The photodegradation of polybrominated diphenyl ethers (PBDEs) in various environmental matrices: kinetics and mechanisms

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Abstract

The fate and transport of polybrominated diphenyl ethers (PBDEs) have raised a great deal of concern due to their persistence, bioaccumulative nature and adverse effects. Photodegradation is one of the important transformation processes for organic contaminants in the environment. In order to understand the photochemical behaviors of PBDEs, this study critically reviews the kinetics and mechanisms of PBDEs photodegradation in different matrices: (i) organic solvent phase; (ii) aqueous phase; (iii) gas phase; (iv) solid phase, and (v) TiO₂-mediated phase. The half-lives of PBDEs in solid and gas phases are significantly longer than those in liquids. The degradation kinetics are affected by the number and positions of the bromines in PBDEs, solvent effects, the composition of any solid matrix, and the presence or absence of common environmental species such as humic substances, metal cations and halide anions. Regarding the photodegradation mechanisms reductive debromination and intermolecular elimination of HBr are the two predominant degradation pathways in direct photolysis to produce lowerbrominated BDEs and polybrominated dibenzofurans (PBDFs), respectively. A variety of derivatives can be formed depending on the medium. Hydroxylated PBDEs (OH-PBDEs) and bromophenols are produced through the reaction of PBDEs with •OH radicals in aqueous and atmospheric systems. Chlorinated BDEs form in the presence of chloride in water, and hydroxylated PBDFs (OH-PBDFs) and methoxylated PBDFs (MeO-PBDFs) form in methanol. Thus, it is important to scrutinize the photodegradation products and photochemical mechanisms of PBDEs under field-relevant conditions in environmental health monitoring and cleaning up contaminated sites.

Keywords: Polybrominated diphenyl ethers ; photodegradation; kinetics; mechanisms

1. Introduction

Polybrominated diphenyl ethers (PBDEs), a group of brominated flame retardants with 209 congeners differing in the brominated substitutions in the aromatic rings (Fig.1), have been widely applied in electronics, textiles and other everyday products since 1970s [1]. The worldwide production of all PBDEs from 1970 to 2005 is estimated to have been 1.3 to 1.5million tonnes, including approximately 100,000 tonnes of penta-BDEs, 100,000 tonnes of octa-BDEs, and over 1.1million tonnes of deca-BDEs [2]. In the recent 30 years, many countries have successively enforced restrictions for the use of commercial PBDEs (Fig. 2) [3]. The production of penta-BDEs and octa-BDEs was banned in 2005 but continued use of deca-BDE is still permitted in the major industrialized countries, such as China, Japan and the USA [3-6]. PBDEs can be released into the environment during their production, application, disposal and recycling processes [6,7]. Numerous studies have reported their presence in water, air, soil, sediment, fish, birds, and human blood [8-13]. PBDEs are identified as endocrine disruptors that can impact liver enzyme reactivity, affect thyroid hormone levels, induce immunotoxicity, hinder neurodevelopment, and cause DNA damage [14-17]. Because of their prevalence in various environmental matrices and potential toxicity to wildlife and humans, there have been lots of recent investigations into the environmental fate and treatment technologies for PBDEs,, such as biodegradation [18,19], adsorption [20,21], photodegradation [22,23], zero-valent iron dehalogenation [24,25] and advanced oxidation processes [26] .

Among those environmental processes, photodegradation is an important abiotic transformation for PBDEs, leading to the formation of lowerbrominated congeners and other derivatives, some of which are even more toxic and have greater bioaccumulation potential than the parent pollutants [22,27-29]. The physicochemical properties of environmentally relevant PBDEs are summarized in Table 1 [30-33]. The PBDEs especially the highly-brominated congeners, show strong affinity for organic matter with $\log K_{ow}$ ranging from 5.55 to 12.11 [33]. Since organic solvents are used for simulating lipophilic environments, photolysis in such solvents has received the most attention. Among the PBDEs, BDE-209 is the most investigated congener due to its environmental abundance, particularly in solids. The phototransformation process of BDE-209 is known to lead to the accumulation of less brominated congeners (especially BDE-153, BDE-99 and BDE-47) in the environment, and this has attracted extensive research interest [34,35].

Available reviews about PBDEs in the literature focus on the analytical methods applicable in various media (water, dust, soil, sediment, polymers, biological samples and food) [36-39], their regional environmental occurrence (especially in European countries, the USA, China and Japan) [40-43], human exposure through inhalation and ingestion [44-47], biotic and abiotic transformation in the environment [48], and the degradation technologies of PBDEs in liquid systems [49]. However, the photochemical behavior of PBDEs in different natural and artificial media under various environmental conditions still has not been critically evaluated and compared. In this review, we focus on the photodegradation kinetics and mechanisms of PBDEs in (i) organic solvents; (ii) aqueous media; (iii) gas phase; (iv) solid phase; and (v) TiO_2 -mediated phase. Factors affecting the photodegradation rates are

summarized such that the similarity and disparity in PBDE photodegradation pathways in various matrices can be clearly illustrated. This review is significant for advancing our understanding of the fate and transport of PBDEs in the environmental matrices and provides guidance for developing photochemically enhanced treatment for open wetland and contaminated sites.

2. Absorbance spectra of PBDEs

Direct photolysis of PBDEs depends on their absorption spectra. The pollutant's absorption spectrum must overlap with the emission spectrum of the light source. Eriksson et al.[50] measured absorption spectra of 11 PBDE congeners in tetrahydrofuran (THF) and Raff and Hites [51] obtained UV absorption spectra of 25 congeners in isooctane. As shown in Fig. 3, all of the PBDEs tested absorb light with 280–400 nm wavelength. Their molar absorptivity in the UV-B region (280-315 nm) is much greater than that in the UV-A region (315-400 nm), suggesting that PBDEs can undergo direct photodegradation through exposure to solar light [52,53]. The UV absorbance spectra varied among PBDEs depending on the number of bromine atoms and the bromine substitution positions. The PBDEs containing more bromine atoms can absorb UV light with longer wavelengths [54,55]. In addition, indirect photolysis is promoted by photosensitizers (e.g., organic matter and ferric ions) in the environment which can absorb light to produce reactive oxygen species such as $^1\text{O}_2$, $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$ and H_2O_2 . They then react with PBDEs and result in their photooxidation [22,29].

3. Photodegradation in organic solvents

3.1 Kinetics in organic solvents

Strong hydrophobicity and low solubility in water cause PBDEs to show strong partitioning affinity to organic matrices [20]. This is why the majority of studies of the photochemical behavior of PBDEs in liquids have focused on organic solvents such as methanol, acetonitrile and hexane as a proxy media simulating the natural environment. The photolysis kinetics generally follow the pseudo-first order reaction model. Table 2 summarizes the photolysis rates of PBDEs in various organic solvents. The degradation rates and quantum yields are highly dependent on the molecular structure of PBDEs and the solvent effects, as discussed below.

3.1.1 Molecular structures

In general, the higher brominated BDEs degrade faster than the less-brominated ones. The first-order rate constant for BDE-209 ($k = 40 \times 10^6 \text{ s}^{-1}$) in methanol/water reported by Eriksson et al. [50] was nearly 600 times of that of BDE-47 ($k = 0.07 \times 10^6 \text{ s}^{-1}$). Two reasons may account for this difference. First, there is greater overlap between the irradiation spectrum and the absorption spectra of heavier PBDEs, while the absorption spectra of the less-brominated congeners are relatively narrow (Fig. 3). Then, the energy of the highest occupied molecular orbital (HOMO), which is related to the electron donor ability, generally increases with the bromination degree, enabling greater reactivity in photolysis [59]. But it should be noted that PBDEs with the same number of bromines also exhibit different degradation rates. Compared to BDE-99 (2, 2', 4, 4', 5-penta-BDE), BDE-100 (2, 2', 4, 4', 6-penta-BDE) had the same number of bromine substituents and relatively higher- HOMO

energy, but its degradation rate was 19 times slower than BDE-99 in hexane. Similarly, BDE-75 (2, 4, 4', 6-tetra-BDE), a byproduct of BDE-100 photolysis, had also been found to degrade more slowly than BDE-47 (2, 2', 4, 4'-tetra-BDE) [59]. This may be attributed to the more stable brominated phenyl ring with 2, 4, 6-substitution in BDE-100 and BDE-75. Eriksson et al. [50] also reported that the degradation of BDE-190 (2, 3, 3', 4, 4', 5, 6-hepta-BDE) and BDE-181 (2, 2', 3, 4, 4', 5, 6-hepta-BDE), both of which have one fully-brominated phenyl ring, was about 5 times faster than that of BDE-183 (2, 2', 3, 4, 4', 5', 6-hepta-BDE).

A quantitative structure-property relationship (QSPR) model has been developed to predict the quantum yields and direct photodegradation rate constants of PBDEs in methanol and hexane considering molecular structural descriptors [60-62]. The structural factors predominantly governing the quantum yields of PBDEs are the average atomic charges on the hydrogen atoms (q_H) and bromine atoms (q_{Br}) as well as the gap of frontier molecular orbital energy ($E_{HOMO} - E_{LUMO}$). This suggests that the quantum yields are correlated with the bromine substitution patterns of PBDEs [60-62]. At the same time, molecular weight (M_w), average molecular polarizability (α), molecular surface area (S_m), total energy (TE) and q_{Br} are used to characterize the photodegradation rate constants of PBDEs in QSPR models, reflecting the fact that bromination degree also plays an important role [60-62].

