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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 $\mu\text{g/g}$, and were higher in the summer than in the winter (average of 10.2 and 5.3 $\mu\text{g/g}$, 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 $10^{-2}/\text{min}$. 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. © 2017 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

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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 octa-

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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 ultraviolet (UV-vis) 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 Σ PBDE (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 (54–30000)	2006	~97	Thuresson et al., 2012
UK ^b	28, 47, 49, 66, 99, 100, 153, 154, 183, 196, 197, 203, 209	340000 (140–2600000)	July 2006–June 2007	~100	Harrad et al., 2008
USA	28, 47, 99, 100, 153, 154, 183, 209	276800 (5237–3571961)	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 (193–22955)	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	30337 (912–345540)	–	~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 (20–33728)	June–July, 2009	~84	Kalachova et al., 2012
Kuwait	28, 47, 66, 85, 99, 100, 138, 153, 154, 183, 208, 207, 206, 209	2065 (68–17200)	April 2011	~89	Gevao et al., 2016
Egypt	17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 209	6943 (171–37440)	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	14951 (70–65874)	September–October, 2014	~67	Harrad et al., 2016
Israel	47, 99, 209	Summer: 10211 (3290–28284) Winter: 5333 (943–21619)	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 \times 30 cm).

few studies examined debromination of BDE-209 adsorbed on solid substrate (Lagalante et al., 2011; Söderström et al., 2004; Stapleton and Dodder, 2008), and to the best of our knowledge no quantitative data are available on photolysis of particle-bound lower-brominated PBDEs (in particular, BDE-47, BDE-99). Since PBDE photolysis rates highly depend on the irradiation nature (e.g., intensity and wavelength spectra) and on the matrix on which the PBDE are adsorbed, simulating in-vehicle PBDE degradation using the reported rate constants for dissolved PBDEs is problematic.

High concentrations of highly brominated particulate PBDEs (e.g., BDE-209, BDE-206, BDE-183) in the winter, and high gaseous-phase concentrations of the more volatile PBDEs (e.g., BDE-28, BDE-47 and BDE-99) in the hot season have been reported in vehicles (Li et al., 2009). The higher summer concentrations of the lighter PBDEs were attributed to enhanced leaching from the vehicle interior due to the higher ambient temperatures. In warm and sunny regions, like the Middle East and North Africa, vehicles parked in the sun are exposed to high solar radiation and can heat up to above 70°C. Hence, people living in such regions may be exposed to high in-vehicle dust-bound concentrations of PBDEs due to both thermally enhanced leaching of PBDEs from the vehicle interior and insolation enhanced photo-debromination of the highly polybrominated congeners. This study tests this hypothesis by examining the concentration of three major PBDEs (BDE-47, BDE-99 and BDE-209) in car dust under varying Mediterranean climate conditions.

1. Material and methods

1.1. Chemicals

Analytical standards of three common PBDEs: BDE-209 (deca-BDE), BDE-99 and BDE-47 (major congeners of penta-BDE and tetra-BDE, respectively) were used (Cambridge isotope laboratory, purity level of 98%–99%).

1.2. Study area

All the cars sampled in this study were from the Haifa area, which is located in northern Israel along the eastern Mediterranean coast. The Mediterranean climate in this area is characterized by hot and dry summers and cool and rainy winters. The rainy season extends from October to March, and rainfall peaks in December through February. Average ambient temperature and insolation during our summer/winter campaigns were 26.4/14.3°C and 630/362 W/m², respectively.

