaner in April 2011. The vehicles included in the study were not vacuumed for at least 2 weeks prior to sampling. Each participant was asked to complete a questionnaire about the make and model of the vehicle, year and country of manufacture, fabric for internal furnishing, and odometer reading. The temperature inside the car during sampling was also measured. The entire interiors of the car, including seats, dashboard, and floor were vacuumed. Dust samples collected from each vehicle were immediately transferred to hexane-rinsed amber glass bottles and stored at -20 ^{o}C prior to further processing. The dust samples were sieved through a 250 µm stainless steel mesh (Retsch, Germany) and immediately transferred to clean solvent rinsed amber glass bottles and kept at -20 ^{o}C until analysis.

Dust samples (~2g) were Soxhlet-extracted with hexane overnight. Before extraction the samples were spiked with 100 µl BDE-205 (645 pg/µl) to monitor analytical recovery. The extract was rotary evaporated to ~ 5 ml and subjected to sulfuric acid cleanup. The extracts were back-extracted with 5% NaCl solution and passed throw sodium sulfate (baked at 450˚C for 24 h and stored at 130˚C prior to use), to remove residual water. The volume of the sample reduced under a gentle stream of nitrogen and 50 µl of dodecane was added as keeper. The volume of the sample was increased to 500 µl with iso-octane and spiked with 10-µl BDE-35 (62 pg/µl) as internal standard, used for volume correction and to adjust for variations in instrument response. Some samples which required further cleanup were subjected to column chromatography using 3g silica (baked at 450˚C for 24 h and stored at 130˚C prior to use) and eluting the compounds of interest with 15 ml (9:1, v/v) mixture of hexane:dichloromethane (DCM).

The sample extracts were analysed on a Shimadzu GC 2010 (Shimadzu, Tokyo, Japan) gas chromatograph using splitless injection on a 15 m DB5-ms column (0.25 mm i.d., 0.25 µm film thickness) and helium as carrier gas. The oven program was 150 ^{o}C for 1 min, ramped at 20 ^{o}C min^{-1} to 250 ^{o}C, 4^{o}C min^{-1} to 290 ^{o}C, and held for 25 min. This gas chromatograph was coupled to a Shimadzu 2010 Mass Selective Detector

operated in electron capture negative chemical ionization (ECNCI) using selected ion monitoring (SIM), with methane as reagent gas. The ions m/z 79 and 81 were monitored for all target compounds. The ions m/z 484.7, 486.7, and 488.7 were also monitored for BDE 209. Operating conditions were as follows: injector temperature was set at 250°C; ion source at 230°C; transfer line at 300°C. Identification and quantification was carried out against five calibration standards of known concentrations. A peak was positively identified if it was within ±0.05 min of the retention time in the calibration standard and quantified only if the S/N≥3 and the ratio of the target ion to its qualifier ion was within ±20% of the standard value.

Results and discussion

The concentrations of ΣPBDEs in dust from vehicles were log normally distributed and ranged from 85 – 40109 ng/g. The geometric mean, median and range in concentrations of the individual congeners are presented in Table 1. Also given in Table 1 are the frequency of detection of each congener. The compounds routinely detected in vehicles with frequency > 90% in decreasing order of importance are: As shown in Table 1, the major congener was BDE 209 (83%), with a geometric mean concentration of 702 ng/g (median, 466 ng/g) with the other congeners contributing 17% of the total measured compounds. The maximum $\sum_{17}$PBDEs was measured in a 2009 Mitsubishi Pajero manufactured in Japan (40,108.4 ng/g) with the lowest in a 2007 Toyota Yaris (84.6 ng/g) also manufactured in Japan.

Table 1. Summary of PBDE concentrations (ng/g) found in car dust

Congener	% Detection	Geometric mean	Median	Range
17	16	0.2	0.3	< d. l. - 0.6
28	72	0.5	0.5	< d. l. - 5.1
71	96	4.5	7.4	< d. l. - 685
47	96	5.7	4.8	< d. l. - 47.6
66	88	0.4	0.2	< d. l. - 10.6
100	96	2.0	1.4	< d. l. - 2713
99	100	18.1	10.9	1.7 - 2225
85	88	0.5	0.5	< d. l. - 2.3
154	92	0.9	0.8	< d. l. - 3.4
153	96	1.7	1.5	< d. l. - 18
138	84	1.2	1.4	< d. l. - 115
183	100	2.7	3.1	0.47 - 11.8
190	64	0.8	0.4	< d. l. - 932
208	100	11.6	12.3	1.8 - 192
207	100	21.0	19.7	2.9 - 414
206	100	68.5	78.8	5.0 - 3488
209	100	702.6	465.7	52.3 - 33143