3.1.2 Solvent effects

There are also significant differences in the photoreactivity of PBDEs in various solvents. Slow photodegradation rate constants and low quantum yields are observed in poor hydrogen-donating solvents. Eriksson et al. [50] revealed that the photolytic degradation rates

of 15 individual PBDEs in 8:2 methanol/water mixtures were 1.7 times slower than those in pure methanol and 2–3 times slower than those in tetrahydrofuran (THF). This corresponds to the order of hydrogen donor ability (THF > methanol > water). Similarly, the photolytic rates and quantum yields of 12 PBDEs in hexane were found to be higher than those in methanol [62].

However, Davis and Stapleton [63] report that the photoreactivity of BDE-209 and nona-BDEs in toluene was about 1.5 times higher than that in THF, although THF has the better hydrogen-donating ability. This may be ascribed to the aromatic ring in toluene being a chromophore which produced electron transition energy under irradiation, promoting the indirect photolysis of PBDEs. The detailed mechanism was illuminated from a molecular perspective by Pan et al. [64]. The two excited states ($\pi_{tolu}\sigma^*$ and $\pi_{cpx}\sigma^*$) photo-induced by the face-to-face π - π interactions between toluene and the penta-bromine-substituted phenyl groups of BDE-209 contributed to this photocatalytic process. Depending on the $\pi_{tolu}\sigma^*$ state, the C-Br bond at the *para* or *meta* position of BDE-209 elongated and was more easily broken due to intramolecular charge transfer; depending on the $\pi_{cpx}\sigma^*$ state, electronic excitation from the π orbital in the BDE-209 and toluene complex stimulates the σ^* orbital of phenyl in BDE-209 and probably lead to debromination at the *ortho*-, *meta*-, or *para*- position [64].

The solvent also affects the molecular properties of PBDEs. Xie et al. [65] studied the photodegradation of BDE-209 in tetrahydrofuran, dichloromethane, isopropanol, ethanol, methanol, acetonitrile and dimethylsulfoxide. They found that the lowest singlet vertical excitation energy (E_{ex}) and the average formal charge on the bromine atoms (q_{Br}^+) of

BDE-209 (which reflect the energy barriers for the excitation and the cleavage of C-Br bonds, respectively) can be changed by the reaction fields produced by the solvent. The linear relationships between E_{ex} , q_{Br}^{+} and the log-transformed photoreactivity of BDE-209 were observed [65].

3.2 Mechanisms in organic solvents

Consecutive debromination is known to be the main mechanism of PBDEs photolysis in organic solvents, as shown in Scheme 1. Other derivatives, including PBDFs, OH-PBDFs, MeO-PBDFs and bromophenol are also observed depending on conditions such as the irradiation time, the bromination degree of the PBDEs and the solvent medium. In this section, the photochemical transformation pathways of PBDEs are summarized with respect to the solvents used.

3.2.1 Hexane

The photolysis of 13 common PBDEs (BDE-209, 208, 207, 206, 196, 183, 154, 153, 100, 99, 85, 47 and 28) in hexane have been investigated to identify the complete pathway of the consecutive reductive debromination starting from BDE-209 (Scheme 1a) and 183 (Scheme 1b) [59,66]. The distribution of the bromine substitutions in the two phenyl rings is a significant factor affecting the stability of PBDEs. For example, no congener with a fully-brominated phenyl ring can be observed as a photoproduct except BDE-181 and 190, which are generated briefly from BDE-209 followed by their instantaneous degradation [66]. Thermodynamic calculations suggest that a fully bromine-substituted ring in a PBDE should be unstable [67]. Moreover, debromination usually occurs more readily on more

bromine-substituted rings in the unsymmetrically-substituted PBDEs. The dominant products (e.g., BDE-201 and BDE-202 from BDE-208; BDE-153 from BDE-183; BDE-47, BDE-66 and BDE-49 from BDE-99; and BDE-15 from BDE-28) are all formed by the loss of one bromine atom from the more substituted rings [59,66].

The different bromine positions (*meta*-, *ortho*-, and *para*-) in the phenyl ring also affect the degradation products. Wei et al. [66] found that molecules with *para*-brominated substitution showed relatively greater stability than those with *ortho*- or *meta*-substitution. The observed order of photoreactivity is generally $meta \geq ortho > para$, particularly for BDEs with less than 8 bromines, but this is not evident for more highly-brominated congeners [59,66]. Net charge theory predicts that *meta*- and *ortho*-bromine atoms should have higher net positive charges than those in *para*-positions in all PBDEs, and that the net charges of bromines at *meta*-positions should be higher than those in *ortho*- positions for the congeners with 7 bromines or less [68]. The lower energy of an *ortho* bromine and the more elongated C-Br bond at an *ortho* position than at a *para* position also supports the bromine substitution order [67,69].

Besides the lower brominated PBDE congeners as photoproducts in hexane, Fang et al. [59] detected a few PBDFs. No brominated benzene or PBDE-solvent adducts via the cleavage of inter-ring bonding was observed during the photolysis reaction, possibly due to the good hydrogen donor ability of hexane. However, the total molar mass of PBDEs before and after irradiation was not balanced. With BDE-209, 208 and 206, less than 31% of the original molar mass of PBDEs was left after 4 h of exposure to sunlight, implying that some unknown photolytic mechanisms formed non-PBDE derivatives [66].

3.2.2 Acetonitrile

The photolysis of BDE-15 has been investigated in CH₃CN and 1:1 CH₃CN/water mixtures by Rayne et al. [70], showing the same debromination pathway in spite of different photolysis rates. Only BDE-3 and diphenyl ether (DE) were formed by C-Br bond cleavage in debromination, while the no products formed via C-O bond cleavage could be found.

The photoinduced debromination pathway of BDE-153 in CH₃CN was similar to that in hexane. BDE-99, 101 and 118 are generated as primary photoproducts and BDE-47, 49, 66 and 77 as secondary products (Scheme 1) [71]. But no mono- to tri-BDEs were detected on the experimental time-scale, and 70% of the molar mass of the PBDEs remained unaccounted for after 5 min of irradiation, demonstrating that non-debromination pathways played an important role in the photochemical transformation in CH₃CN. Mono- to penta-BDFs and tetra-brominated-2-hydroxybiphenyl congeners were observed as the byproducts [71]. The PBDFs, formed by the intramolecular elimination of HBr from PBDEs, can subsequently generate lower brominated BDFs via consecutive debromination due to their instability under irradiation (Route a of Scheme 2) [72]. The C-O bond homolytic cleavage in BDE-153 provided a diaryl system for photo-Fries rearrangement to form hexabrominated-2-hydroxybiphenyls, which were proposed as precursors of tetrabrominated-2-hydroxybiphenyl congeners (Route b of Scheme 2) [71]. However, such precursors could not be detected (even with the mono- to tri-brominated congeners as the secondary products), probably due to their rapid photodegradation or impurities in the analyses. Moreover, from a mechanistic point of view, the transformation pathway from brominated hydroxybiphenyl to PBDFs via the loss of HBr should not be neglected (Route c

of Scheme 2) [71].

3.2.3 Methanol

The detected less-brominated BDEs suggested that the consecutive debromination pathway of BDE-209 in methanol was little different from that in hexane (Scheme 1). But note that no mono- to penta-BDEs was observed while di- to penta-BDFs were found [50,73]. These results prove that a furan ring can be generated not only from PBDEs with less than six bromine substituents, but from PBDEs with any level of bromination if there is an un-brominated *ortho* position. Methoxylated-PBDFs (MeO-PBDFs) and hydroxylated PBDFs (OH-PBDFs) were also observed [73], probably resulting from a reaction between PBDFs and surrounding methanol molecules due to the high photoreactivity of PBDFs (Route a of Scheme 3). However, neither methoxylated-PBDEs (MeO-PBDEs) nor hydroxylated PBDEs (OH-PBDEs) were found, implying that the intramolecular elimination to generate PBDFs from PBDEs may be more favorable than the reaction with methanol.

In addition, bromophenols and their hydrodebromination products were also identified as photoproducts [28,73], suggesting that bromophenolate ions produced by heterolytic ether bond cleavage subsequently reacted with methanol molecules (Route b of Scheme 3). But bromobenzenes, the other products formed via the cleavage of ether bonds, had been observed only in trace amounts close to the limit of detection [28].

A new debromination mechanism for BDE-209 in methanol involving the addition of carboxylates has also been demonstrated by Sun et al. [74]. It depends on the generation of a halogen-binding complex between carboxylates and PBDEs. The C-Br bond can then be more easily broken by photoinduced electrons transfer from the carboxylate sites to PBDE

sites in the complex under visible light irradiation.

4. Photodegradation in aquatic systems

The majority of previous studies have elucidated the photochemical transformation of PBDEs in organic solvents using high initial concentrations(mg/L), but in natural aquatic environments PBDEs exist at extremely low concentrations (ng/L) and in the form of the low brominated congeners which are relatively more soluble in water [9,75]. The photochemical behavior then depends strongly on the chemical species in the aquatic system, such as humic substances, metal ions and halide ions. Thus, the photodegradation of PBDEs in water is separately summarized in Table 3.

4.1 Kinetics in aquatic systems

The photodegradation of BDE-47, 99, 100, 153 and 154 in pure water follows pseudo-first-order kinetics under simulated or natural sunlight [76]. For the less-brominated BDEs in aqueous solutions, the indirect photolytic contributions of $^1\text{O}_2$ and $\bullet\text{OH}$ radicals have been shown to be 18.8% and 4.9% for BDE-47 and 17.3% and 6.6% for BDE-28, respectively [77]. This demonstrated that $^1\text{O}_2$ played a more important role than $\bullet\text{OH}$ in the indirect photodegradation of the low brominated congeners.