1.3. Sampling

Two major sampling campaigns were conducted, in which dust from the upholstery of 11–16 cars (Table 2) collected 3–4 months after the vehicles were cleaned. Specifically, vehicle cleaning was done at the beginning of each campaign at the same commercial car wash business throughout the study. The cars were normally used by their owners throughout the study period, but during the cleaning and throughout the study period no odorant/freshening spray was applied in the vehicles interior. Sampling of car dust that accumulated

during summer was done in early October, 2014. Sampling of car dust that accumulated during winter took place in early April, 2015. An intermediate shorter autumn sampling was also performed (Table 2). Dust collection was performed by attaching pre-weighed dried (for overnight at 105°C) glass microfiber filters (GF/A, Whatman Inc.) to the inlet of a vacuum cleaner hose (700 W, Prusman, Israel) using a stainless steel filter holder. Dust was collected only from the cars seats, since a preliminary sampling revealed that dust accumulation over the relevant time period of 2–3 months occurred mostly on these rough surfaces (on average, about 30 mg dust were collected from smooth dashboard areas compared to about 500 mg dust from the upholstery). As a result, PBDEs detected in the dashboard dust were below the level of quantification. Used filters were stored at –20°C until analysis, with the weighing done at room temperature after acclimatization.

1.4. Analytical methods

Filters extraction was carried out by sonication for 30 min at room temperature using 20 mL of hexane:dimethylchloride (1:1 vol.%) mixture as the extraction solvent. The extraction process was repeated twice to enhance recovery. The extract was then concentrated to 1 mL using a TurboVap II system (TurboVap II, Caliper Life Sciences, USA). Prior to chemical analysis, extracts were centrifuge at 4500 r/min to remove any dust residues. Analysis was done using gas chromatograph (GC) (CP-3800, Varian, USA) equipped with electron capture detector (ECD) and a 15 m TG SQC capillary column (15 m × 0.25 mm × 0.25 μm). The oven temperature was held at 200°C for 2 min and then increased to 300°C at a rate of 20°C/min, where it was held for 17 min. The injector temperature was 200°C. PBDEs concentrations were determined based on peak area in the chromatogram using external calibration curves obtained with analytical standards of each compound.

1.5. Quality assurance and quality control

The linearity of the signal for all three BDEs gave R² of 0.966–0.999 for concentrations that ranged between 0.1–6 mg/L. The limits of detection (LOD) of the target analytes were about 5 μg/L (i.e., 5 ng in the dust samples). The presence of the target PBDEs in dust samples was confirmed by comparing retention times and peak areas relative to the calibration signals of the analytical grade analogs. In each field campaign, filter blanks (unexposed GF/A filters) were also analyzed and yielded BDE concentrations below the LOD. Recovery was assessed using GF/A filters spiked with different concentrations (0.2, 1.5, and 3 μg/mL) of the three PBDEs standards. Based on 6 repetitions, the average recoveries were 54% ± 7% for BDE-47, 47% ± 2% for BDE-99 and 57% ± 9% for BDE-209. PBDE concentrations in extracted dust samples were normalized to the average recovery obtained for each PBDE.

1.6. Debromination

Debromination experiments were carried outdoors under clear sky conditions, to study surface loss of adsorbed PBDEs.

Table 2 – Sampled vehicles in the different campaigns.

Car No.	Manufacturing country	Car model	Model year	Summer 2014 July–September	Autumn 2014 October–November	Winter 2014/2015 December–March
1	South Korea	Daewoo Matiz	2000	+		
2	South Korea	Kia Rio	2001		+	+
3	Germany	Volkswagen Bora	2001		+	+
4	South Korea	Hyundai Getz	2004		+	+
5	Japan	Suzuki Liana	2005	+	+	+
6	Turkey	Renault Megan	2006		+	+
7	Japan	Toyota Prius	2007	+	+	+
8	Turkey	Toyota Corolla	2007		+	+
9	Italy	Fiat Punto	2008	+	+	+
10	Japan	Daihatsu Sirion	2008	+	+	+
11	South Korea	Kia Forte	2010	+	+	+
12	Czech Republic	Hyundai-i30CW	2011	+	+	+
13	South Korea	Chevrolet Spark	2011	+	+	+
14	South Korea	Kia Rio	2011	+	+	+
15	India	Nissan Micra	2011	+		
16	Japan	Suzuki Swift	2012		+	+
17	Japan	Toyota Prius	2013	+	+	+
18	UK	Nissan Versa	2014		+	+

