Environ Sci Pollut Res (2009) 16:312–321
DOI 10.1007/s11356-009-0150-4

AREA 6.4 • PERSISTENT CHEMICALS • RESEARCH ARTICLE

Identification and quantification of products formed via photolysis of decabromodiphenyl ether

Anna Christiansson · Johan Eriksson · Daniel Teclechiel · Åke Bergman

Received: 9 April 2008 / Accepted: 21 March 2009 / Published online: 10 April 2009

Abstract

Background, aim, and scope Decabromodiphenyl ether (DecaBDE) is used as an additive flame retardant in polymers. It has become a ubiquitous environmental contaminant, particularly abundant in abiotic media, such as sediments, air, and dust, and also present in wildlife and in humans. The main DecaBDE constituent, perbrominated diphenyl ether (BDE-209), is susceptible to transformations as observed in experimental work. This work is aimed at identifying and assessing the relative amounts of products formed after UV irradiation of BDE-209.

Materials and methods BDE-209, dissolved in tetrahydrofuran (THF), methanol, or combinations of methanol/water, was exposed to UV light for 100 or 200 min. Samples were analyzed by gas chromatography/mass spectrometry (electron ionization) for polybrominated diphenyl ethers (PBDEs), dibenzofurans (PBDFs), methoxylated PBDEs, and phenolic PBDE products.

Results The products formed were hexaBDEs to nonaBDEs, monoBDFs to pentaBDFs, and methoxylated tetraBDFs to pentaBDFs. The products found in the fraction containing halogenated phenols were assigned to be pentabromophenol, dihydroxytetrabromobenzene, dihydroxydibromodibenzofuran, dihydroxytribromodibenzofuran, and dihydroxytetrabromodibenzofuran. The PBDEs accounted for approximately 90% of the total amount of substances in each sample and the PBDFs for about 10%.

Discussion BDE-209 is a source of PBDEs primarily present in OctaBDEs but also to some extent in PentaBDEs, both being commercial products now banned within the EU and in several states within the USA. It is notable that OH-PBDFs have not been identified or indicated in any of the photolysis studies performed to date. Formation of OH-PBDFs, however, may occur as pure radical reactions in the atmosphere.

Conclusions Photolysis of decaBDE yields a wide span of products, from nonaBDEs to hydroxylated bromobenzenes. It is evident that irradiation of decaBDE in water and methanol yields OH-PBDFs and MeO-PBDFs, respectively. BDE-202 (2,2′,3,3′,5,5′,6,6′-octabromodiphenyl ether) is identified as a marker of BDE-209 photolysis.

Recommendations and perspectives BDE-209, the main constituent of DecaBDE, is primarily forming debrominated diphenyl ethers with higher persistence which are more bioaccumulative than the starting material when subjected to UV light. Hence, DecaBDE should be considered as a source of these PBDE congeners in the environment.

Keywords Chemical reactivity · Photolysis · Polybrominated dibenzofurans · PBDFs · Polybrominated diphenyl ethers · PBDEs · UV degradation

1 Background, aim, and scope

Polybrominated diphenyl ethers (PBDEs) have been a dominating type of brominated flame retardants (BFRs) during the last few decades (Alaee et al. 2003). The world production of the commercial perbrominated diphenyl ether, DecaBDE, reached 56,000 tons in 2003 (Andersson et al. 2006), while the lower brominated, PentaBDE and

---

Electronic supplementary material The online version of this article (doi:10.1007/s11356-009-0150-4) contains supplementary material, which is available to authorized users.

A. Christiansson · J. Eriksson · D. Teclechiel · Å. Bergman (✉)
Department of Environmental Chemistry, Stockholm University,
Svante Arrhenius väg 12,
106 91 Stockholm, Sweden
e-mail: ake.bergman@mk.su.se

OctaBDE, have been banned by the European Union (EU) (Cox and Efthymiou 2003) and their commercial production have been ceased in the U.S. (Great Lakes Flame Retardants 2005). The environmental occurrence of PBDEs is dominated by tetraBDEs—hexaBDEs as a primary consequence of PentaBDE uses and due to their unfavorable physicochemical characteristics (Law et al. 2003; Hites 2004; de Wit et al. 2006; Law et al. 2006). Both OctaBDE and DecaBDE products are discussed as potential sources of the lower brominated diphenyl ethers (He et al. 2006; Gaul et al. 2006).

BDE-209, making up as much as 92–98% of the PBDE congeners in DecaBDE (Alaee et al. 2003; La Guardia et al. 2006), is a significant contaminant in some river estuaries (Chen et al. 2007b), in sediments (Moon et al. 2007), and in air (ter Schure et al. 2004; Gouin et al. 2006). BDE-209 has been shown in rather high concentrations in window films (Butt et al. 2004) and in dust from homes (Wilford et al. 2005; Stapleton et al. 2005; Gevao et al. 2006; Karlsson et al. 2007; Tan et al. 2007). The compound is less frequently reported in biota but still found in high levels in terrestrial birds of prey (Lindberg et al. 2004; Chen et al. 2007a), and in variable concentrations in terrestrial mammals (de Wit et al. 2006; Voorspoels et al. 2006), but rarely in marine mammals (Verreault et al. 2005; Thomas et al. 2005).

The perbromination of BDE-209 makes it vulnerable to a range of chemical reactions, such as substitution, reduction, and photolysis (Eriksson et al. 2004b; Rahm et al. 2005; Ahn et al. 2006a; Li et al. 2007). The latter two reaction pathways are leading to, among other products being formed, lower brominated diphenyl ether congeners (Söderström et al. 2004; Ahn et al. 2006a; Ahn et al. 2006b; Li et al. 2007). Anaerobic reductive debromination of decaBDE has been shown in sediment (Parsons et al. 2004), sewage sludge (Gerecke et al. 2005) and by anaerobic bacteria (He et al. 2006).