Organic matter in natural aquatic environments has a significant influence on the photolysis of PBDEs. Leal et al. [23] studied the effect of XAD-4, fulvic acid, and humic acid on the photodegradation of BDE-209 in water and found that photoreactivity was significantly inhibited by the presence of fulvic acid and humic acid (8 mg/L), while XAD-4 fraction (8

mg/L) had little effect. Other than light attenuation by the humic substances, this was probably a result of BDE-209 partitioning into the hydrophobic compartments of humic substances [23]. However, the photosensitized effect via the generation of reactive oxygen species (eg. $^1\text{O}_2$, $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, and H_2O_2) should not be neglected [78-81]. As for the photodegradation of BDE-47 in aqueous solution, the photolysis rate increased with increasing concentration of fulvic acid from 0.25 to 5 mg/L, but then decreased up to 10mg/L [22]. Zhao et al. [22] indicated that the enhancement of photodegradation was attributed to the photogenerated $\bullet\text{OH}$ radicals, while the quenching effect of fulvic acid for $\bullet\text{OH}$ became predominant with increasing amount of humic substances. Yet, whether ROS other than $\bullet\text{OH}$, like $^1\text{O}_2$, H_2O_2 and $^3\text{DOM}^*$ contributed to the degradation or not remained unclear [82].

Besides humic substances, Zhao et al. [29] showed that the phototransformation of BDE-47 can be promoted by the presence of ferric ion (Fe(III)), and that the co-existence of chloride ion (Cl^-) further enhanced its degradation because of the iron redox cycle. Hydroxyl radicals ($\bullet\text{OH}$) can be produced via the transformation of Fe(III) to Fe(II) in an aquatic system under irradiation, while the chlorine radicals subsequently formed by the reaction between Cl^- and $\bullet\text{OH}$ radicals would promote iron redox cycling and facilitate continuous $\bullet\text{OH}$ generation [29,83]. On the other hand, an increased photolysis rate of BDE-47 and BDE-99 was observed in the presence of various non-ionic surfactants (Brij 35, Brij 58, and Tween 80) compared with the rate in pure water, which had been attributed primarily to the more effective hydrogen donor ability of the surfactants. Such promotion was inhibited in the presence of cations but hardly affected by pH or dissolved oxygen [84,85].

4.2 Mechanisms in aquatic systems

Only the lower brominated PBDEs and trace amounts of PBDFs have been identified as photoproducts in pure water and surfactant solutions [71,76,84-86], suggesting that two similar phototransformation pathways occur in aqueous solution, shown as Scheme 1 and Route a of Scheme 2. Photoreactions via aryl-ether rearrangement or cleavage which occurred in methanol and acetonitrile were not observed, probably due to rapid photohydrodebromination or the low initial concentrations of PBDEs in aquatic systems [71,76,84-86].

In the presence of Fe(III) and Cl⁻, some chlorinated PBDEs compounds had been detected besides the less-brominated BDEs. This is probably due to reactions of chlorinated radicals and the aryl radicals via homolytic C-Br bond cleavage. A phototransformation pathway for BDE-47 was proposed in Scheme 4 [29]. The mechanisms of photochemical formation of OH-PBDEs from PBDEs had also been studied in aqueous Fe(III) and/or fulvic acid solutions using BDE-47 as a model compound (Scheme 5) [22]. 6-OH-BDE-47 and 2'-OH-BDE-68 were products which had been observed and attributed to the reaction of *ortho*-tetra-BDE radicals and •OH radicals. Meanwhile, 6-OH-BDE-47 might transform into 2'-OH-BDE-68, a more stable product via a Smiles rearrangement reaction, including hydroxyl ionization and nucleophilic attack by O⁻. Experiments with O¹⁸ isotopic tracer suggested that the aqueous solution and dissolved oxygen were the two sources of hydroxyl groups for these two OH-PBDEs [22].

5. Photodegradation in gas phase

There have been a few experimental studies of the photolysis of PBDEs in gas phase (Table 4). Work by Yang et al. [10] revealed that more than 80% of the PBDEs detected in air samples from 15 sites across China consisted of BDE-17, -28, -47 and -99 in gas phase due to their relatively high vapor pressure. This is in contrast with the particle phase that was dominated by BDE-209 (more than 90%). In general, the photochemical transformation of PBDEs in the atmosphere can be described as direct photolysis and photooxidation by $\bullet$ OH radicals [51,87].

5.1 Kinetics in gas phase

The atmospheric lifetimes of PBDEs resulting from direct photodegradation and $\bullet$ OH radical photoreaction are presented in Fig. 4. The photolytic lifetime decreases with the number of bromine substituents (from >20h for 1 or 2 bromines PBDEs to <0.1h for BDE-209), but the photooxidation lifetime shows the opposite trend [51]. These results illustrate that direct photolysis may be more important in the removal of highly brominated PBDEs (with ≥ 3 Br), while the less-brominated congeners (1 or 2 Br) react preferentially with $\bullet$ OH radicals in the gaseous environment. Wang et al. [88] used BDE-47 (100 ug/mL) to investigate the photochemical transformation in n-nonane or isooctane vapor (50 μ L) under UV irradiation (280-400 nm) in a two-film environment (gas and liquid phase). Interestingly, the photodegradation of BDE-47 in isooctane was much slower than that in n-nonane [88]. The higher vapor pressure of isooctane led to greater partition of BDE-47 into the gas phase during irradiation. In the gas phase, hydroxyl radicals were produced by the UV light and BDE-47 underwent relatively slow photo-oxidant compared to the direct

photolysis in the liquid phase [88].

5.2 Mechanisms in gas phase

Raff and Hites [51] found that the direct photolysis of BDE-3 and BDE-7 in helium gas under 307 nm irradiation followed pseudo-first-order kinetics. Besides diphenyl ether, dibenzofuran and 2-bromodibenzofuran were detected as the photoproducts, indicating that dibenzofuran can also be formed in the gas phase photolysis of BDEs [51]. In a two-film environment, apart from the less-brominated PBDEs (BDE-1, -3, -4, -8, -15, -17, and -28), generated via the reductive debromination dibromophenols and monobromophenol were observed to derive from the photooxidation of BDE-47 (Scheme 6) [88]. Dibromophenols could be formed by the direct cleavage of BDE-47 at C-O bonds and photooxidation by $\bullet\text{OH}$ radicals via BDE-28 and BDE-17.

Concerning the $\bullet\text{OH}$ photooxidation of PBDEs in gaseous environment, Zhou et al. [89] employed density functional theory to simulate its kinetics and mechanisms using BDE-15 as a model compound, which were consistent with experimental results. The proposed photooxidation pathway for BDE-15 was accordingly shown in Scheme 7, indicating that OH-PBDEs can be formed via Br substitution by $\bullet\text{OH}$ (Route a of Scheme 7) and the hydrogen atom abstraction by $\bullet\text{OH}$ and O_2 (Route b of Scheme 7). Bromophenol was also generated in this photooxidation process [89]. Moreover, Cao et al. [90-92] subsequently used quantum chemical methods to study the $\bullet\text{OH}$ -initiated oxidation mechanisms of BDE-7, BDE-28 and BDE-47. Their work revealed [90-92] that hydrogen-substituted hydroxyl addition (Route b of Scheme 7) was the dominant pathway due to the energy barriers being

lower than those of bromo-substituted addition (Route a of Scheme 7).

6. Photodegradation in solid phase

Previous studies of the photochemical behavior of PBDEs in solid phase have particularly focused on deca-BDE. BDE-209 can readily be adsorbed onto the solid matrices such as bulk soil, clay minerals and atmospheric dust, thus they can be transported long distances attached to fine suspended particles [93]. The photodegradation rates of PBDEs vary significantly with respect to solid characteristics and different irradiation conditions (Table 5).

6.1 Kinetics in solid phase

The photolysis rates of PBDEs depend strongly on solid properties such as porosity, water content, organic matter content, mineral composition and the presence of metal oxides. Soderstrom et al. [34] found that the half-lives of BDE-209 photodegradation under UV irradiation (300-400nm) followed the order silica gel (< 0.25h) < sand (12h) < sediment (40–60h) < soil (150–200 h). This was because sediment and soil had interior pores that shielded BDE-209 from UV radiation, and they were also enriched with natural organic matter that could attenuate light intensity and slow down the photolysis rate [34]. Hua et al. [94] also reported the similar role for humic acid in the heterogeneous photolysis of BDE-209.

In addition, Ahn et al. [95] found that the photodegradation of BDEs varied on different mineral surfaces and that the half-lives of BDE-209 photodegradation followed the order of

montmorillonite (36d) < kaolinite (44d) < sediment (150d) < aluminum hydroxide (178d) < birnessite (1423d) < ferrihydrite (no degradation). In spite of the significantly different bonding affinity of BDE-209 towards montmorillonite and kaolinite, similar degradation rates were observed in the two phases, implying that bonding force do not play an important role in the photoreactivity [95]. Some clay minerals such as montmorillonite and kaolinite may enhance the photodegradation of BDE-209 due to their strong electron-donating ability which should enhance the reductive debromination. Montmorillonite produces electrons through the bridging oxygen in Si-O-Al or at crystal edges under irradiation, whereas aluminum hydroxide, birnessite and ferrihydrite give no sign of catalytic promotion of photoreactions of BDE-209 [95].

Water content is also a key factor affecting PBDE photodegradation in solid matrices. Kajiwara et al. [27] studied the photodegradation of BDE-209 on high-impact polystyrene (HIPS) under natural sunlight and found that the photolysis of BDE-209 was faster in the hydrated HIPS samples than in un-hydrated ones during 112 days of irradiation. This suggested that water acted as a hydrogen donor and enhanced the debromination. However, Sanchez-Prado et al. [86] investigated the photodegradation of BDE-100 in D₂O solution and found that the products of the photolysis did not support the involvement of hydrogen. So any promotion was likely due to a bathochromic shift of the UV absorption spectra of PBDEs in water [96]. Sanchez-Prado et al. [86] further showed that the photolysis rate was very similar in solid ice and ultrapure water. And the half-lives of BDE-100 were 3.9 min and 4.3 min, respectively.