Three sets of six replicate glass-fiber filters were spiked with 1.5 µg of each PBDE (i.e., 30 µL of 50 mg/L solution in ethanol). After solvent evaporation, the filters were placed in a covered Petri glass dish under direct sunlight. After prescribed exposure to solar radiation of 0, 4, 10, 24, 32, or 40 hr (with maximum of 8 hr per day, hence 40 hr of exposure was obtained over five consecutive days) the samples were extracted and analyzed as described above. In experiments that ran over multiple days, samples were stored at –20°C during the night and re-exposed to sunlight in the following day. Light absorption spectra ($\lambda = 220\text{--}800$ nm) of the three PBDE compounds (BDE-47, BDE-99, BDE-209) dissolved in dichloromethane were measured using UV spectrophotometer (GENESYS™ 10, Thermo Scientific, USA).

1.7. Chemical actinometry

Solar UV photon flux was measured during the photolysis experiments using chemical actinometry with 2-nitrobenzaldehyde (2NBZ) dissolved in distilled water. The 2NBZ solution was placed in a stirred jacket beaker covered with glass cover and aluminum foil with a 0.75 cm² hole at its top, and maintained at 20°C. Samples were taken 4–5 times per day and analyzed using high performance liquid chromatograph with a 150 mm × 4.6 mm C₁₈ reverse phase 5 mm column (Hypersyl gold) (230 solvent delivery, 410 autosampler, and 335 photo-diode array detector, Agilent, USA). Detection was done at 235 and 320 nm. The mobile phase was 60:40 (V/V) distilled water (18.2 M Ω) and acetonitrile, with flow rate of 1.0 mL/min.

Incidence actinic UV flux (I_0 , photons/(cm²·sec)) was calculated from the first-order degradation rate of 2NBZ as follows:

$$I_0(300\text{--}400\text{ nm}) = \frac{C \times k \times N_A \times V}{\Phi \times \alpha \times (1 - 10^{-\epsilon Cl})}, \quad (1)$$

where, C (0.33 mmol/L) is the initial concentration of 2NBZ, k (sec⁻¹) is the measured first-order decay rate constant of 2NBZ, N_A (molecules/mol) is Avogadro number, ϵ (202 L/(mol·cm)) is 2NBZ

weighted averaged molar absorption coefficient for 300–400 nm, Φ (0.41 molecules/photon; Galbavy et al., 2010) is its direct photolysis quantum yield, α (cm²) is the area of solution exposed to sunlight, and 'l' and 'V' are the optical path-length and volume of the actinometry solution, respectively.

2. Results and discussion

Total PBDE concentrations (i.e., sum of BDE-47, BDE-99 and BDE-209) in car dust during the three sampling campaigns (July–September 2014; October–November 2014; December–April 2014/2015) are presented in Fig. 1. Analysis of variance (ANOVA) revealed that the summer total PBDE concentrations were significantly higher ($p < 0.05$) while the difference between the autumn and the winter PBDE concentrations were not substantial. The seasonal trends are clearer when only the vehicles that participated in all three sampling campaigns (Group A, $n = 9$) are analyzed (Fig. 1). The higher PBDE content in dust during the summer is in line with the higher prevailing temperatures in this season (the average temperature during the summer campaign was 26.5°C vs. 18.5°C and 14.3°C in the autumn and winter campaigns, respectively), which is expected to enhance the leaching of flame retardants from upholstery. It is noteworthy that in the East Mediterranean, transitional seasons are rather short and highly varying from year to year and from day to day in both temperature and cloudiness (i.e., solar irradiation). Hence, the uncertainty in the autumn's results is likely to be higher.