The concentrations of PBDEs in this study are 44 times higher than those reported previously for house dust in Kuwait *(4)* collaborating findings by Harrad et al., *(8)* in Birmingham, United Kingdom that vehicles are more contaminated than homes. When the data is compared with similar studies around the world it can be they are similar to those reported in Portugal *(9)*, Chicago *(10)*, Washington, DC, *(11)* and Singapore *(12)* but far lower than those reported from Birmingham, UK *(8)*. In this study we were unable to correlate concentration data with make, model or year of manufacture; odometer reading and/or type of fabric used in the interior . This is, in part, due to the sample size and possible differences in flame retardancy policy between manufacturers as have been the case in similar previous studies *(6, 8-9, 13)*

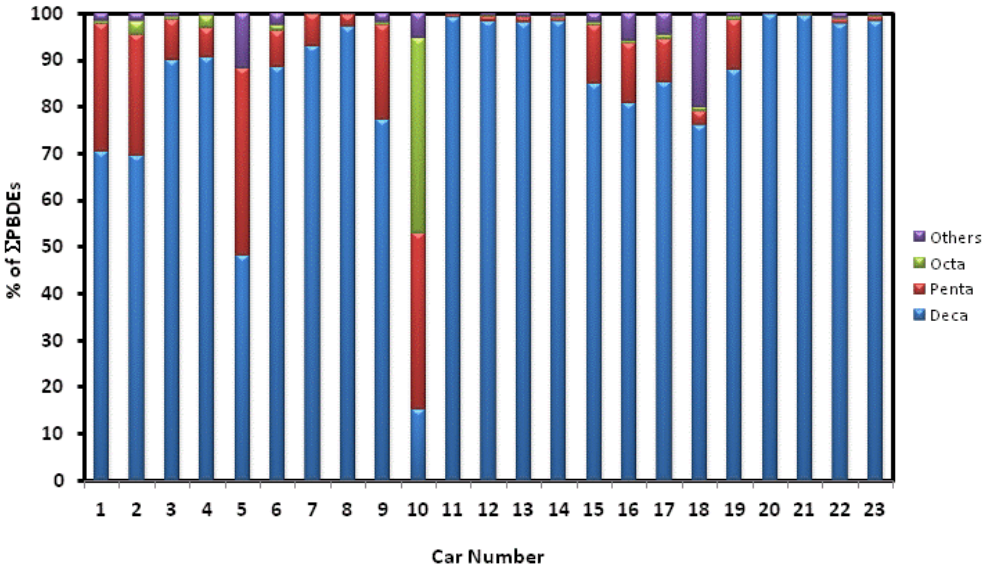

Figure 1. Contribution of various commercial mixtures to the ΣPBDE concentration measured in cars in Kuwait. % deca =100 × [BDEs(207+208+206+209)/ Σ_{17}PBDEs]; (% octa =100 × [BDEs(183+190)/Σ_{17}PBDEs], % penta =100 × [BDEs(47+99+100+154+153) / Σ_{17}PBDEs], and % Others = 100 BDEs(17+28+71+66+85+138)/ Σ_{17}PBDEs]

PBDEs were manufactured at three degrees of bromination (penta-, octa-, and deca- mixtures). The dust data was dominated by the deca formulation contributing 84.5% of the ΣPBDEs measured (median, 90%, range 15-99 %). In 70% of the cars investigated the contribution of deca formulation exceeded 85% of the ΣPBDEs measured. This was followed in decreasing order of magnitude by penta technical formulation with 10 % of the measured PBDEs (median, 6.9 %, range 0 – 40%) and the Octa formulation accounting for just 2.4% of the ΣPBDEs. There were two notable exceptions to these general observations. The most significant departure to the general trend in this study was observed in a 2006 Nissan Altima manufactured in Japan (Car 10) for which the octa-BDE formulation was the dominant mixture contributing 41.6% of the ΣPBDEs followed by the penta (37.8%) with the deca formulation contributing the least (15%). The second departure from the trend was observed for a 1994 Toyota Corolla manufactured in Japan (vehicle number 5) in which the deca- and penta-formulations (48% and 40% respectively) contributed similar proportions.