Stapleton and Dodder [97] studied the photodegradation of BDE-209 in clean dust spiked

with BDE-209 in toluene and in natural dust originally containing BDE-209. The results showed a longer half-life in the natural dust (408h versus 301h), which could result from different partitioning or distribution on the dust and the different origins of the BDE-209. Lagalante et al. [98] also reported that the photolysis rate of BDE-209 in dust from automobiles was much slower than that in house dust. BDE-209 arising from abrasion of fabric was found to be heterogeneously distributed within vehicle dust, while the BDE-209 in house dust was present as homogeneous, clear inclusions [99].

6.2 Mechanisms in solid phase

The photodegradation mechanisms of PBDEs on different solid substrates do not exhibit big differences. Two photodegradation pathways have been reported [27,95]. One is the formation of the lower brominated PBDE congeners through stepwise reductive debromination (Scheme 1). Recent research employing positive matrix factorization of a data set describing 24 BDEs in 233 sediment samples proved that the less-brominated BDEs were produced by photochemical debromination and that the degradation was therefore measurable and quantifiable in the environment [101].

It should be noted that consecutive reductive debromination does not predominate throughout the whole photodegradation processes. Kajiwara et al. [27] investigated the photodegradation of BDE-209 in HIPS and found that after exposure to sunlight for 7 days the concentration of photoproducts (hexa- to nona-BDE congeners) remained relatively stable, while BDE-209 still declined continuously. But the secondary debromination products such as BDE-47, 99 and 100 were not detected [27].

Apart from stepwise reductive debromination, another pathway involves the formation of dibenzofurans (PBDFs) through the intramolecular elimination of HBr on PBDEs for cyclization (Route a of Scheme 2). Kajiwarra et al. [27] indicated that the total concentration of PBDFs (di- to octa-BDFs) increased rapidly by about 40 times when BDE-209 in HIPS was exposed to sunlight for 7 days. But such photoproducts were unstable and degraded gradually after a week of irradiation. Sanchez-Prado et al. [86] also reached a similar conclusion that di-BDFs and tri-BDFs produced from the photodegradation of BDE-100 in solid ice increased rapidly followed by quick reduction. The time-scale of whole process was less than 10min. Although the PBDF concentration was low, their brief appearance nevertheless merits attention because of their high toxicity for humans and wildlife [102].

7. Photodegradation in TiO₂-media phase

TiO₂ when irradiated generates both oxidative and reductive species, so there have been extensive studies on the TiO₂ photocatalytic degradation of various organic contaminants [103-105]. The photodegradation of PBDEs in the presence of TiO₂ has two important pathways: (i) reductive debromination by the conduction band electrons (e_{CB}^-) and (ii) the hole-initiated oxidation. Upon photoexcitation of TiO₂, conduction band electrons are produced leaving holes in the valence band (h_{VB}^+) (eq. 1) [104,106]. The electrons can enable C-Br bond cleavage and thus promote the reductive debromination of PBDEs [107], while the holes can be scavenged by water in the photoreaction system to generate •OH radicals (eq. 2) that give rise to strong oxidation and even mineralization [108,109].

7.1 Kinetics in TiO_2 -media phase

The photocatalysis reactions of PBDEs by TiO_2 are compiled in Table 6. The relative significance of reductive and oxidative processes depends on the generation of CB electrons (e_{CB}^-) and $\bullet\text{OH}$ radicals. This section addresses the influencing factors for the main degradation process and photocatalytic reactivity.

Oxygen plays an important role in the generation of e_{CB}^- . Sun et al. [107] investigated the TiO_2 -mediated photocatalysis of BDE-209 in CH_3CN with isopropyl alcohol added as a quencher for $\bullet\text{OH}$ radicals. The results showed fast reaction with argon-purged samples, but degradation was only barely observed in air-saturated solutions, which was consistent with the results of a study published by Li et al. [110]. Compared to BDE-209, oxygen was more competitive in capturing CB electrons (eq. 3). Thus, in order to ensure reductive efficiency it is necessary to eliminate oxygen from the system.

The production of $\bullet\text{OH}$ radicals and e_{CB}^- depends on the type of solvent. Huang et al. [108] studied the formation of $\bullet\text{OH}$ radicals and e_{CB}^- in mixtures with different ratios of water and CH_3CN . The generation of e_{CB}^- significantly decreased with the addition of even 0.1% water, and it disappeared with 1% water content. Sun et al. [107] also reported that the addition of 1% water to CH_3CN prevented the photocatalytic removal of BDE-209 by TiO_2 , possibly because a water layer on the surface of the TiO_2 blocked electron transformation and

decreased the accumulation of electrons [107,111] . However, PBDEs pre-loaded on a TiO₂ surface or photocatalyzed by a modified TiO₂ (e.g., graphene oxide and montmorillonite-TiO₂) can still be reduced in an aqueous system [109,112,113].

In contrast, •OH radicals were significantly enhanced with increasing water content. This was because the increased adsorption of water molecules on a TiO₂ surface can facilitate the conversion of VB holes (h_{VB}^{+}) to •OH (eq. 2) [108]. To enhance the accumulation of e_{CB}^{-} , alcohols (e.g., methanol and isopropyl alcohol) can be added as electron donors to scavenge VB holes and prevent charge recombination (eq. 4) [107,112,113]. However, oxygen species such as •OH can be quenched by alcohols as well, considerably weakening the oxidation efficiency.

The photocatalytic reactivity also depends on the TiO₂ dose, the structure of the catalyst, the presence of humic acid, and pH. More TiO₂ provides more active sites on the interface and better degradation efficiency. Huang et al. [108] found that the debromination efficiency of BDE-209 greatly increased from 21.2% to 95.6% with an increase of TiO₂ dosage from 0 to 0.1g/L, but decreased again to less than 50% when the dose was increased to 1g/L. The increased turbidity of the TiO₂ suspension shortened the penetration depth of the irradiation and limited the photoexcitation of the TiO₂ [108,113].

Several crystalline forms of TiO₂, including anatase, rutile and mixtures of anatase and rutile, exhibit different photocatalytic performance. Chow et al. [114] found that both the production of reactive oxygen species (ROS) and the degradation of BDE-209 through TiO₂-mediated photocatalysis were highest in a mixture of anatase and rutile. This may be

because anatase acted as an oxidative center and rutile acted as a reductive one, promoting electron transfer and leading to a higher yield of ROS [114-116].

On the other hand, the debromination of PBDEs becomes more efficient as the concentration of humic acid in a TiO₂ suspension increased from 0 to 20mg/L, but it declined with a further increase to 40mg/L [114]. Humic acid can act as photosensitizers to produce reactive species that promote the breakdown of organic contaminants [79,117,118]. Too much humic acid may, however, reduce adsorption on the surface of the TiO₂ and thus inhibit photosensitization [114].

The presence of bases and acids can enhance or suppress the TiO₂-mediated photocatalysis of PBDEs [107,114]. The reduction of BDE-209 in CH₃CN is much faster in solutions containing bases (pyridine, trimethylamine, and dimethylformamide) than with the addition of formic, acetic or trifluoroacetic acid [107]. The Fermi level of TiO₂ can be shifted toward a negative potential by the adsorption of bases on the surface, whereas the adsorption of acids can shift the conduction band edge to the positive end [119,120]. In terms of oxidation process, the highest yield of ROS and the most efficient degradation BDE-209 was observed at pH 12 [114], suggesting that OH⁻ can enhance the transformation of VB holes to •OH radicals (eq. 2).

7.2 Mechanisms in TiO₂-mediated phase

In reductive degradation less-brominated BDEs are produced via the cleavage of C-Br bonds, but the debromination order at the *meta*, *para* and *ortho* positions may be different in aqueous and organic solvents. Concerning the *mono*-debrominated intermediates in BDE-209

degradation, the major nona-BDE in aqueous environments is BDE-207 [112]. In organic solvents (e.g. CH₃CN and CH₃OH) BDE-206 is the predominant mono-debrominated product [107], indicating different bromine reactivity of BDE-209 in these two photocatalytic systems. As has been mentioned in Section 3.2, bromines at the *ortho* position seem to be more active due to the lower dissociation energy of *ortho* C-Br bonds [67,107]. However, BDE-209 adsorption on TiO₂ is limited by its low solubility in an aqueous environment. Strong interaction due to the steric effects in water may cause the *meta* C-Br bond energy to be reduced to even lower than that of *ortho* C-Br bonds. Or the breaking of C-Br bonds may change from the stepwise mechanism of eq. 5 to the concerted one of eq. 6 with the polarization of C-Br bonds by trapped electrons [112,121].

Besides lower brominated BDEs, some phenolic intermediates such as 2,4-dibromophenol and pentabromophenol were also detected as byproducts of the fast photocatalytic degradation of BDE-209 over surface-palladized TiO₂ [110], indicating that the cleavage of C-O ether bonds also occurred. However, few phenolic intermediates can be observed on an untreated TiO₂ surface under the same irradiation, implying that the cleavage of ether bonds may be photoinduced by the Pd-catalyzed hydrogenation of oxygen [110].

Lei et al. [113] suggested a multi-electron induced debromination pathway for BDE-209 over graphene oxide-TiO₂. Graphene oxide can enhance the charge separation of TiO₂ (eq. 1) by storing and shuttling electrons to initiate multi-electron transfer to attack BDE-209. Unlike stepwise reduction, multi-electron induced debromination skips some reduction steps and

produces smaller amounts of less-brominated BDE congeners, thus achieving higher debromination efficiency [113].