Overall, the average of the total PBDE concentration (10.2, 6.3, and 5.3 µg/g_{dust} for summer, autumn and winter, respectively) is similar to that reported previously in countries that are characterized by a comparable climate: 2.1 µg/g_{dust} in Kuwait (April, 2011) (Gevao et al., 2016), 6.9 µg/g_{dust} in Egypt (Hassan and Shoeib, 2015) and 15.0 µg/g_{dust} in Nigeria (September–October, 2014) (Harrad et al., 2016). Olukunle et al. (2015) reported lower levels in Nigeria (0.72 µg/g_{dust}; April–June, 2014), which could result from

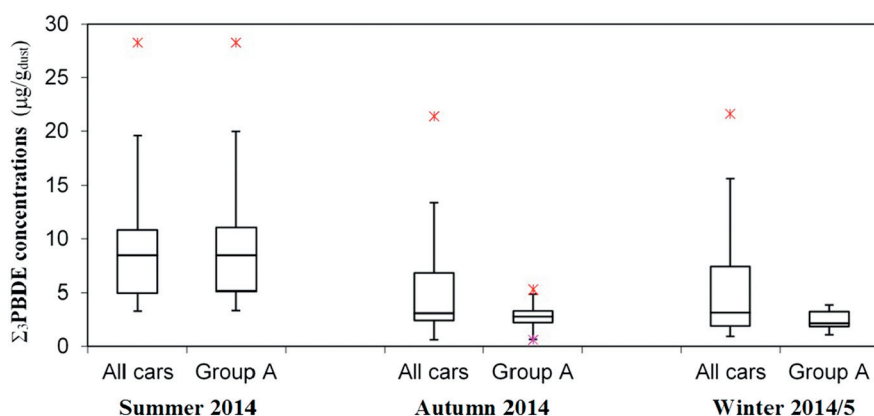


Fig. 1 – Seasonal variation of the total concentrations of the three dust-bound polybrominated diphenyl ethers (Σ_3 PBDEs) congeners in car. Box lower and upper borders represent the 25th and 75th percentiles of the observed concentrations, respectively (i.e., the inter quartile range (IQR)). The inner line is the median. The upper whisker represents the smaller value between the 75th percentile + 1.5 \times IQR and the maximum observation. The lower whisker represents the larger value between the 25th percentile – 1.5 \times IQR and the minimum observation. The red asterisk represents the maximum observation outside this range (i.e., the extreme outlier). All cars: summer $n = 11$, autumn and winter $n = 16$; Group A: only vehicles that participated in the three campaigns, $n = 9$. There are no significant differences among the paired columns for all seasons.

the weaker vacuum cleaner they used for dust sampling (90 W Hoover, HSV40) (Olukunle et al., 2015). No clear trend in total PBDEs concentrations was observed with regard to the vehicle model year or manufacturing country (Appendix A. Figs. S1 and S2).

However, despite the similarity in the total PBDE concentrations among the above studies, there is a clear difference in congener-specific concentrations. Namely, while BDE-209 concentrations in car dust collected in Israel in the summer were very low (Appendix A Figs. S1 and S2), in the other studies it was the major component. This discrepancy could be attributed to the fact that in the present study dust was collected only from car seats and not from vehicle interior plastic surfaces. Although our measurements showed that considerably less dust accumulates on the smooth dashboard than in the upholstery (see Section 1), dashboard dust may contain larger fraction of BDE-209 since deca-BDE has been mainly used in plastics whereas penta-BDEs were added to polyurethane foam PUF (EPA, 2010). Hence, most of the BDE-209 detected in the present study likely originated from inner-vehicle plastic furnishings (e.g., dashboard, knobs, etc.) and accumulated as dust-bound PBDE on the upholstery. It is noteworthy that BDE-209 has been detected also in cars that were manufactured in Europe (UK, Italy, Germany, and Czech Republic) after the 2008 EU ban on the use of deca-BDE, which may suggest that the vehicles' interior fittings have been manufactured in countries that allowed using deca-BDE.

A clear difference in the distribution of the three PBDE congeners is seen between the summer and winter campaigns (Fig. 2). BDE-209 levels were higher in the winter than in the summer in both Group A cars (those that participated in all the campaigns) and when analyzing all the sampled cars ($p < 0.02$). BDE-99 revealed an opposite seasonal trend, with significantly higher concentrations in the summer than in the winter ($p < 0.04$). Seasonal variability of BDE-47 was also observed but the patterns were non-significant ($p > 0.18$) in

spite of the large seasonal variability (Fig. 2). In particular, while BDE-47 was the major component in the winter (and the fall) in all the sampled vehicles, its fraction out of the total three PBDE concentration was >0.5 in only 45% of the vehicles in the summer.