The findings of this study are similar to those reported in other studies. Gearhart and Posselt *(6)*, for example, reported that deca-BDE was the dominant PBDEs formulation in car interiors and was five times higher than its contribution in dust from homes and offices. Similar technical mixtures have also been reported by Cunha et al., *(9)* although Lagalante et al. *(13)*, found the penta-BDE formulation as the dominant formulation in automobiles at a car dealership in the United States. The differences in the proportions of technical mixtures in each of these studies may be due, in part to the type(s) and quantities of each flame retardant used by the manufacturers. An assessment of the proportion of various technical mixtures present in vehicles of different manufacturers over time is presented in Fig. 2. Although caution is to be exercised in the interpretation of the results in this study because of the limitations of the sample size, it can be seen that there is a trend towards the use of deca technical mixture by all manufacturers and a phasing out of the penta and octa mixtures. This trend is more explicitly observed for Toyota and Nissan vehicles which shows a gradual phase out of the penta technical mixture since the mid 1990s. These observations would need to be examined further before any firm conclusions can be reached on the practices of various companies on their use of flame retardants in the manufacture of vehicles as other co-founding factors can influence the concentrations in dust and because of the small sample size in this study. Following a recent report of PBDEs in 133 randomly selected cars from 11 leading car manufacturers by the Ecology Center, a non-profit organization in the United States, the Japanese Automobile Manufacturers Association (JAMA) announced guidelines for a voluntary

reduction of 13 volatile organic chemicals, including PBDEs in their products. The data in Figure 3 appears to suggest that the manufacturers have indeed begun to implement these changes.

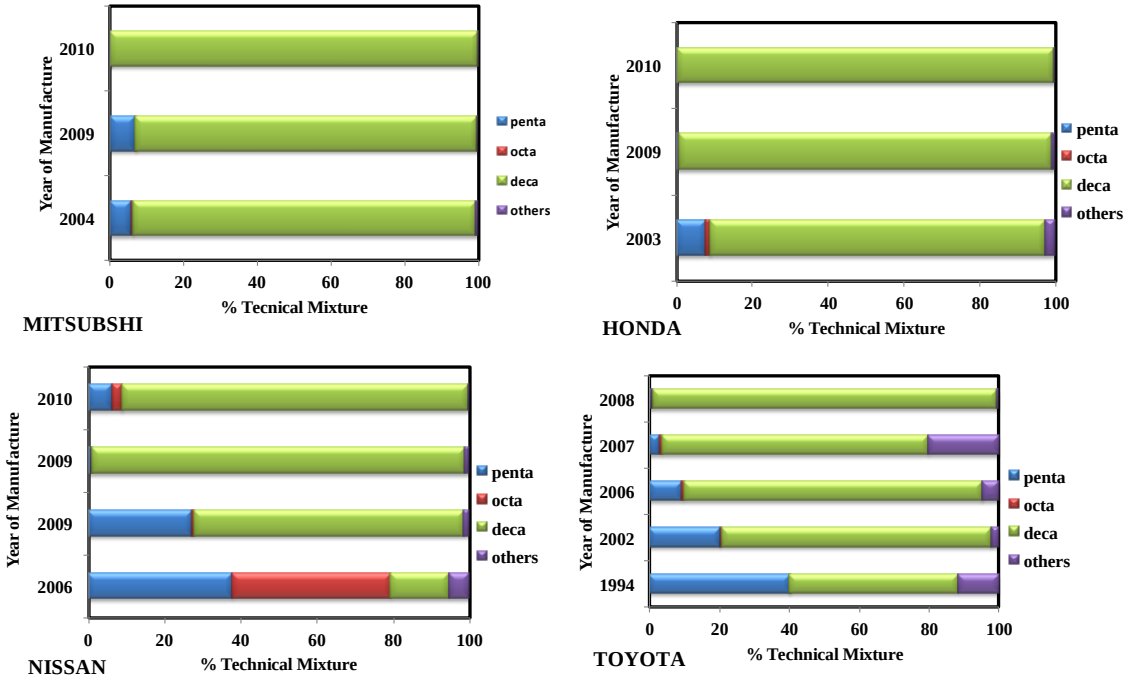

Figure 2. Changes in proportions of commercial PBDE technical mixtures in Japanese cars as a function of year of manufacure

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