The main oxidative degradation mechanisms of BDE-209 are illustrated in Scheme 8, including the $\bullet\text{OH}$ addition and HBr/Br elimination pathways [108]. The oxidative degradation of BDE-209 involved photogenerated holes (h^+) and $\bullet\text{OH}$ radicals and proceeded through three stages: parent pollutant $\rightarrow$ aromatic intermediates $\rightarrow$ aliphatic intermediates $\rightarrow$ $\text{CO}_2 + \text{H}_2\text{O} + \text{Br}^-$. Aromatic-OH adduct radicals were first formed by the addition of $\bullet\text{OH}$ or the reaction of holes (h^+) and water. Subsequently, due to the initial attack of $h^+/\bullet\text{OH}$ at the different carbon positions, pentabromophenol and pentabromophenoxy radicals were generated via the cleavage of ether bonds, while BDE-phenoxy radicals were formed by the rapid loss of HBr . After several steps of $h^+/\bullet\text{OH}$ addition and consecutive HBr/Br elimination, the phenyl rings were broken to produce brominated dienoic acids [108]. Only the aliphatic intermediates such as brominated dienoic acid were detected in experiments, implying that the transformation of aromatic intermediates was much faster than their generation due to the greater reactivity of lower brominated congeners toward $\bullet\text{OH}$ radicals [51,89,108].

A novel TiO_2 -immobilized hydrophobic montmorillonite was developed such that BDE-209 can be adsorbed into the montmorillonite to prevent blockage by the water layer during the photocatalytic reaction [109]. The degradation pathways involve reactions with CB electrons and $\bullet\text{OH}$ radicals (i.e., both reductive and oxidative processes). Highly-brominated BDEs tend to proceed through reductive debromination, while the lowerbrominated species were more active toward $\bullet\text{OH}$ radicals due to the electronic and steric effect of bromine on the aromatic system [109]. The localization of the substrates

(BDE-209) in the montmorillonite layers may also affect the degradation pathway. In addition to the less-brominated BDEs formed via reductive debromination, An et al. [109] also observed brominated phenoxy phenols, phenoxy phenols and small carboxylic acid as photoproducts, which likely originated from further reaction with $\bullet\text{OH}$ radicals. The whole degradation pathway is shown in Scheme 9.

The debromination efficiency (Y_{Br^-}) is generally used to evaluate the mineralization rate of BDE-209 in TiO_2 -photocatalytic studies (eq. 7). The oxidative processes occur in aqueous system without quenchers for $\bullet\text{OH}$ (e.g., alcohols), they can lead to more than 95% debromination efficiency after 12 h [108]. Regarding to the reductive pathways in deaerated solutions with added alcohols as activator, the debromination efficiency was only 45.7% after 24 h, unless grapheneoxide- TiO_2 photocatalyst had been used (90% after 24 h) [113].

$$Y_{\text{Br}^-}(\%) = \frac{[\text{Br}^-]_t / 80}{([\text{BDE-209}]_0 / 939.17) \times 10} \times 100 \quad (7)$$

where $[\text{Br}^-]_t$ is the mass concentration of Br^- at exposure time t , $[\text{BDE-209}]_0$ is the initial mass concentration of BDE-209.

8. Toxicity assessment.

As discussed earlier, a series of potentially more harmful products, such as lower brominated BDEs and PBDFs, are formed when PBDEs are exposed to irradiation [122]. Thus, toxicological evaluation is necessary for the mixture after photolysis of PBDEs. Hagberg et al. [123] and Olsman et al. [124] applied bioassays to assess the toxicological characterization of photolytic BDE-209 in toluene after irradiation with UV-A, UV-AB and UV-ABC. As revealed in Fig 5, the level of bioassays derived

2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents (bio-TEQs) after 16 h UV exposure increased with wider spectra, which was in agreement with the increased concentration of PBDFs [123]. Initially the UV-ABC experiment showed the same patterns as the UV-A and UV-AB but the formation of PBDFs was enhanced after complete degradation of BDE-209 at 8 h, which led to a significant increase of bio-TEQs. Similarly, Su et al. [125] found that the photolysis of BDE-209 resulted in the increased cytotoxicity and large mRNA alterations in chicken embryonic hepatocytes. In addition to the toxic photoproducts, some free radicals could be formed from the UV-AB photodecomposition of BDE-209, which potentially caused harmful effect to human skin [126].

9. Conclusions and recommendations

The kinetics and mechanisms of PBDE photodegradation in various environments have been critically reviewed and summarized. The photolytic kinetics are mostly pseudo-first order. Despite the different experimental conditions employed in the literature, the half-lives of PBDEs in solids and gases are consistently much longer than those in liquids, probably due to the relative lack of hydrogen donors and light screening effect. Reductive debromination and intermolecular elimination of HBr are the two common degradation pathways. The lower brominated PBDEs and PBDFs can be observed in almost all situations except TiO_2 -photocatalyzed degradation. The formation of other derivatives, such as OH-PBDEs, bromophenol, brominated-hydroxybiphenyl, and chlorinated BDEs depends on the matrix and the coexisting chemical species. TiO_2 -mediated photocatalytic oxidation shows the best degradation performance, resulting in more debromination and mineralization of PBDEs.

Existing knowledge of the photodegradation of PBDEs is still insufficient to fully illustrate the photochemical transformation kinetics and mechanisms in the natural environment. Further research is recommended to better identify the photodegradation products, elucidate the photochemical behavior of the derivatives, and analyze environmental samples under field-relevant conditions. No good mass balance of PBDEs after photodegradation has yet been reported. More complete identification of the photodegradation products is needed, especially for PBDE derivatives and non-PBDE byproducts. Further efforts are needed to better elucidate the photochemical behaviors of the derivatives resulting from PBDEs such as OH-PBDEs and MeO-PBDEs, as their toxicological consequences are more serious than those of PBDEs and carry greater potential risks for ecosystems. The detailed mechanisms of phototransformation in environmentally-relevant conditions remain uncertain and need further investigation. Experiments with authentic environmental samples should be prioritized, since humic substances, clay minerals, ferric ion, chloride ion and carboxylate can significantly influence the photochemical kinetics and mechanisms of degradation. And evaluation in field-relevant concentrations (e.g., ng/L in water) may better reflect the real scenarios in the environment.

Acknowledgements

We thank the National Basic Research Program of China (2015CB459000), National Science Foundation of China (21577178) and Science and Technology Planning Project of Guangdong Province of China (2014A020216010), for their financial support of this study.

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Table 1. The physicochemical properties of environmentally relevant PBDEs

Congener	T _m ^a (°C)	S _{w,25} ^b (ug/L)	Log K _{ow} ^c	H ₂₅ ^d (Pa m ³ /mol)	LC ₅₀ ^e (mg/L)
2,4,4'-Tribromodiphenyl ether (BDE-15)	57-58	130	5.55	21	3.6
2,4,4'-Tribromodiphenyl ether (BDE-28)	64-64.5	70	5.98	5.1	3.6
2,2',4,4'-Tetrabromodiphenyl ether (BDE-47)	83.5-84.5	15	6.55	1.5	4.2
2,2',4,4',5-Pentabromodiphenyl ether (BDE-99)	90-94.5	9.4	7.13	0.23	5.2
2,2',4,4',6-Pentabromodiphenyl ether (BDE-100)	100-101	40	6.86	0.069	8.4
2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153)	160-163	0.87	7.62	0.067	N/A
2,2',4,4',5,6'-Hexabromodiphenyl ether (BDE-154)	131-132.5	0.87	7.39	0.24	N/A
2,2',3,4,4',5',6-Heptabromodiphenyl ether (BDE-183)	171-173	1.5	8.27	0.0074	N/A
Decabromodiphenyl ether (BDE-209)	302.5	0.28	12.11	0.04	N/A

^a melting points, data from Ref. [31,32]^b aqueous solubilities at 25°C, data from Ref. [31,32]^c octanol–water partition coefficients, data from Ref. [32,48]^d Henry's law constants at 25°C, data from Ref. [30,32]^e the median lethal concentration of embryonic zebrafish, N/A=not available, data from Ref. [33]

Table 2. Summary of the photodegradation of PBDEs in organic solvent phase.

PBDE congeners	Matrix	Radiation source	Analytical Method	Photodegradation kinetics and mechanism	Ref
BDE-209	Hexane: benzene: acetone (8:1:1, v/v)	Mercury lamp (254 nm); Sunlight	GC-ECD GC-MS	Degradation products: octa- to tri-BDEs, hexa- to mono-BDFs, penta- to tetra- bromophenol Main mechanism: consecutive reductive debromination, intramolecular elimination of HBr and the cleavage of ether bond	[56]
BDE-15	MeOH; ACN; ACN:H ₂ O (1:1)	16-300 nm lamps	GC-MS ¹ H-NMR	Rate constants: $1.98 \times 10^{-2} \text{ min}^{-1}$ (ACN), $3.10 \times 10^{-2} \text{ min}^{-1}$ (MeOH) Degradation products: BDE-3, DE Main mechanism: consecutive reductive debromination	[70]
BDE-209	Toluene	Mercury UV-lamp (1.6 mW/cm ² , 300-400 nm)	GC-MS	Half-life: <0.25 h Degradation products: nona- to penta-BDEs Main mechanism: consecutive reductive debromination	[34]
BDE-209	Hexane	Sunlight	GC- μ ECD GC-MS	Rate constants: $1.86 \times 10^{-3} \text{ s}^{-1}$ (July of 2003), $1.11 \times 10^{-3} \text{ s}^{-1}$ (October of 2003) Degradation products: lower brominated BDEs Main mechanism: consecutive reductive debromination	[35]
BDE-209, 208, 207 206, 203, 190, 183 181, 155, 154, 139 138, 99, 77, 47	MeOH: H ₂ O (80:20, v/v); MeOH; THF	UV lamp (20W)	HPLC-UV GC-MS	Rate constants in MeOH:H₂O ($10^5 \times \text{s}^{-1}$): 40 (BDE-209), 17 (BDE-208), 19 (BDE-207), 8.3 (BDE-206), 3.7 (BDE-203), 3.0 (BDE-190), 0.67 (BDE-183), 3.2 (BDE-181), 0.41 (BDE-155), 0.33 (BDE-154), 0.40 (BDE-139), 0.62 (BDE-138), 0.3 (BDE-99), 0.06 (BDE-77), 0.07 (BDE-47) Rate constants in MeOH ($10^5 \times \text{s}^{-1}$): 65 (BDE-209), 30 (BDE-208), 32 (BDE-207), 13 (BDE-206), 5.9 (BDE-203), 1.1 (BDE-183), 5.6 (BDE-181), 0.67 (BDE-139), 0.12 (BDE-47) Rate constants in THF ($10^5 \times \text{s}^{-1}$): 83 (BDE-209), 46 (BDE-207), 9.4 (BDE-181), 0.2 (BDE-47) Degradation products: nona- to hexa-BDEs, penta- to di-BDFs and Meo- PBDFs Main mechanism: consecutive reductive debromination and intramolecular elimination of HBr	[50]
BDE-153	ACN	UV-lamp (6W, 302 nm)	GC-MS	Half-lives: 1.6 min Degradation products: lower brominated BDEs, penta- to mono-BDFs, tetrabrominated 2-hydroxybiphenyls Main mechanism: consecutive reductive debromination, intramolecular elimination of HBr and photo-Fries rearrangement	[71]