These observations suggest that apart from temperature-driven leaching, photo-debromination due to exposure solar insolation (Söderström et al., 2004; Stapleton and Dodder, 2008) and partitioning to the gas phase probably affected the summer in-vehicle PBDE concentrations. The seasonal variation of the concentrations of the three congeners could represent faster debromination than leaching rates of BDE-209 in the summer, and higher leaching than debromination rates of BDE-209 in the winter. For the penta-BDE and tetra-BDEs (i.e., BDE-99 and BDE-47, respectively), the effect of photo-debromination is more complex as they are both generated by debromination of different highly brominated congeners and, at the same time, are also subjected to photo-debromination themselves. Furthermore, due to the higher volatility of lower brominated BDEs, seasonal variations in their partitioning between dust and gas phase may be important. For example, high summer BDE-47 concentrations could be expected due to enhanced leaching and photo-debromination of BDE-209, BDE-99, and other highly brominated congeners (Lagalante et al., 2011). The high variability in the summer BDE-47 concentrations (Fig. 2) may represent, in part, the partitioning of BDE-47 into the gas phase (which unfortunately was not measured in this study). Such an equilibrium between leaching, evaporation and debromination, is likely taking place in vehicles that are exposed to high solar radiation (e.g., parked in the summer sun). The latter affects the seasonal trend of the total dust-bound PBDE as well as the relative distribution of different congeners. To study in-vehicle photo-debromination of PBDEs, photolysis of the three PBDEs was investigated while they were deposited on glass-fiber filters and exposed to solar radiation through glass interface, i.e., simulating in-vehicle conditions.

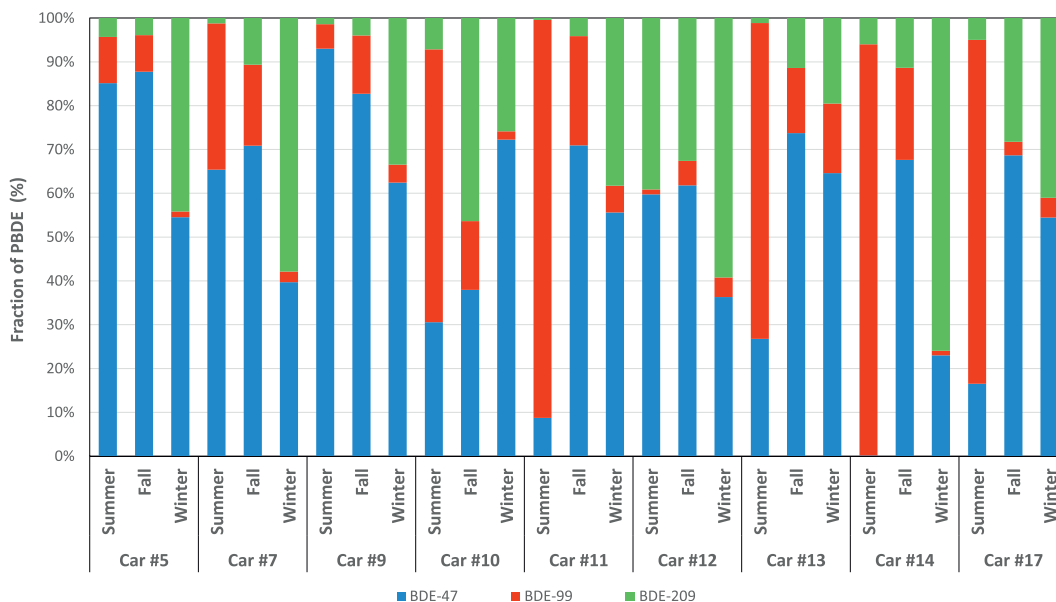


Fig. 2 – Seasonal distribution of the three dust-bound PBDE congeners in Group A cars (see Table 2 for vehicle-specific information). The cars are ordered according to their manufacturing year from the oldest (#5) to the newest (#17).