The present study should be related to few previous studies on photolysis of DecaBDE and/or BDE-209 (Watanabe and Tatsukawa 1987; Ohta et al. 2001; Hua et al. 2003; Söderström et al. 2004; Bezares-Cruz et al. 2004; Palm et al. 2004; Eriksson et al. 2004b; Hagberg et al. 2006; Olsman et al. 2006; Ahn et al. 2006b). The first, performed in the late 1980s by Watanabe and Tatsukawa (Watanabe and Tatsukawa 1987), indicated the formation of debrominated diphenyl ethers. OctaBDEs down to triBDEs were reported as major products. Further, also monoBDFs to hexaBDFs were reported as products in their study as well as tetra- and pentabromobenzenes. A solvent mixture of hexane/benzene/acetone (8:1:1) was applied. Ohta et al. (2001) dissolved DecaBDE in toluene to detect a large number of lower brominated diphenyl ethers, mainly monoBDEs—nonaBDEs. DecaBDE dissolved in toluene or adsorbed to silica gel, sand, sediment or to soil and subjected to UV light reported similar transformations without matrix-related effects on the product profile (PBDEs and PBDFs) but with effects on BDE-209 degradation rate (Söderström et al. 2004). Similarly, it has been shown that sand particles coated with humic acid may decrease degradation rates of DecaBDE when irradiated with UV light (Hua et al. 2003). In contrast, Ahn et al. (2006b) showed increased photolytic transformation rates when decaBDE was adsorbed to clay minerals (montmorillonite and kaolinte). Palm et al. (2004) showed consecutive debromination of BDE-209 when subjected to UV light and adsorbed to silica in an aqueous suspension. Also, the formation of PBDFs was confirmed under their photolytic experiment. Another few studies showed similar products being formed from BDE-209 (Bezares-Cruz et al. 2004; Hagberg et al. 2006; Olsman et al. 2006). Degradation rates of 15 PBDE congeners, dissolved in 80% methanol exposed to UV light, were determined by Eriksson et al. (2004b) showing decreasing rates with decreased bromination degree of the diphenyl ethers. HexaBDEs to octaBDEs and diBDFs to pentaBDFs were shown. One product was also identified as a methoxylated tetraBDF.

Photolysis of decaBDE have accordingly been investigated in numerous different studies (Watanabe and Tatsukawa 1987; Ohta et al. 2001; Hua et al. 2003; Söderström et al. 2004; Bezares-Cruz et al. 2004; Palm et al. 2004; Eriksson et al. 2004b; Hagberg et al. 2006; Olsman et al. 2006; Ahn et al. 2006b), but there is still a gap of knowledge regarding structural identities of products being formed. Hitherto, the most extensive product information has been reported by Söderström et al. (2004) and by Bezares-Cruz et al. (2004), while other studies have only reported the general occurrence of PBDE and PBDF transformation products (Watanabe and Tatsukawa 1987; Ohta et al. 2001; Hua et al. 2003; Palm et al. 2004; Eriksson et al. 2004b; Hagberg et al. 2006; Olsman et al. 2006; Ahn et al. 2006b). The aim of this work was to identify and to assess the relative amounts of products formed after UV irradiation of BDE-209 dissolved in tetrahydrofuran, methanol–water, or methanol, and further, if possible, to identify markers of BDE-209 photolysis.

The present study is relying on methodology previously presented in detail by Eriksson et al. (2004a, b). DecaBDE, dissolved in different solvent mixtures, was exposed to UV light, and the products were identified and quantified using Gas chromatography-mass spectrometry (GC/MS).

2 Materials and methods

2.1 Instruments

GC/MS with electron ionization (EI) was performed by an ion trap GCQ Finnigan Mat instrument equipped with a fused silica capillary column, DB-5HT, 15 m×0.25 mm i.d., 0.1 µm film thickness, J&W Scientific (Folsom, USA). The temperature program was 80°C for 1 min, raised with 15°C min^{-1} to 300°C and finally increased by 2°C min^{-1} to 320°C. The injections were made in the splitless mode using an autosampler, the injector temperature was 220°C, and the injection volume was 1.0 µl. Helium was used as carrier gas. For identification of compounds formed from BDE-209, mass spectra were recorded at *m/z* 150–1000, between 5 and 24 min at an ion source temperature of 180°C, an electron energy of 70 eV, and a transferline temperature at 275°C. For quantification purposes, mass spectra were recorded at *m/z* 240–420, between 5.00 and 11.10 min, at *m/z* 470–650 between 11.10 and 17.20 min, at *m/z* 640–820 between 17.20 and 20.00 min, and at *m/z* 300–1000 between 20.00 and 22.00 min.

2.2 Chemicals

Authentic reference standards 2,7-diBDF, 2,3,8-triBDF, BDE-196, BDE-197, BDE-198, BDE-201, BDE-204, and BDE-205 were purchased from Campro Scientific (Veenendaal, The Netherlands) and 2,8-diBDF, 2,4,8-triBDF, 2,3,7,8-tetraBDF, 2,4,6,8-tetraBDF, 2,3,4,7,8-pentaBDF were purchased from Cambridge Isotope Laboratories (Andover, USA). BDE-153, BDE-154, BDE-155, BDE-169, BDE-181, BDE-183, BDE-194, BDE-202, BDE-203, BDE-206, BDE-207, BDE -208, and Cl-BDE-208 were synthesized in house as reported elsewhere (Marsh et al. 1999; Christiansson et al. 2006; Teclechiel et al. 2007). Decabromodiphenyl ether was purchased from Fluka Chemie AG (Buchs, Switzerland).

n-Hexane for pesticide residue analysis, and toluene analytical grade, were bought from Scharlau Chemie (Barcelona, Spain). *n*-Hexane, for gas chromatography and methanol, for high performance liquid chromatography (HPLC), were purchased from Merck KGaA, (Darmstadt, Germany). Tetrahydrofuran, for HPLC, was purchased from Acros Organics, (New Jersey, USA). Water for HPLC was bought from VWR International (Poole, England), hydrochloric acid from VWR International (Fontenary Sous Bois, France), ethanol 99.5% from Kemetyl AB (Haninge, Sweden), and potassium hydroxide from Eka Chemicals AB (Bohus, Sweden).

2.3 Experimental section

2.3.1 Method

All glass equipment used was carefully washed prior to the experimental work. A decaBDE stock solution of 2 mM was prepared by dissolving decaBDE (19.2 mg) in THF (10 mL) in a pyrex glass test tube.

The experimental procedure is based on the work previously described by Eriksson et al. (2004a, b).

One milliliter of the decaBDE stock solution was taken out and diluted to 2.0 L with the appropriate solvent as described in Table 1, giving a final solution of 1 µM. The experimental container was a cylindrical glass vessel with a UV-lamp (fluorescent tube TL 20 W/09N from Philips (Holland)) placed in the middle of the vessel (Eriksson et al. 2004a; Eriksson et al. 2004b). The experimental container was filled up (1.7 L) with the 1 µM decaBDE solution, and nitrogen was bubbled through the solution. The solution was illuminated for either 100 or 200 min, as described in Table 1. A portion of the solution (500 mL) was taken out into a measuring glass before being transferred to a round bottle. The measuring glass was rinsed with the respective solvent used (30–50 mL) and added to the round bottle. The solvent was evaporated to a residue of 5–10 mL under reduced pressure at room temperature. The residue was then transferred to a pyrex glass test tube. The round bottle was rinsed with the appropriate solvent used (5–10 mL) for the experiment and transferred to the test tube. The solvent was finally evaporated to dryness using a gentle stream of nitrogen at 40°C.