BDE-209, 99, 47	Isooctane	Sunlight	GC-MS	Half-lives: 0.6 h (BDE-209), 34 h (BDE-99), 204 h (BDE-47)	[57]
BDE-183, 153, 100, 99, 47, 28	Hexane	Mercury lamp (500W, >290 nm)	GC-ECD GC-MS	Half-lives: 0.26 h (BDE-183), 0.29 h (BDE-153), 6.46 h (BDE-100), 0.32h (BDE-99), 2.53 h (BDE-47), 4.97 h (BDE-28) Degradation products: lower brominated BDEs, few PBDFs Main mechanism: consecutive reductive debromination	[59]
BDE-209	THF; MeOH; MeOH:H ₂ O	UV-lamp (20W)	GC-MS	Degradation products: nona- to hexa- BDEs, penta- to mono-BDFs, penta- to tetra- MeO-PBDFs, tetra- to di-OH-PBDFs, bromophenol Main mechanism: consecutive reductive debromination, intramolecular elimination of HBr and the cleavage of ether bond	[73]
BDE-209, 208, 206, 207	Toluene; MeOH; THF	Sunlight	GC-MS LC-MS-MS	Rate constants in Toluene: 0.108 min ⁻¹ (BDE-209), 0.181 min ⁻¹ (BDE-208), 0.202 min ⁻¹ (BDE-207), 0.151 min ⁻¹ (BDE-206) Rate constants in MeOH: 0.0554 min ⁻¹ (BDE-209), 0.096 min ⁻¹ (BDE-208), 0.119 min ⁻¹ (BDE-207), 0.0678 min ⁻¹ (BDE-206) Rate constants in THF: 0.0751 min ⁻¹ (BDE-209), 0.046 min ⁻¹ (BDE-208), 0.0546 min ⁻¹ (BDE-207), 0.0307 min ⁻¹ (BDE-206) Degradation products: lower brominated BDEs Main mechanism: consecutive reductive debromination	[63]
BDE-209	THF; Ethanol; DCM; DMSO; Isopropanol; ACN; MeOH; Acetone	Xenon lamp (500 W)	GC-μECD HPLC-UV	Half-lives: 25.3 min ⁻¹ (THF), 35.1 min ⁻¹ (Ethanol), 37.7 min ⁻¹ (DCM), 41.7 min ⁻¹ (DMSO), 41.9 min ⁻¹ (Isopropanol), 45.4 min ⁻¹ (ACN), 51.5 min ⁻¹ (MeOH), 593.8 min ⁻¹ (Acetone)	[65]
BDE-183, 154, 153, 119, 100, 99, 85, 66, 52, 47, 33, 28, 17, 15, 8, 3, 2, 1	Hexane; MeOH	RPR-3000A lamp	GC-ECD	Rate constants in MeOH: 0.428 min ⁻¹ (BDE-183), 0.33 min ⁻¹ (BDE-154), 0.449 min ⁻¹ (BDE-153), 0.13 min ⁻¹ (BDE-119), 0.153 min ⁻¹ (BDE-100), 0.414 min ⁻¹ (BDE-99), 0.31 min ⁻¹ (BDE-85), 0.227 min ⁻¹ (BDE-66), 0.167 min ⁻¹ (BDE-52), 0.204 min ⁻¹ (BDE-47), 0.138 min ⁻¹ (BDE-33), 0.136 min ⁻¹ (BDE-28), 0.137 min ⁻¹ (BDE-17), 0.06 min ⁻¹ (BDE-15), 0.063 min ⁻¹ (BDE-8), 0.051 min ⁻¹ (BDE-3), 0.037 min ⁻¹ (BDE-2), 0.0395 min ⁻¹ (BDE-1) Rate constants in Hexane: 0.523 min ⁻¹ (BDE-183), 0.444 min ⁻¹ (BDE-154), 0.664 min ⁻¹ (BDE-153), 0.183 min ⁻¹ (BDE-119), 0.192 min ⁻¹ (BDE-100), 0.488 min ⁻¹ (BDE-99), 0.426 min ⁻¹ (BDE-85), 0.254 min ⁻¹ (BDE-66), 0.177 min ⁻¹ (BDE-52), 0.277 min ⁻¹ (BDE-47), 0.17 min ⁻¹ (BDE-33), 0.193 min ⁻¹ (BDE-28), 0.163 min ⁻¹ (BDE-17), 0.053 min ⁻¹ (BDE-15), 0.063 min ⁻¹ (BDE-8), 0.04 min ⁻¹ (BDE-3), 0.047 min ⁻¹ (BDE-2), 0.036 min ⁻¹ (BDE-1)	[62]

Technical octa-BDEs (DE-79)	MeOH	Sunlight simulator (SOL 500, 400 W, >280 nm)	HPLC-UV GC-ECD GC-MS	Half-lives in DE-79: 24.2 min (BDE-154), 15.1 min (BDE-153), 17.3 min (BDE-183), 7.2 min (BDE-197), 7.3 min (BDE-196) Half-lives of isolated congener: 9.4 min (BDE-154), 7.4 min (BDE-153), 9.0 min (BDE-183), 6.1 min (BDE-197), 4.6 min (BDE-196) Degradation products: lower brominated BDEs Main mechanism: consecutive reductive debromination	[58]
BDE-209, 208, 207, 206, 196, 183, 154, 153, 100, 99, 85, 47, 28	Hexane	Sunlight	GC-MS	Rate constants: 2.09 h ⁻¹ (BDE-209), 2.38 h ⁻¹ (BDE-208), 2.31 h ⁻¹ (BDE-207), 1.34 h ⁻¹ (BDE-206), 1.2 h ⁻¹ (BDE-196), 0.28 h ⁻¹ (BDE-183), 0.11 h ⁻¹ (BDE-154), 0.21 h ⁻¹ (BDE-153), 0.02 h ⁻¹ (BDE-100), 0.18 h ⁻¹ (BDE-99), 0.19 h ⁻¹ (BDE-85), 0.025 h ⁻¹ (BDE-47), 0.02 h ⁻¹ (BDE-28) Degradation products: lower brominated BDEs Main mechanism: consecutive reductive debromination	[66]
BDE-209	MeOH:H ₂ O (100:1, v/v); DMSO: H ₂ O (100:1, v/v) containing oxalate	PLS-SXE 300 Xe lamp (> 420 nm)	HPLC-UV GC-μECD	Half-lives in MeOH:H₂O: 21 min (ammonium oxalate), 12 min (potassium oxalate), 139 min (oxalic acid), 231 min (ammonium oxalate and hydrochloric acid) Half-lives in DMSO:H₂O: 173 min (ammonium oxalate) Degradation products: lower brominated BDEs Main mechanism: consecutive reductive debromination based on the halogen binding interaction	[74]
Technical octa-BDEs (DE-79)	MeOH; MeOH/H ₂ O	SOL 500 sunlight simulator (400 W, >280 nm)	GC-MS	Half-lives of BDE-183: 9 min (pure MeOH), 24 min (MeOH containing 20% H ₂ O), 44 min (MeOH containing 50% H ₂ O) Degradation products: lower brominated BDEs, bromophenol, bromo-benzene Main mechanism: consecutive reductive debromination, the cleavage of ether bond	[28]

Table 3. Summary of the photodegradation of PBDEs in aqueous phase.