2.1. Debromination

The UV-vis absorbance spectra of BDE-47, BDE-99 and BDE-209 in DCM (Appendix A Fig. S3) shows that most of the absorption occurs in the UV-C wavebands, with a maximum absorption at ~230 nm (Lagalante et al., 2011 obtained a similar spectral signature for PBDEs dissolved in hexane). However, UV-C solar radiation does not reach the lower atmosphere, since it is completely absorbed by the stratospheric ozone layer. Moreover, while both UV-B (290–315 nm) and UV-A (315–400 nm) may be relevant for outdoor photolysis of PBDEs, only the latter can penetrate the vehicle windows and induce in-vehicle PBDE debromination. Hence, to study PBDE debromination under irradiation conditions similar to those found in vehicle cabins, BDE-doped glass fiber filters were placed in closed glass petri dishes and exposed for up to 40 hr to solar radiation. Concentrations of all three BDEs decreased, following first order reaction kinetics with rate constants on the

order of 10^{-2} min^{-1} (Table 3), with BDE-99 presenting a slightly higher degradation rate. As seen in Table 3, data on the kinetics of PBDE photo-debromination is very limited. The debromination rate of BDE-209 on a porous glass filter (for solar UV irradiation of 16 W/m^2) is similar to that reported by Söderström et al. (2004) for debromination of BDE-209 attached to sand and sediment (for solar UV irradiation of 23 W/m^2), but is larger by one order of magnitude than that reported by Stapleton and Dodder (2008) for BDE-209 sorbed on complex matrix of natural dust. We are unaware of any previous studies that measured photodegradation rates of BDE-99 and BDE-47 sorbed on solid surfaces.

In agreement with Fang et al. (2008) and Lagalante et al. (2011), photo-degradation of higher-brominated PBDE resulted in the formation of lower-brominated congeners. Specifically, the buildup of BDE-47 concentrations formed following BDE-99 debromination ceased after ~10–12 hr of irradiation (Fig. 3), probably due to its own debromination into lower-brominated

Table 3 – Debromination rates of the three investigated PBDEs.

BDE-47 (hr ⁻¹)	BDE-99 (hr ⁻¹)	BDE-209 (hr ⁻¹)	Note	Solar flux	Source
0.065 ± 0.02	0.083 ± 0.011	0.035 ± 0.006	Glass filter in glass Petri dish	16 W/m ² (300–400 nm)	This study
–	–	0.0015 ± 0.0001	Adsorbed on sodium sulfate	545 W/m ² (340 nm)	Lagalante et al., 2011
0.3	1.83	–	in hexane, mercury lamp (253.7 nm)	–	Fang et al., 2008
–	0.41–0.536	–	mercury lamp + nonionic surfactants	0.11 W/(L-sec) (mainly 253.7 nm)	Li et al., 2009
–	–	4.038–6.0	In hexane, sunlight	714–896 W/m ² (UV-vis)	Shih and Wang, 2009
–	–	0.0017–0.0023	Spiked natural-dust, sunlight	61–929 W/m ² (average 545 W/m ²)	Stapleton and Dodder, 2008
–	–	0.019–0.053	Sand, sunlight	(UV-vis)	
–	–	0.009–0.023	Sediment, sunlight	23 W/m ² (UV only)	Söderström et al., 2004

UV-vis: ultraviolet-visible.

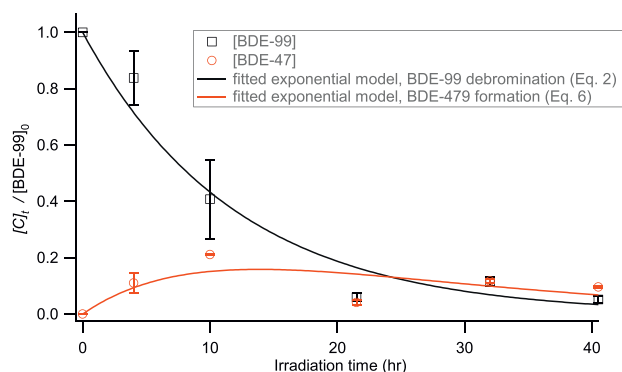


Fig. 3 – Photodegradation of BDE-99, spiked on glass fiber filters, and its photoproduct BDE-47 as a function of the exposure time to UV-A solar radiation. All concentrations are normalized to initial BDE-99 concentration ($[BDE-99]_0$). $[C]_t$ represents concentration at time t .