n-Hexane (4 mL) was added before analysis. Identification and quantification of products formed through UV-induced reactions of decaBDE were performed by GC/MS. The analyses were performed by applying authentic standard mixtures of PBDEs and PBDFs. Cl-BDE-208 and BDE-77 were used for comparing the relative retention times (Table 2). Identification was done by both comparing relative retention times and by comparison of mass fragmentation pattern. For the quantification, a portion of the sample (0.2 mL) was added to a vial spiked with Cl-BDE-208 (17.10 µg) and BDE-77 (1.56 µg). The unknown monoBDFs and the diBDFs were quantified using the response factor of 2,8-diBDF, the triBDFs

Table 1 Experimental conditions

Solvent	Time (min)	Sample	Concentration of decaBDE	Corresponding to *x* half-lives[a]
THF	100	I	1 µM	7
THF	100	Blank	–	
100% MeOH	100	II	1 µM	6
100%MeOH	100	Blank	–	
90% MeOH	100	III a	1 µM	
90% MeOH	200	III b	1 µM	
90% MeOH	200	Blank	–	
80% MeOH	100	IV a	1 µM	3
80% MeOH	200	IV b	1 µM	7
80% MeOH	200	Blank	–	
80% MeOH	–	Control	1 µM	

[a] Eriksson et al. (2004b)

Table 2 Relative retention times versus BDE-77 (3,3′,4,4′-tetrabromodiphenyl ether) for the PBDFs and against Cl-BDE-208 (4-chloro-2,2′,3,3′,4′,5,5′,6,6′-nonabromodiphenyl ether) for the PBDEs used as standards

RRT BDE-77	
2,8-Dibromidibenzofuran (2,8-diBDF)	0.764
2,4,8-Tribromodibenzofuran (2,4,8-triBDF)	0.913
2,3,8-Tribromodibenzofuran (2,3,8-triBDF)	0.928
2,4,6,8-Tetrabromodibenzofuran (2,4,6,8-tetraBDF)	1.040
2,3,7,8-Tetrabromodibenzofuran (2,3,7,8-tetraBDF)	1.085
2,3,4,7,8-Pentabromodibenzofuran (2,3,4,7,8-pentaBDF)	1.231
RRT Cl-BDE-208	
2,2′,4,4′,6,6′-Hexabromodiphenyl ether (BDE-155)	0.659
2,2′,4,4′,5,6′-Hexabromodiphenyl ether (BDE-154)	0.669
2,2′,4,4′,5,5′-Hexabromodiphenyl ether (BDE-153)	0.690
3,3′,4,4′,5,5′-Hexabromodiphenyl ether (BDE-169)	0.726
2,2′,3,4,4′,5,′6-Heptabromodiphenyl ether (BDE-183)	0.749
2,2′,3,4,4′,5,6-Heptabromodiphenyl ether (BDE-181)	0.778
2,2′,3,3′,5,5′,6,6′-Octabromodiphenyl ether (BDE-202)	0.806
2,2′,3,3′,4,5′,6,6′-Octabromodiphenyl ether (BDE-201)	0.810
2,2′,3,4,4′,5,6,6′-Octabromodiphenyl ether (BDE-204)	0.815
2,2′,3,3′,4,4′,6,6′-Octabromodiphenyl ether (BDE-197)	0.817
2,2′,3,3′,4,5,5′,6-Octabromodiphenyl ether (BDE-198)	0.823
2,2′,3,4,4′,5,5′,6-Octabromodiphenyl ether (BDE-203)	0.825
2,2′,3,3′,4,4′,5,6′-Octabromodiphenyl ether (BDE-196)	0.830
2,3,3′,4,4′,5,5′,6-Octabromodiphenyl ether (BDE-205)	0.842
2,2′,3,3′,4,4′,5,5′-Octabromodiphenyl ether (BDE-194)	0.856
2,2′,3,3′,4,5,5′6,6′-Nonabromodiphenyl ether (BDE-208)	0.905
2,2′,3,3′,4,4′,5,6,6′-Nonabromodiphenyl ether (BDE-207)	0.915
2,2′,3,3′,4,4′,5,5′,6-Nonabromodiphenyl ether (BDE-206)	0.936
2,2′,3,3′,4,4′,5,5′,6,6′-Decabromodiphenyl ether (BDE-209)	1.066

From GC/MS chromatogram recorded in the EI mode on a non-polar GC-column (DB-5HT, 15 m×0.25 mm i.d., 0.1 μm film thickness)

against 2,4,8-triBDF, the tetraBDFs and the MeO-tetraBDFs against 2,4,6,8-tetraBDF, the pentaBDFs and the MeO-pentaBDF against 2,3,4,7,8-pentaBDF. The unknown hexaBDEs were quantified relative to BDE-153 or BDE-154. The unknown heptaBDEs were quantified using the response factor of either BDE-183 or BDE-181. The octa-decaBDEs were all quantified relative to their respective authentic standard except for BDE-202 that was quantified by comparison to BDE-201.

2.3.2 Separation of neutral and phenolic PBDE products

Separation of phenolic and neutral compounds was done for the samples with water–methanol mixtures as follows. Potassium hydroxide in 50% ethanol (2 mL, 1 M) was added to the sample diluted in *n*-hexane (10 mL). After rocking and centrifugation, the organic phase was transferred to a new test tube. The alkaline solution was re-extracted with *n*-hexane (2×4 mL), and the organic phases, containing the neutral substances, were combined. The solvent was evaporated to dryness, and *n*-hexane (4 mL) was added.

The alkaline solution was acidified with hydrochloric acid (2 M, 2 mL) and extracted with 10% diethyl ether in *n*-hexane (2×4 mL). The organic phases, containing the phenolic compounds, were transferred to a new test tube, and the solvent was evaporated. The potential phenols dissolved in *n*-hexane (0.5 mL) were methylated by adding a solution of diazomethane in diethyl ether (0.5 ml). The samples were analyzed by GC/MS.

3 Results

The quantities of hexa- to nonabrominated diphenyl ethers, mono- to pentabrominated dibenzofurans, and methoxylated tetra- to pentabrominated dibenzofurans were estimated after UV irradiation of dissolved BDE-209. The percentage relative to the total amount in each sample for the PBDE, PBDF, and MeO-PBDF congeners formed in each experiment were calculated and are listed in Tables 3, 4, and 5 for the actual solvents and irradiation times applied. The product profiles of BDE-209 irradiated by UV light in THF and in 80% methanol, as determined by GC/MS, are shown in Fig. 1a, b, respectively. Acidic products were detected in a separate fraction of UV-irradiated decaBDE mixture when dissolved in diluted methanol. The product profile as determined by GC/MS is shown in Fig. 2. The major products were assigned to be pentabromophenol, dihydroxytetrabromobenzene, dihydroxydibromodibenzofuran, dihydroxytribromodibenzofuran, and dihydroxytetrabromodibenzofuran according to GC/MS. Mass spectra of the assigned products are shown in Fig. 3 in supplementary information.