PBDE congeners	Matrix	Radiation source	Analytical Method	Photodegradation kinetics and mechanism	Ref
BDE-153	Distilled water; Seawater	UV-lamp (6W, 302 nm)	GC-MS	Half-lives: 4.6 min (seawater); can not be calculated in distilled water Degradation products: lower brominated BDEs Main mechanism: consecutive reductive debromination	[71]
BDE-154, 153, 100, 99, 47	Water	Xenon lamp (1500 W); Sunlight	GC-MS	Half-lives under simulated sunlight: 2.41 min (BDE-154), 2.07 min (BDE-153), 4.62 min (BDE-100), 2.18 min (BDE-99), 4.16 min (BDE-47) Degradation products: lower brominated BDEs, PBDFs Main mechanism: consecutive reductive debromination, intramolecular elimination of HBr	[76]
BDE-209, 99 47	Baltic sea; Atlantic ocean	Sunlight	GC-MS	Half-lives at surface water: 0.02 d (BDE-209), 1.4 d (BDE-99), 8.4 d (BDE-47) Half-lives in Baltic sea (60 N°): 1.8 d (BDE-209), 121 d (BDE-99), 526 d (BDE-47) Half-lives in Atlantic ocean(60 N°): 0.4 d (BDE-209), 27 d (BDE-99), 115 d (BDE-47)	[57]
BDE-47	Nonionic surfactant solution (Brij 35, Brij 58 and Tween 80)	Low pressure mercury lamp (253.7 nm, 2.28×10^{-7} Einstein L ⁻¹ s ⁻¹)	GC-μECD GC-MS	Rate constants : 5.12×10^{-4} s ⁻¹ in water, $7.97-8.33 \times 10^{-4}$ s ⁻¹ in Brij 35, $7.33-7.92 \times 10^{-4}$ s ⁻¹ in Brij 58, $2.44-11.9 \times 10^{-4}$ s ⁻¹ in Tween 80 Degradation products: tri- to mono- BDEs, tri- to mono- BDFs Main mechanism: consecutive reductive debromination, intramolecular elimination of HBr	[84]
BDE-99	Surfactant solution (Brij 35, Brij 58)	Low pressure mercury lamp (253.7 nm, 2.28×10^{-7} Einstein L ⁻¹ s ⁻¹)	GC-μECD GC-MS	Rate constants : 6.1×10^{-4} s ⁻¹ in water/O ₂ , 12.8×10^{-4} s ⁻¹ in water/N ₂ , 12.2×10^{-4} s ⁻¹ in 0.4mM Brij 35/O ₂ , 14.6×10^{-4} s ⁻¹ in 0.4mM Brij 35/N ₂ , 11.4×10^{-4} s ⁻¹ in 0.4mM Brij 58/O ₂ , 13.1×10^{-4} s ⁻¹ in 0.4mM Brij 58/N ₂ Degradation products: tetra- to mono- BDEs, tetra- to mono- BDFs Main mechanism: consecutive reductive debromination, intramolecular elimination of HBr	[85]
BDE-100	Water	Low-pressure mercury lamp (254 nm)	GC-MS	Half-life: 4.3 min Degradation products: lower brominated BDEs, PBDFs Main mechanism: consecutive reductive debromination, intramolecular elimination of HBr	[86]
BDE-209	Water Ethanol	Xenon lamp (1500 W, 290-400 nm)	HPLC-UV	Half-lives: 69 min (water), 3.3 min (ethanol)	[23]

BDE-47	Water(containing ferric and chloride Ions)	Xenon lamp (500 W, > 300 nm)	GC-MS	<p>Degradation percentage (6 h): 11% in pure water, 52% (1 uM Fe(III), 34% (2.3 mgC/L humic acid), 11% (16.9 g/L Cl⁻), 77% (1 uM Fe(III) and 16.9 g/L Cl⁻)</p> <p>Degradation products: tri- to mono- BDEs, chlorinated-BDEs</p> <p>Main mechanism: consecutive reductive debromination and the reaction with chlorine radicals.</p>	[29]
BDE-47	Water(containing ferric ions and fulvic acid (FA))	Xenon lamp (>290 nm, 125 mW/cm ²)	GC-μECD GC-MS	<p>Rate constants: 0.18 h⁻¹ (2 uM Fe(III), pH=5.6), 0.22 h⁻¹ (5uM Fe(III), pH=5.6), 0.27 h⁻¹ (10uM Fe(III), pH=5.6), 0.18 h⁻¹ (5 uM Fe(III), pH=7.1), 0.16 h⁻¹ (5 uM Fe(III), pH=8.2), 0.16 h⁻¹ (0.2 mg/L FA, pH=5.6), 0.38 h⁻¹ (1 mg/L FA, pH=5.6), 0.56 h⁻¹ (5 mg/L FA, pH=5.6), 0.21 h⁻¹ (10 mg/L FA, pH=5.6), 0.27 h⁻¹ (5 uM Fe(III), 0.2 mg/L FA, pH=5.6), 0.46 h⁻¹ (5 uM Fe(III), 1 mg/L FA, pH=5.6), 0.57 h⁻¹ (5 uM Fe(III), 5 mg/L FA, pH=5.6), 0.26 h⁻¹ (5 uM Fe(III), 10 mg/L FA, pH=5.6)</p> <p>Formation products: OH-PBDEs</p> <p>Mechanism: the reaction with •OH radicals</p>	[22]
BDE-154, 153, 99, 47, 28	Water	Mercury and Xenon lamp (> 290 nm)	GC-μECD HPLC-UV	<p>Rate constants under Xe lamp: 0.128 h⁻¹ (BDE-154), 0.11 h⁻¹ (BDE-153), 0.078 h⁻¹ (BDE-99), 0.0463 h⁻¹ (BDE-47)</p> <p>Rate constants under Hg lamp: 18.42 min⁻¹ (BDE-47), 9.65 min⁻¹ (BDE-28), 17.52 min⁻¹ (BDE-47 in 100 mM IPA), 9.01 min⁻¹ (BDE-28 in 100 mM IPA), 14.05 min⁻¹ (BDE-47 in 5 mM NaN₃), 7.34 min⁻¹ (BDE-28 in 5 mM NaN₃)</p> <p>Mechanism: the reaction with •OH radicals and ¹O₂</p>	[77]

Table 4. Summary of the photodegradation of PBDEs in gaseous phase.

PBDE congeners	Matrix	Radiation source	Analytical Method	Photodegradation kinetics and mechanism	Ref
BDE-15, 11, 7, 4, 3, 2, 1 and DE	He-air mixture		GC-MS	•OH reaction rate constants ($10^{-12}\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$, 298K): 5.14 (BDE-15), 3.23 (BDE-11), 3.88 (BDE-7), 1.33 (BDE-4), 5.75 (BDE-3), 4.6(BDE-2) 4.7 (BDE-1), 7.45 (DE)	[87]
BDE-209, 99, 47	Lake superior air	Sunlight		Estimated photolysis rate constants: $0.047 \times 10^{-6}\text{s}^{-1}$ (BDE-209), $43 \times 10^{-6}\text{s}^{-1}$ (BDE-99), $26 \times 10^{-6}\text{s}^{-1}$ (BDE-47) Estimated •OH reaction rate constants: 0 (BDE-209), $0.31 \times 10^{-6}\text{s}^{-1}$ (BDE -99), $0.81 \times 10^{-6}\text{s}^{-1}$ (BDE-47)	[51]
BDE-15	Atmospheric Environment		Density functional theory	Estimated •OH reaction rate constants: $7.02 \times 10^{-12}\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ Degradation products: OH-PBDEs, bromophenol Main mechanism: Br substitution by•OH, abstraction of H gem to•OH in BDE-OH adducts by O ₂ .	[89]
BDE-7			Computational methods	Estimated •OH reaction rate constants: $3.76 \times 10^{-12}\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ (298K, title reaction) Main mechanism: hydroxyl addition and hydrogen abstraction	[91]
BDE-28	Atmospheric Environment		Computational methods	Estimated •OH reaction rate constants: $1.79 \times 10^{-12}\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ Estimated •OH reaction life time: 6.7 d Degradation products: OH-PBDEs, PBDDs, PBDFs Main mechanism: hydroxyl addition	[92]
BDE-47	Atmospheric Environment		Computational methods	Estimated •OH reaction rate constants: $0.83 \times 10^{-12}\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ Main mechanism: hydroxyl addition and hydrogen abstraction	[90]
BDE-47	Isooctane and Nonane (solution and their vapor phase)	UV-lamp (300 W, 30 mW/cm ²)	GC-MS	Degradation percentage(80 mL chamber): 100 % (nonane,24h), more than 70% (isooctane, 24h) Degradation products: tri- to mono- BDEs, bromophenols Main mechanism: consecutive reductive debromination and the reaction with•OH radicals	[88]

Table 5. Summary of the photodegradation of PBDEs in solid phase.

PBDE congeners	Matrix	Radiation source	Analytical Method	Photodegradation kinetics and mechanism	Ref
BDE-209	Quartz glass; Humic acid-coated sand	Sunlight phosphor lamp (RPR-3000A, 250-305 nm); Black-light phosphor lamp (RPR-3500A, 305-440 nm);Sunlight	HPLC-UV	Degradation percentage: 70.8% in quartz glass hydrated with water (72 h sunlight irradiation); 29.6% in quartz glass hydrated with humic acid solution (72 h sunlight irradiation); 69% in quartz glass hydrated with water (60 h 3000 A lamp irradiation); 43.8% in quartz glass hydrated water (240 h 3500 A lamps irradiation); 10.9% in humic acid-coated sand (96 h sunlight irradiation)	[94]
BDE-209	Silica gel; Sand; Soil; Sediment	Mercury UV-lamp (1.6 mW/cm ² , 300-400 nm); Sunlight	GC-MS	Half-lives (artificial UV light): <0.25 h (silica gel); 12 h (sand); 40-60 h (sediment); 150-200 h (soil) Half-lives (sunlight): 37 h (sand); 80 h (sediment) Degradation products: nona- to tetra-BDEs and penta- to tetra-BDFs Main mechanism: consecutive reductive debromination and intramolecular elimination of HBr	[34]
BDE-209	Montmorillonite; Kaonilite; Sediment; Al hydroxide; Mn dioxide; Fe oxide	Black light-phosphor UV-lamp (300-400 nm); Sunlight	HPLC-UV GC-ECD	Half-lives (artificial UV light): 36 d (montmorillonite), 44 d (kaonilite), 150 d (sediment), 178 d (Al hydroxide), 1423 d (Mn dioxide), no degradation in Fe oxide after 14 days irradiation. Half-lives (sunlight): 261 d (montmorillonite); 408 d (kaonilite), 990 d (sediment), no degradation in Al hydroxide, Mn dioxide, Fe oxide after 101 days irradiation. Degradation products: nona- to tri-BDEs Main mechanism: consecutive reductive debromination	[95]
BDE-209	TV casing; High-impact polystyrene (HIPS)	Sunlight	GC-MS	Half-lives: 51 d (pulverized HIPS); no obvious degradation in TV casing after 224 days irradiation Degradation products: nona- to hexa-BDEs and octa- to di-BDFs Main mechanism: consecutive reductive debromination and intramolecular elimination of HBr	[27]
BDE-209	House dust	Sunlight	GC-MS	Half-lives: 301 h (spiked dust); 408 h (natural dust) Degradation products: nona- to hepta-BDEs Main mechanism: consecutive reductive debromination	[97]
BDE-209	Personal vehicle dust; Sodium sulfate	UVA-340 lamp (17.5±1.5 W m ⁻²)	GC-MS	Half-lives: 18.7±1.8 d (sodium sulfate), no obvious degradation in personal vehicle dust after 56 d irradiation Degradation products: lower brominated BDEs Main mechanism: consecutive reductive debromination	[98]