congeners. Similarly, debromination of BDE-209 results in the formation of BDE-99, which further debrominate and formed BDE-47 and probably also other unmeasured congeners (Fig. 4). Peak BDE-99 concentrations were obtained after ~15 hr of irradiation. The limited buildup of BDE-99 concentrations during BDE-209 debromination probably represents its fast degradation (Table 3). Furthermore, the consistently higher BDE-47 and lower BDE-99 concentrations during the photolysis of BDE-209 also represents the relatively higher BDE-99 photodegradation rates. Similar (yet weaker) trends were observed also when the BDEs were deposited as dry films on the inner wall of sealed glass vials (e.g., Appendix A Fig. S4).

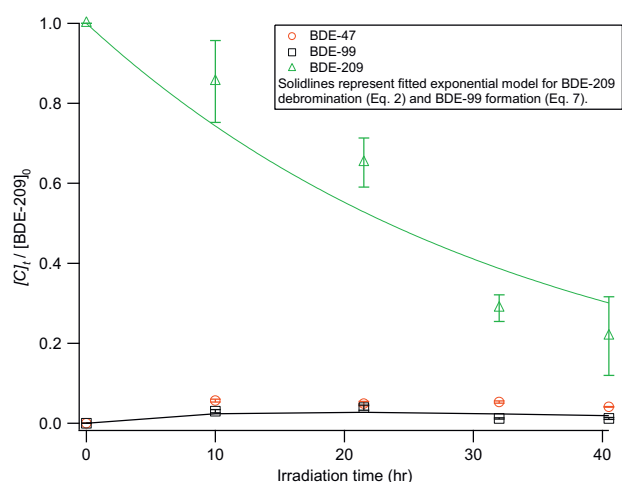


Fig. 4 – Photodegradation of BDE-209, spiked on glass fiber filters, and of its photoproducts BDE-99 and BDE-47, as a function of the exposure time to UV-A solar radiation. All concentrations are normalized to $[BDE-209]_0$. BDE-47 is formed due to debromination of BDE-99 and thus the model that describes its concentrations is more complex and is not provided.

The decay rates were estimated by fitting to the experimental debromination data a first-order kinetic model:

$$[D] = [D]_0 \times \exp(-k_d t), \quad (2)$$

where $[D]$ is the concentration of the debrominating (i.e., parent) PBDE at time t , $[D]_0$ is its initial concentration, and k_d is the debromination rate constant of the debrominating PBDE (D). The temporal evolution of the concentration of the photodegradation products (P) can be expressed by:

$$\frac{d[P]}{dt} = f k_d [D] - k_p [P], \quad (3)$$

where $[P]$ is the concentration of the formed PBDE, f is the fraction of D that degraded to P (i.e., the formation yield of P), and k_p is the degradation rate constant of P . Substituting Eq. (2) in Eq. (3) gives:

$$\frac{d[P]}{dt} = f k_d [D]_0 \times \exp(-k_d t) - k_p [P]. \quad (4)$$

Integration of Eq. (4) provides the concentration of P as a function of the exposure time to solar UV-A radiation:

$$[P] = \frac{f k_d [D]_0}{k_p - k_d} \times (\exp(-k_d t) - \exp(-k_p t)) + [P]_0 \times \exp(-k_p t), \quad (5)$$

where $[P]_0$ is the initial concentration of the formed product. Since $[P]_0$ was zero in our experimental setup, the right term in Eq. (5) cancels.