Photolysis of BDE-209 is well known to lead to PBDE and PBDF congeners with variable number of bromines (Watanabe and Tatsukawa 1987; Ohta et al. 2001; Hua et al. 2003; Söderström et al. 2004; Bezares-Cruz et al. 2004; Palm et al. 2004; Eriksson et al. 2004b; Hagberg et al. 2006; Olsman et al. 2006; Ahn et al. 2006b), but little has been done in relation to their structural identities earlier. The photolysis of BDE-209 is fastest in THF, while considerably slower in diluted methanol (Eriksson et al. 2004b). Illumination for 200 min in 80% MeOH and 100 min in pure THF corresponds to almost seven half-lives for BDE-209 (Eriksson et al. 2004b). Since the reactions are consecutive, longer radiation times lead to increased relative amounts of heptaBDEs and octaBDEs and decreased amounts of nonaBDEs and decaBDE itself. This is also true for the PBDFs. The more highly

Table 3 Percentage of total amount of substances in each sample for the brominated diphenyl ethers

	Identified substances	RRT	THF 100min I	100% MeOH 100min II	90% MeOH 100min III a	90% MeOH 200min III b	80% MeOH 100min IV a	80% MeOH 200min IV b
Yield percent			104	105	65	33	54	42
HexaBDE		0.669	0.4					
HexaBDE	BDE-154	0.672	0.09			0.09		
HexaBDE		0.674	0.01					
HexaBDE		0.677	0.1					
HexaBDE		0.681	0.4					
HexaBDE	BDE-153	0.691	0.5	0.1		0.1		
HexaBDE		0.694	0.07			0.06		
HexaBDE		0.698	0.1					
HexaBDE		0.703	0.1					
HexaBDE		0.707	0.04					
HexaBDE		0.716	0.1					
Sum hexaBDE			1.9	0.13		0.29		
HeptaBDE		0.733	0.5					
HeptaBDE		0.739	0.5	0.1	0.08	0.3	0.05	0.2
HeptaBDE		0.745	10	3	1	7	0.6	4
HeptaBDE	BDE-183	0.749	12	5	2	9	0.9	6
HeptaBDE		0.754	0.2	0.1	0.08	0.4	0.03	0.2
HeptaBDE		0.760	0.2	0.05	0.02	0.2		0.1
HeptaBDE		0.764	0.6	0.08	0.04	0.3	0.03	0.2
HeptaBDE		0.773	1	0.4	0.2	1	0.1	0.5
HeptaBDE	BDE-181	0.780	0.6	0.2	0.08	0.4	0.03	0.3
HeptaBDE		0.784	0.5	0.2	0.08	0.5	0.03	0.3
Sum heptaBDE			26	9.3	3.6	20	1.9	6.0
OctaBDE	BDE-202	0.805	4	2	2	3	1	3
OctaBDE	BDE-201	0.810	10	7	5	10	4	9
OctaBDE	BDE-197, BDE-204	0.816	6	5	4	7	3	7
OctaBDE	BDE-198, BDE-203	0.825	17	13	10	19	7	18
OctaBDE	BDE-196	0.830	10	8	7	11	5	11
OctaBDE	BDE-205	0.843		0.2	0.1			0.2
OctaBDE	BDE-194	0.856		0.5	0.4	0.6	0.2	0.5
Sum octaBDE			46	36	28	50	21	48
NonaBDE	BDE-208	0.904	2	5	7	2	8	4
NonaBDE	BDE-207	0.913	2	9	12	3	14	6
NonaBDE	BDE-206	0.935	10	28	31	17	30	27
Sum nonaBDE			15	42	51	21	51	37
DecaBDE	BDE-209	1.065	0.34	2.8	8.7	1.6	15	2.6
Sum PBDEs			90	90	91	93	88	93

The yield is calculated as total amount of substance formed/start amount of decaBDE. Relative retention times (RRT) versus Cl-BDE-208

brominated PBDFs, like pentaBDFs, decreases on the benefit of less brominated ones, like di- and monoBDFs. It is well known that highly halogenated dibenzofurans are very photosensitive with high quantum yields and high absorption coefficients (Lenoir et al. 1991; Watanabe et al. 1994). It is therefore difficult to say whether the pentaBDFs are a product of the hexaBDEs or if they are products from hepta to nonaBDEs. It is in principal a possibility that BDE-206 can form an octabrominated BDF. MeO-tetraBDFs and MeO-pentaBDFs are formed in trace amounts and only when methanol is used as a solvent. When diluted methanol is used as a solvent, it is possible to also detect phenolic transformation products. Hence, photochemically induced reactions between methanol or water on

Table 4 Percentage of total amount of substances in each sample for the brominated dibenzofuranes

	Identified substances	RRT	THF 100 min I	100% MeOH 100 min II	90% MeOH 100 min III a	90% MeOH 200 min III b	80% MeOH 100 min IV a	80% MeOH 200 min IV b
MonoBDF		0.588	2	0.07				
MonoBDF		0.597	0.09					
Sum monoBDF			2.4	0.068				
DiBDF		0.749	0.01	0.04				
DiBDF		0.753	0.5	0.4		0.1		
DiBDF	2,8-DiBDF	0.765	3	2	0.1	0.4	0.1	
DiBDF		0.770	2	2	0.1	0.4	0.1	
Sum diBDF			6.1	4.3	0.24	0.94	0.20	
TriBDF		0.896	0.04					
TriBDF		0.899	0.09	0.4	0.5	0.7	0.5	0.4
TriBDF		0.904		0.03		0.1		
TriBDF		0.907	0.5	2	3	3	3	2
TriBDF		0.911				0.02		
TriBDF	2,4,8-TriBDF	0.914	0.6	1	2	2	3	2
TriBDF		0.930			0.02			
TriBDF		0.939			0.06			0.05
Sum triBDF			1.3	3.8	5.3	5.2	6.0	4.7
TetraBDF		1.029	0.05	0.4	0.8	0.2	1.4	0.6
TetraBDF	2,4,6,8-TetraBDF	1.039	0.2	0.5	1	0.2	2	0.6
TetraBDF		1.052	0.02	0.06	0.09		0.1	0.02
TetraBDF		1.056	0.03	0.03	0.03		0.03	
TetraBDF		1.065		0.2	0.4	0.001	0.6	0.1
Sum tetraBDF			0.25	1.1	2.3	0.37	4.3	1.3
PentaBDF		1.164		0.2	0.3	0.1	0.5	0.2
PentaBDF		1.189			0.1		0.4	0.1
PentaBDF		1.191		0.1	0.1	0.07		
PentaBDF		1.202		0.01	0.03		0.04	
Sum pentaBDF				0.28	0.5	0.19	0.94	0.31
Sum PBDFs			10	9.6	8.4	6.7	11	6.3

Relative retention times (RRT) versus BDE-77

one side and PBDFs or PBDEs on the other, are indicated. The formation of MeO-PBDFs under natural conditions is highly unlikely, while OH-PBDFs, pentabromophenol, and other polybrominated phenols are expected products in the environment. However, OH-PBDEs that have been reported in environmental samples (Marsh et al. 2004; Verreault et al. 2005; Malmvärn et al. 2005; Mas et al. 2007) were not indicated in this study.