BDE-209	Textile	UVA-340 lamp (1.25 W m ⁻²)	HPLC-UV	Rate constant: $3.94 \times 10^{-2} \text{ d}^{-1}$ Degradation products: BDE-208 to -206 Main mechanism: consecutive reductive debromination	[100]
BDE-100	Ice	Low-pressure mercury lamp (254 nm)	GC-MS	Half-life: 3.9 min Degradation products: tetra- to di-BDEs and tri- to di-BDFs Main mechanism: consecutive reductive debromination and intramolecular elimination of HBr	[86]

Table 6. Summary of the photodegradation of PBDEs in TiO₂-mediated phase.

PBDE congeners	Matrix	Experimental conditions	Analytical Method	Photocatalytic kinetics and mechanism	Ref
BDE-209	ACN; THF; Hexane; Toluene; Acetone; MeOH; DMSO; DMF	Xenon lamp (> 360 nm); 1 g/L TiO ₂ ; 0.33 M isopropyl alcohol; Purged with argon	HPLC-UV GC-MS	Rate constants: 0.33 min ⁻¹ , 90% degradation after 7.5 min (UV/TiO ₂ /ACN/ Ar) Degradation percentage (3 min): 0 % (hexane, toluene, THF, DMSO, acetone, ACN+1% H ₂ O, ACN+formic acid, ACN+acetic acid, ACN + TFA), 43.8% (MeOH), 85.9% (DMF), 63.6% (ACN), 43.6% (ACN+ 0.1% H ₂ O), 5.7% (ACN+0.2 % H ₂ O), 4.3% (ACN+0.5 % H ₂ O), 85.8 % (CAN +pyridine), 87.2% (ACN+ triethylamine), 95.6% (ACN+ DMF) Degradation products: nona- to tetra- BDEs Main mechanism: consecutive reductive debromination	[107]
BDE-209	Water:THF (95:5, v/v)	High pressure mercury lamp (125W); 0.3 g TiO ₂ immobilized hydrophobic montmorillonite	GC-MS LC-MS/MS	Rate constants: 1.3 h ⁻¹ for TiO ₂ : clay (1:4), 1.9 h ⁻¹ for TiO ₂ : clay (2:3), 2.0 h ⁻¹ for TiO ₂ : clay (3:2), 4.1 h ⁻¹ for TiO ₂ : clay (4:1) Degradation products: hexa- to mono- BDEs, OH-PBDEs, phenoxy phenols, small carboxylic acid Main mechanism: consecutive reductive debromination and oxidative process	[109]
BDE-209	MeOH; MeOH: H ₂ O (5:95)	Xenon lamp (> 360 nm); BDE-209 preloaded on TiO ₂ ; Purged with argon	HPLC-UV	Degradation percentage : 30% in MeOH: H ₂ O (5:95) by TiO ₂ after 4 h Degradation products: lower brominated BDEs Main mechanism: stepwise reductive process (MeOH), concerted process (aqueous system)	[112]
BDE-209	Water: ACN with 1% THF	0.1 g/L TiO ₂ ; Xenon lamp (360-400nm);	HPLC-UV LC-MS GC-MS	Debromination efficiency: 95.6 % (12 h, UV/TiO ₂ /H ₂ O) Degradation products: brominated dienoic acids, carboxylic derivatives, hydroxylated compounds Main mechanism: oxidative process	[108]
BDE-209	Water with 0.1% DMSO	Visible light; 1% nano-size TiO ₂	GC-MS	Half life: 3.05 d (1% TiO ₂), 4.05 d (0% TiO ₂) Degradation percentage (6 d) : 93% (pH=12), 91.6-93% (5-20 mg/L humic acid), 82% (anatase/rutile TiO ₂) Degradation products: penta- to tetra- BDEs Main mechanism: oxidative process	[114]
BDE-209	MeOH with 1% THF	Mercury lamp (100W, > 360 nm); 0.2 g/L Pd/ TiO ₂ ;Purged with argon	GC-μECD HPLC-UV	Degradation percentage: 100% after 4 min (Pd/ TiO ₂), 40% after 4 min (TiO ₂) Degradation products: lower brominated BDEs, diphenyl ether, bromo-phenol Main mechanism: consecutive reductive debromination and the cleavage of ether bond	[110]

BDE-209	Water with 2% MeOH and 1% THF	Xenon lamp (> 340 nm), 0.1 g/L grapheneoxide- TiO ₂ , Purged with nitrogen	HPLC-UV GC-MS	Degradation percentage: 100% after 24 h (grapheneoxide-TiO ₂ , TiO ₂) Debromination efficiency: 90% after 24 h (grapheneoxide-TiO ₂), 45.7% after 24 h (TiO ₂) Degradation products: lower brominated BDEs, Brominated carboxylic acids Main mechanism: multi-electron reductive debromination	[113]
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Figure

Figure 1. Chemical structure of polybrominated diphenyl ethers

Figure 2. Global PBDE restriction action in the recent 30 years. Reprinted with permission from Ref. [3]. Copyright 2015 Springer.

Figure 3. UV-vis absorption spectra of 25 PBDE congeners measured at 298 K in isoctane. Adapted with permission from Ref. [51]. Copyright 2007 American Chemical Society.

Figure 4. Atmospheric lifetimes of PBDEs as a function of bromine substitution with respect to OH radical reactions (τ_{OH}) and photolysis (τ_{photo}). The values of τ_{OH} were estimated from a structure-activity relationship [$\log \tau_{OH} = 0.2333(\#Br) + 1.472$; $R^2=0.941$, $N=48$]. The τ_{photo} values for 25 PBDE congeners (gray circles) were fitted with a straight line [$\log \tau_{photo} = -0.4031 (\#Br) + 2.527$; $R^2=0.838$, $N=25$]. Reprinted with permission from Ref. [51]. Copyright 2007 American Chemical Society.

(a)

(b)

Figure 5. (a) Comparison of bioassay derived TEQs (bio-TEQ) and estimated chemical TEQ (chem-TEQ) in UV-irradiated decaBDE solutions. (b) Change in concentrations of different PBDF homologue groups in UV irradiated decaBDE solution after different exposure times. Mono- and di-BDFs are included but not visible. Reprinted with permission from Ref. [123]. Copyright 2006 Elsevier.

(a)

(b)

Scheme 1. (a) Proposed photo-debromination scheme starting with BDE-209. Highlighted congeners are dominant in commercial mixtures. (b) Proposed photo-debromination scheme starting with BDE 183. Highlighted congeners are dominant in commercial mixtures. Reprinted with permission from Ref. [66]. Copyright 2013 Elsevier.

Scheme 2. Photodegradation mechanism of BDE-153 in acetonitrile, of which Route a stands for the intramolecular elimination of HBr, Route b stands for photo-Fries rearrangement, and Route c stands for the transformation pathway from brominated hydroxybiphenyl to PBDFs. Reproduced with permission from Ref. [71]. Copyright 2006 Elsevier.

Scheme 3. Photodegradation mechanism of BDE-209 in methanol, of which Route a stands for the formation mechanism of MeO-PBDFs and OH-PBDFs, and Route b stands for the cleavage of ether bond to produce bromophenols and bromobenzenes [28,50,73].

Scheme 4. Photodegradation mechanism of BDE-47 in aqueous solutions in the presence of ferric and chloride ions, of which Route a stands for consecutive debromination process, and Route b stands for the reaction with chlorine radicals to produce chlorinated BDEs. Reproduced with permission from Ref. [29]. Copyright 2014 Elsevier.

Scheme 5. Proposed pathway for the formation of 6-OH-BDE-47 and 2'-OH-BDE-68 from BDE-47. Reprinted with permission from Ref. [22]. Copyright 2015 American Chemical Society.

Scheme 6. Transformation pathway of BDE-47 under UV radiation in a two-film environment (gas and liquid phase). Reproduced with permission from Ref. [88]. Copyright 2013 Elsevier.

Scheme 7. Reaction channels for single $\bullet\text{OH}$ -initiated photooxidation of BDE-15 in the presence of O_2 (The width of the arrows indicates the relative importance of the reaction channel), of which Route a stands for bromo-substituted hydroxyl addition and Route b stands for hydrogen-substituted hydroxyl addition. Adapted with permission from Ref. [89]. Copyright 2011 American Chemical Society.

Scheme 8. Possible pathways for the photocatalytic oxidative degradation of BDE-209 over TiO_2 in aqueous dispersions. The brominated dienoic acids (bold characters) were detected in LC-MS measurements. Reprinted with permission from Ref. [108]. Copyright 2012 American Chemical Society.