The concentrations of BDE-47 and BDE-99, which result from debromination of BDE-99 and BDE-209, respectively, can be fitted by Eq. (5) using the rate constants reported in Table 3. Thus, BDE-47 concentrations that result from debromination of BDE-99 can be calculated by:

$$[BDE-47] = \frac{f k_{99} [BDE-99]_0}{k_{47} - k_{99}} \times (\exp(-k_{99} t) - \exp(-k_{47} t)), \quad (6)$$

and BDE-99 concentrations due to debromination of BDE-209 can be estimated by:

$$[BDE-99] = \frac{f k_{209} [BDE-209]_0}{k_{99} - k_{209}} \times (\exp(-k_{209} t) - \exp(-k_{99} t)). \quad (7)$$

It is noteworthy that the formation yield, f , is specific for each product of debromination of a parent PBDE under given conditions. As f is unknown, it was estimated by fitting the estimated concentrations (Eq. (5)) to the experimental data. The estimated concentrations of the two photoproducts, Eqs. (6)–(7), are shown as solid line in Figs. 3 and 4. As can be seen, the fitted model predicts very well the concentrations of both products using a formation yield of $f = 39\% \pm 1\%$ for BDE-47 formation as a result of BDE-99 debromination, and $f = 12\% \pm 1\%$ for BDE-99 formation as a result of BDE-209 debromination. Considering the multiple pathways possible for debromination of BDE-209 (Lagalante et al., 2011), the low value of f obtained for the formation of BDE-99 from debromination of BDE-209 seems reasonable.

3. Conclusions

Due to the physicochemical properties of PBDEs, they tend to go through a dynamic surface–air exchange as a result of seasonal and diurnal temperature and insolation variations. Such processes are known to result in long-range atmospheric transport through a series of deposition/volatilization hops, *i.e.*, the “grasshopper” effect, but here we show that these processes also have a local impact on the seasonality of in-vehicle PBDE concentrations.

Despite recent regulations regarding the phasing out of PBDEs, the three BDEs were detected in almost any dust sample collected from the upholstery of the 16 examined cars. We did not find any clear effect of the vehicle’s model year or manufacturing country on the in-vehicle PBDE concentrations, yet significant seasonal variability in dust-bound total PBDE and in the congener-specific distribution was observed. Lower levels of BDE-209 and higher levels of BDE-99 were observed during the summer, with BDE-47 showing mixed results. Among the three PBDE congeners studied, BDE-99 was the dominant congener in the summer whereas BDE-47 was the dominant congener in the winter and the fall. These patterns likely result from a complicated co-occurring processes of PBDEs leaching from the vehicle interior fixtures, gas–particle partitioning, and photodebromination, with all processes affected by the ambient conditions (mainly temperature and solar irradiance). Our results support the assumption that debromination and volatilization can be very important processes in vehicles, especially when exposure to the high temperatures and intense solar radiation that characterize the Israeli/Mediterranean summer. In the winter, the lower temperatures result in slower PBDEs leaching and evaporation, which leads to lower total dust-bound PBDE levels, higher (than in the summer) concentrations of highly brominated congeners (*e.g.*, BDE-209), and higher concentrations of volatile congeners (*e.g.*, BDE-47) that tend to remain in the particulate phase during winter.

Controlled debromination experiments showed that the three PBDEs debrominate to lower-brominated congeners by photolysis. Concentrations of both the parent debrominating compounds and the photoproducts were fitted by a first-order reaction kinetic model. Using debromination rate constants derived from the photolysis experiments, the model fitted reasonably well the data and revealed (by mean of tuning the model) the formation yield of the debromination products in the examined pathways. Comparisons of the kinetic data from the current study to previously reported rate constants is difficult due to variability in the irradiation intensity, wavelength spectra, and the matrices in which the PBDE resided in the different studies. Overall, the debromination rate constant of BDE-209 doped on glass-fiber filter was of the same order of magnitude as those reported by Söderström *et al.* (2004) for debromination of BDE-209 attached to sand and sediment. To the best of our knowledge, the present study is the first to report photolysis rate constants for sorbed BDE-47 and BDE-99. In general, we showed that local climatic conditions can affect the in-vehicle concentrations of- and exposure to dust-bound PBDEs, with higher exposure to total dust-bound PBDEs in the summer.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jes.2017.11.022>.

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