The most abundant nonaBDEs is #206 (see Table 3 and Fig. 1), but also the other two isomers are formed. This is in accordance with previous observations (Söderström et al. 2004; Bezares-Cruz et al. 2004; Eriksson et al. 2004b; Ahn et al. 2006b). In microbial reductive debromination of decaBDE, it seems like BDE-206 are formed in minor amounts compared to BDE-207 and BDE-208 (Gerecke et al. 2005). A group of seven to nine octaBDEs are formed by UV light (see Table 3). The uncertainty is due to co-elution of the BDEs #197/#204 and #198/#203. BDE-202, a hitherto unknown compound in any of the commercial PBDE products, is detected and identified in the present study. A GC peak, most likely corresponding to BDE-202, can also be seen in other previous studies where BDE-209 has been subjected to UV light. Stapleton et al. found BDE-202 when decaBDE-spiked house dust was exposed to sunlight (Stapleton and Dodder 2008). Hence, the BDE-202 may be a marker for UV induced degradation of BDE-209 when analyzing environmental samples. BDE-202 is also formed via reductive debromination as shown by Konstantinov et al. (2007), and according to data from Gerecke et al. (2005), it seems likely that BDE-202 is also formed via anaerobic degradation of decaBDE. BDE-202 was also found in fish exposed to decaBDE (Stapleton et al. 2006) and in fish

Table 5 Percentage of total amount of substances in each sample for the methoxylated brominated dibenzofuranes formed in each experiment

Substance	RRT	100% MeOH 100min II	90% MeOH 100min III a	90% MeOH 200min III b	80% MeOH 100min IV a	80% MeOH 200min IV b
MeO-tetraBDF	1.120		0.001	0.001	0.001	0.005
MeO-tetraBDF	1.132	0.06	0.1	0.2	0.1	0.3
Sum MeO-tetraBDF		0.056	0.10	0.16	0.14	0.29
MeO-pentaBDF	1.251	0.07	0.05	0.2	0.03	0.1
Sum MeOpenta-BDF		0.068	0.049	0.18	0.028	0.12
Sum MeO-PBDFs		0.12	0.15	0.34	0.16	0.40

Relative retention times (RRT) versus BDE-77.

living downstream of a waste water treatment plant for a plastic goods factory (La Guardia et al. 2007). Interestingly, BDE-183 is the major debrominated product identified among the ten heptaBDE isomers indicated in this study. BDE-153, one of the more persistent PBDE congeners, was formed from BDE-209 as indicated herein. Even if as little as 10 ppm (0.01‰) of BDE-209 is transformed to BDE-153, hundreds of kilograms of this persistent hexaBDE is formed abiotically, since DecaBDE is produced in amounts above 56 million kg per year (Andersson et al. 2006). A similar calculation including heptaBDEs to nonaBDEs indicates photolysis of BDE-209 as a significant source thereof.

A large number of PBDFs, 23 or more, are formed under the experimental conditions applied in this study. This is approximately as many PBDFs as reported by Hagberg et al. (2006). The identified PBDF products were 2,4,6,8-tetraBDF, 2,4,8-triBDF, and 2,7-/2,8-diBDF (see Table 4), among which the latter were also identified in the study by

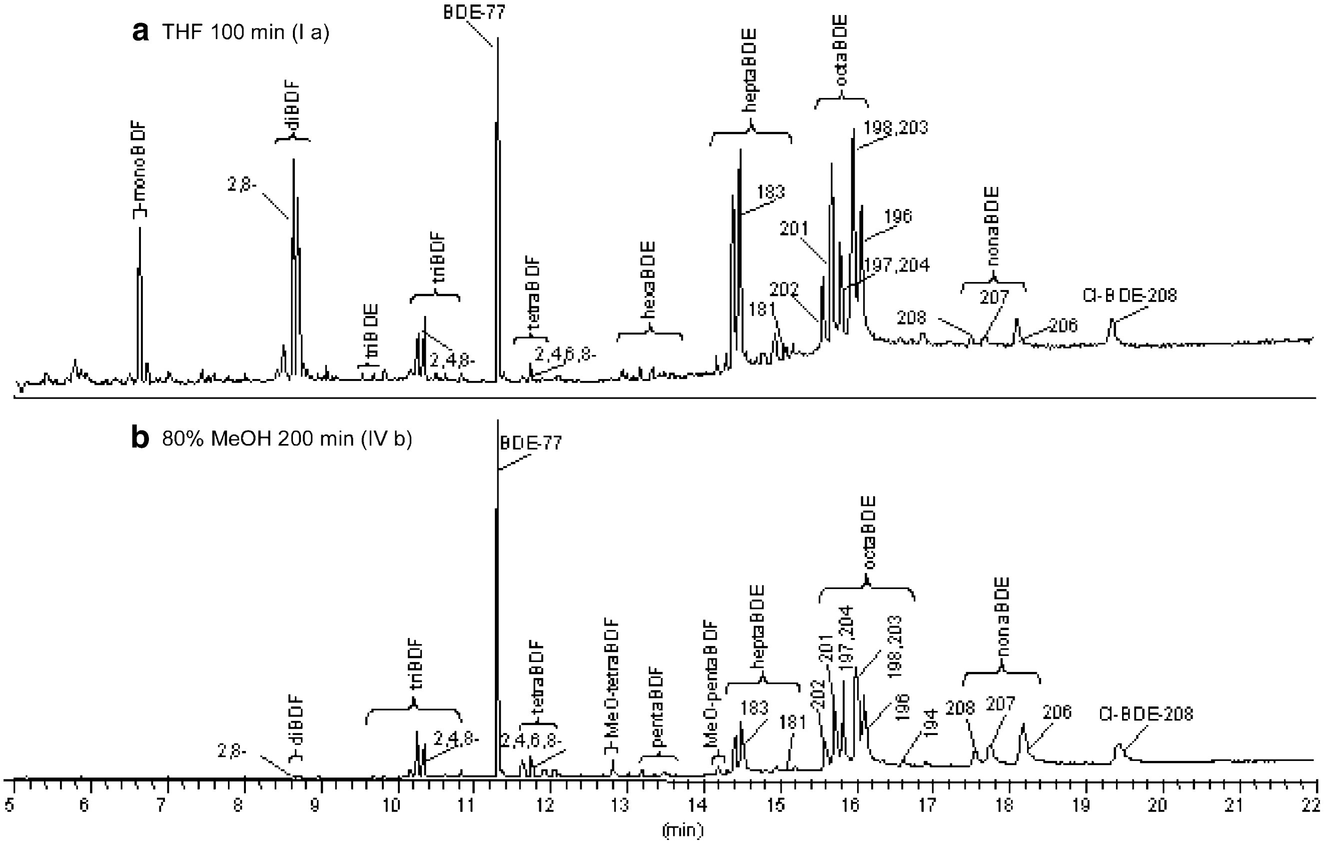

Fig. 1 **a** GC/MS chromatogram recorded in the EI mode on a nonpolar GC-column (DB-5HT, 15 m×0.25 mm i.d., 0.1 µm film thickness) of decaBDE dissolved in 100% THF and exposed to UV light for 100 min. **b** GC/MS chromatogram recorded in the EI mode on a nonpolar GC-column (DB-5HT, 15 m×0.25 mm i.d., 0.1 µm film thickness) of decaBDE dissolved in 80% MeOH:20% water and exposed to UV light for 200 min

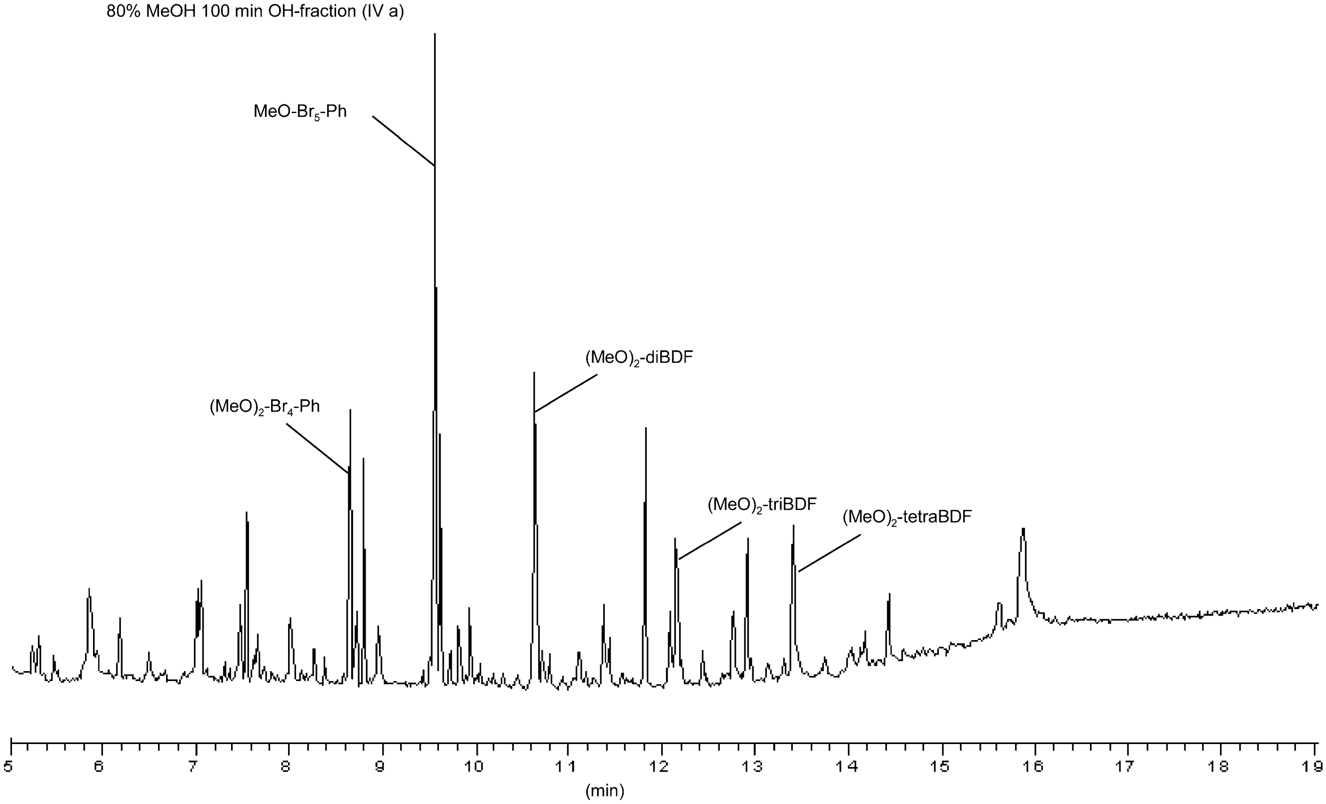

Fig. 2 GC/MS chromatogram recorded in the EI mode on a nonpolar GC-column (DB-5HT, 15 m×0.25 mm i.d., 0.1 μm film thickness) of the hydroxy fraction from decaBDE dissolved in 80% MeOH:20% water and exposed to UV light for 100 min

Hagberg et al. (2006). The overall transformation to PBDFs are estimated to be 6–10% of the products formed (see Table 4). Since the PBDFs may be formed via entirely different routes, not involving BDE-209, it is not possible to identify any of the PBDFs as characteristic of photolysis of decaBDE. On the other hand, PBDFs are photolysis products of decaBDE (BDE-209) as shown herein and in other previous studies, see Section 1.

4 Discussion

It is obvious, based on previous and the present studies, that BDE-209 is a source of lower brominated diphenyl ether congeners and of PBDFs. It is still difficult to calculate the importance of photolysis, since BDE-209 transformations can either be catalyzed or inhibited depending on what the compound is adsorbed to. BDE-209 is at least long-lasting when adsorbed to window surfaces (Butt et al. 2004) that indeed are subjected to sun light, but on the contrary, rapidly transformed if it is in a solution and inside a window (Herrmann et al. 2003). BDE-209 is a source of PBDEs primarily present in OctaBDEs, but also to some extent in PentaBDEs, both being commercial products now banned within EU (Cox and Efthymiou 2003) and in several states within the U.S. (Great Lakes Flame Retardants 2005).

It may be worth stressing that protic solvents, i.e. methanol and water, may lead to the formation of methoxylated or hydroxylated products such as MeO-PBDEs and OH-PBDEs. But neither of those products was found in these experiments. It is a possibility that an excited PBDE undergoes intramolecular reaction to form a PBDF instead of reacting with the surrounding solvent. PBDEs may also fragment to form phenols. Because highly brominated PBDFs are very photosensitive, they could easily react with the surrounding solvent molecules. It is notable that OH-PBDFs have not been identified or indicated in any of the photolysis studies performed up until now. Formation of OH-PBDFs may occur as pure radical reactions in the atmosphere as reported elsewhere (Ueno et al. 2008).

5 Conclusions

Photolysis of decaBDE, dissolved or adsorbed, is yielding a large number of PBDE and PBDF products. The primary individual products are a few heptaBDEs to nonaBDEs with BDE-202 as a possible indicator of environmental transformations of BDE-209, since it is not present in commercial PBDE products. The present study is indicating that environmental photolysis of BDE-209 may lead to formation of both BDE-183 and BDE-153, both being important environmental PBDE congeners. Both hydroxylated and methoxylated products may be formed from BDE-209 when studied under experimental conditions in methanol and methanol/water.

6 Recommendations and perspectives

DecaBDE or BDE-209 has been shown in a large number of studies by now to be converted to lower brominated diphenyl ethers and to low brominated dibenzofurans. DecaBDE is accordingly a source of these more readily bioaccumulative and more persistent PBDEs. It is thus reasonable to limit the production of DecaBDE to promote a cleaner environment.

Acknowledgments We wish to thank Ioannis Athanassiadis for his skillful MS assistance and Maria Athanasiadou for valuable contribution regarding the set up of the study. This study was financed through the Swedish Research Council Formas and from the Swedish foundation for strategic environmental research (MISTRA) through the frame of the NewS program. Financial support was also gained through the European Community within the 6th framework program for research, technological development, and demonstration activities “FIRE” with the contract number QLRT-2001-00596.

References

Ahn MY, Filley TR, Jafvert CT, Nies L, Hua I (2006a) Birnessite mediated debromination of decabromodiphenyl ether. Chemosphere 64:1801–1807

Ahn MY, Filley TR, Jafvert CT, Nies L, Hua I, Bezares-Cruz J (2006b) Photodegradation of decabromodiphenyl ether adsorbed onto clay minerals, metal oxides, and sediment. Environ Sci Technol 40:215–220

Alaee M, Arias P, Sjödin A, Bergman Å (2003) An overview of commercially used brominated flame retardants (BFRs) and their applications, changes in their use pattern in different countries/regions over time and possible modes of release. Environ Int 29:683–689

Andersson PL, Öberg K, Örn U (2006) Chemical characterization of brominated flame retardants and identification of structurally representative compounds. Environ Toxicol Chem 25:1275–1282

Bezares-Cruz J, Jafvert CT, Hua I (2004) Solar photodecomposition of decabromodiphenyl ether: products and quantum yield. Environ Sci Technol 38:4149–4156

Butt CM, Diamond ML, Truong J, Ikonomou MG, ter Schure AFH (2004) Spatial distribution of polybrominated diphenyl ethers in southern Ontario as measured in indoor and outdoor window organic films. Environ Sci Technol 38:724–731

Chen D, Mai B, Song J, Sun Q, Luo Y, Luo X, Zeng EY, Hale RC (2007a) Polybrominated diphenyl ethers in birds of prey from Northern China. Environ Sci Technol 41:1828–1833

Chen SJ, Luo XJ, Lin Z, Luo Y, Li KC, Peng XZ, Mai BX, Ran Y, Zeng EY (2007b) Time trends of polybrominated diphenyl ethers in sediment cores from the pearl river estuary, South China. Environ Sci Technol 41:5595–5600

Christiansson A, Teclechiel D, Eriksson J, Bergman Å, Marsh G (2006) Methods for synthesis of nonabromodiphenyl ethers and a chloro-nonabromodiphenyl ether. Chemosphere 63:562–569

Cox P, Efthymiou P (2003) Directive 2003/11/EC of the European parliament and of the council of February 6 2003 amending for the 24th time Council Directive 76/669/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether). Official Journal of the European Union OJ L 42:45–46

de Wit CA, Alaee M, Muir DCG (2006) Levels and trends of brominated flame retardants in the Arctic. Chemosphere 64:209–233

Eriksson J, Rahm S, Green N, Bergman Å, Jakobsson E (2004a) Photochemical transformations of tetrabromobisphenol A and related phenols in water. Chemosphere 54:117–126

Eriksson J, Green N, Marsh G, Bergman Å (2004b) Photochemical decomposition of 15 polybrominated diphenyl ether congeners in methanol/water. Environ Sci Technol 38:3119–3125

Gaul S, Von der Recke R, Tomy G, Vetter W (2006) Anaerobic transformation of a technical brominated diphenyl ether mixture by super-reduced vitamin B12 and dicyanocobinamide. Environ Toxicol Chem 25:1283–1290

Gerecke AC, Hartmann PC, Heeb NV, Kohler HP, Giger W, Schmid P, Zennegg M, Kohler M (2005) Anaerobic degradation of decabromodiphenyl ether. Environ Sci Technol 39:1078–1083

Gevao B, Al-Bahloul M, Al-Ghadban AN, Al-Omair A, Ali L, Zafar J, Helaleh M (2006) House dust as a source of human exposure to polybrominated diphenyl ethers in Kuwait. Chemosphere 64:603–608

Gouin T, Thomas GO, Chaemfa C, Harner T, Mackay D, Jones KC (2006) Concentrations of decabromodiphenyl ether in air from Southern Ontario: implications for particle-bound transport. Chemosphere 64:256–261

Great Lakes Flame Retardants (2005) http://www.e1.greatlakes com/fr/regupdates/jsp/united_states jsp

Hagberg J, Olsman H, Van Bavel B, Engwall M, Lindstroem G (2006) Chemical and toxicological characterization of PBDFs from photolytic decomposition of decaBDE in toluene. Environ Int 32:851–857

He J, Robrock KR, Alvarez-Cohen L (2006) Microbial reductive debromination of polybrominated diphenyl ethers (PBDEs). Environ Sci Technol 40:4429–4434

Herrmann T, Schilling B, Päpke O (2003) Photolysis of PBDEs in solvents by exposure to daylight in a routine laboratory. Organohalogen Compounds 63:361–364

Hites RA (2004) Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environ Sci Technol 38:945–956

Hua I, Kang N, Jafvert CT, Fabrega-Duque JR (2003) Heterogeneous photochemical reactions of decabromodiphenyl ethers. Environ Toxicol Chem 22:798–804

Karlsson M, Julander A, van Bavel B, Hardell L (2007) Levels of brominated flame retardants in blood in relation to levels in household air and dust. Environ Int 33:62–69

Konstantinov A, Bejan D, Bunce N, McCrindle R, Potter D, Tashiro C, Yeo B (2007) Debromination of PBDEs in DE-83™ Technical Mix by electrolysis. 4th International Workshop on Brominated Flame Retardants, BFR 2007

La Guardia MJ, Hale RC, Harvey E (2006) Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ Sci Technol 40:6247–6254

La Guardia MJ, Hale RC, Harvey E (2007) Evidence of debromination of decabromodiphenyl ether (BDE-209) in biota from a wastewater receiving stream. Environ Sci Technol 41:6663–6670

Law RJ, Alaee M, Allchin CR, Boon JP, Lebeuf M, Lepom P, Stern GA (2003) Levels and trends of polybrominated diphenylethers and other brominated flame retardants in wildlife. Environ Int 29:757–770

Law RJ, Allchin CR, de Boer J, Covaci A, Herzke D, Lepom P, Morris S, Tronczynski J, de Wit CA (2006) Levels and trends of brominated flame retardants in the European environment. Chemosphere 64:187–208

Lenoir D, Schramm K-W, Hutzinger O, Schedel G (1991) Photochemical degradation of brominated dibenzo-*p*-dioxins and -furans in organic solvents. Chemosphere 22:821–834

Li A, Tai C, Zhao Z, Wang Y, Zhang Q, Jiang G, Hu J (2007) Debromination of decabrominated diphenyl ether by resin-bound iron nanoparticles. Environ Sci Technol 41:6841–6846

Lindberg P, Sellström U, Häggberg L, de Wit CA (2004) Higher brominated diphenyl ethers and hexabromocyclododecane found in eggs of peregrine falcons (*Falco peregrinus*) breeding in Sweden. Environ Sci Technol 38:93–96

Malmvärn A, Marsh G, Kautsky L, Athanasiadou M, Bergman Å, Asplund L (2005) Hydroxylated and methoxylated brominated diphenyl ethers in the red algae *Ceramium tenuicorne* and blue mussels from the Baltic Sea. Environ Sci Technol 39:2990–2997

Marsh G, Athanasiadou M, Bergman Å, Asplund L (2004) Identification of hydroxylated and methoxylated polybrominated diphenyl ethers in Baltic Sea salmon (*Salmo salar*) blood. Environ Sci Technol 38:10–18

Marsh G, Hu J, Jakobsson E, Rahm S, Bergman Å (1999) Synthesis and characterization of 32 polybrominated diphenyl ethers. Environ Sci Technol 33:3033–3037

Mas S, Jauregui O, Rubio F, de Juan A, Tauler R, Lacorte S (2007) Comprehensive liquid chromatography-ion-spray tandem mass spectrometry method for the identification and quantification of eight hydroxylated brominated diphenyl ethers in environmental matrices. J Mass Spectrom 42:890–899

Moon HB, Kannan K, Choi M, Choi HG (2007) Polybrominated diphenyl ethers (PBDEs) in marine sediments from industrialized bays of Korea. Mar Pollut Bull 54:1402–1412

Ohta S, Nishimura H, Nakao T, Aozasa O, Miyata H (2001) Characterization of the photolysis of decabromodiphenyl ether and the levels of PBDEs as its photoproducts in atmospheric air of Japan. Organohalogen Compounds 52:321–324

Olsman H, Hagberg J, Kalbin G, Julander A, Van Bavel B, Strid A, Tysklind M, Engwall M (2006) Ah receptor agonists in UV-exposed toluene solutions of decabromodiphenyl ether (decaBDE) and in soils contaminated with polybrominated diphenyl ethers (PBDEs). Environ Sci Pollut Res 13:161–169

Palm W-U, Raimo K, Wiebke S, Wolfgang R, Cornelius Z (2004) Photochemical reactions of brominated diphenyl ethers in organic solvents and adsorbed on silicon dioxide suspension in aqueous suspension. Organohalogen Compounds 66:4104–4109

Parsons J, Zegers B, Skoczynska E, de Voogt P (2004) Reductive debromination of decabromodiphenyl ether (BDE-209) by anaerobic sediment microorganism. Organohalogen Compounds 66:2272–2274

Rahm S, Green N, Norrgran J, Bergman Å (2005) Hydrolysis of environmental contaminants as an experimental tool for indication of their persistency. Environ Sci Technol 39:3128–3133

Söderström G, Sellström U, de Wit CA, Tysklind M (2004) Photolytic debromination of decabromodiphenyl ether (BDE 209). Environ Sci Technol 38:127–132

Stapleton HM, Brazil B, Holbrook DR, Mitchelmore CL, Benedict R, Konstantinov A, Potter D (2006) In vivo and in vitro debromination of decabromodiphenyl ether (BDE 209) by juvenile rainbow trout and common carp. Environ Sci Technol 40:4653–4658

Stapleton HM, Dodder NG (2008) Photodegradation of decabromodiphenyl ether in house dust by natural sunlight. Environ Toxicol Chem 27:306–312

Stapleton HM, Dodder NG, Offenberg JH, Schantz MM, Wise SA (2005) Polybrominated diphenyl ethers in house dust and clothes dryer lint. Environ Sci Technol 39:925–931

Tan J, Cheng SM, Loganath A, Chong YS, Obbard JP (2007) Polybrominated diphenyl ethers in house dust in Singapore. Chemosphere 66:985–992

Teclechiel D, Christiansson A, Bergman Å, Marsh G (2007) Synthesis of octabrominated diphenyl ethers from aminodiphenyl ethers. Environ Sci Technol 41:7459–7463

ter Schure AFH, Larsson P, Agrell C, Boon JP (2004) Atmospheric transport of polybrominated diphenyl ethers and polychlorinated biphenyls to the Baltic Sea. Environ Sci Technol 38:1282–1287

Thomas GO, Moss SEW, Asplund L, Hall AJ (2005) Absorption of decabromodiphenyl ether and other organohalogen chemicals by grey seals (*Halichoerus grypus*). Environ Pollut 133:581–586

Ueno D, Darling C, Alaee M, Pacepavicius G, Teixeira C, Campbell L, Letcher RJ, Bergman Å, Marsh G, Muir D (2008) Hydroxylated polybrominated diphenyl ethers (OH-PBDEs) in the abiotic environment: surface water and precipitation from Ontario, Canada. Environ Sci Technol 42:1657–1664

Verreault J, Gabrielsen GW, Chu S, Muir DCG, Andersen M, Hamaed A, Letcher RJ (2005) Flame retardants and methoxylated and hydroxylated polybrominated diphenyl ethers in two Norwegian arctic top predators: Glaucous gulls and polar bears. Environ Sci Technol 39:6021–6028

Voorspoels S, Covaci A, Lepom P, Escutenaire S, Schepens P (2006) Remarkable findings concerning PBDEs in the terrestrial top-predator red fox (*Vulpes vulpes*). Environ Sci Technol 40:2937–2943

Watanabe I, Kawano M, Tatsukawa R (1994) The photolysis of halogenated dibenzofurans in hexane solutions and on airborne dust by sunlight. Organohalogen compounds 19:235–238

Watanabe I, Tatsukawa R (1987) Formation of brominated dibenzofurans from the photolysis of flame retardant decabromobiphenyl ether in hexane solution by UV and sun light. Bull Environ Contam Toxicol 39:953–959

Wilford BH, Shoeib M, Harner T, Zhu J, Jones KC (2005) Polybrominated diphenyl ethers in indoor dust in Ottawa, Canada: implications for sources and exposure. Environ Sci Technol 39:7027–7035