

Photochemical Formation of Halogenated Dioxins from Hydroxylated Polybrominated Diphenyl Ethers (OH-PBDEs) and Chlorinated Derivatives (OH-PBCDEs)

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The potential photochemical formation of polybrominated and mixed halogenated dibenzo-*p*-dioxins (PBDDs and PXDDs) from hydroxylated polybrominated and polybrominated/chlorinated diphenyl ethers (OH-PBDEs and OH-PBCDEs) in aqueous solution was studied. The ortho-hydroxylated BDE47 derivative 6-OH-BDE47, and chlorinated derivatives 3-Cl-6-OH-BDE47, 5-Cl-6-OH-BDE47, and 3,5-Cl-6-OH-BDE47 were photolyzed under sunlight at 45° N latitude in buffered waters, Mississippi River water, Lake Josephine water, and ultrapure water adjusted to the pH of the natural waters. Chemical actinometry was used to determine reactant quantum yields which were calculated to be between 0.03 and 0.21, with lower yields for the chlorinated derivatives under all conditions. Quantum yields under natural water conditions were not significantly enhanced indicating that direct photolysis is the primary process of photochemical degradation. The formation of halogenated dioxins from the outdoor photolysis of the four OH-PBDEs/OH-PBCDEs under all conditions was confirmed. Dioxin yields of 0.7–3.6% were found, with higher yields for 6-OH-BDE47 under all conditions. This study suggests that photolysis of OH-PBDEs and OH-PBCDEs is a potential formation pathway of PBDDs and PXDDs in the environment.

Introduction

Polybrominated diphenyl ethers (PBDEs) have been used as flame retardants since the 1970s in both commercial and household products, and are susceptible to release during use. Release into the environment also occurs during production, disposal, and recycling of PBDE-containing products. PBDEs are ubiquitous in the environment and have been detected in air, water, wastewater effluent and sludge, sediment, humans, and numerous biological samples (1–4). Although penta- and octa-BDE mixtures are no longer produced in North America and the European Union, there

is evidence indicating that deca-BDE, which is still in production, may undergo photochemical debromination to form lower brominated congeners (5) which, as summarized by McDonald, bioaccumulate and are more bioactive (6). Continued production of deca-BDE, and use and disposal of penta- and octa-BDE-containing products, make it unclear whether the ban on lower brominated congeners will lead to lower levels in the environment (4).

In the environment, PBDEs are expected to primarily associate with air particles, sediment, and soils due to their hydrophobic nature and low vapor pressures. Several studies have shown, however, that PBDEs are present in wastewater influent and effluent (7–11), and thus it is unsurprising that PBDEs are commonly detected in aquatic organisms (1–3). Although >90% removal efficiencies during wastewater treatment (WWT) have been measured (7–9), effluent concentrations up to 0.31–0.90 µg/L (sum (Σ) tetra–hepta congeners) have been measured (8). Ueno et al. hypothesized that oxidation of PBDEs during WWT may occur, leading to the release of hydroxylated polybrominated diphenyl ethers (OH-PBDEs), after detecting higher ratios of ΣOH-PBDEs to ΣPBDEs (0.2–0.4) in surface water samples collected near WWT plants (12). Furthermore, it is possible that hydroxylation may activate the PBDEs toward chlorination during wastewater disinfection with chlorine. Many phenolic compounds are known to undergo electrophilic substitution (13), and triclosan, a hydroxylated polychlorinated diphenyl ether, has been shown to undergo chlorination in the positions ortho and para to the hydroxyl group when exposed to hypochlorous acid under drinking water treatment conditions (14). We hypothesize that chlorination of OH-PBDEs at nonbrominated ortho and/or para positions by free chlorine under WWT disinfection conditions may occur, leading to OH-PBCDEs.

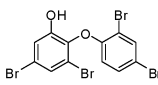
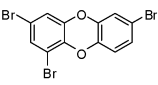
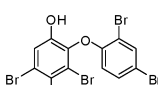
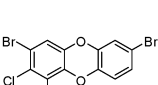
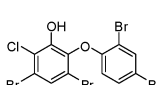
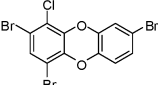
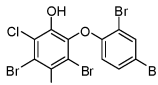
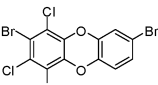
There is mounting evidence that suggests OH-PBDEs are ubiquitous in aquatic environments. In saltwater systems OH-PBDEs/OH-PBCDEs are primarily hydroxylated in the ortho position, and OH-PBDEs have been detected in aquatic organisms including sponges (15–17), tunicates (18, 19), red algae and blue mussels (20), Baltic Sea salmon (21, 22), and OH-PBCDEs have also been found in Baltic Sea salmon and marine sponge (22, 23). Evidence for natural production in saltwater systems is supported by radiocarbon data (24, 25), and cyanobacteria are likely one of the producers (26, 27). Although OH-PBDEs/OH-PBCDEs are not known natural products in freshwater systems, OH-PBDEs have been detected in fish from the Detroit River at ΣOH-PBDE concentrations of 2.7–198 pg/g wet weight (28). OH-PBDEs are known metabolites of PBDEs in rats and mice (29, 30), and in one study OH-PBDE concentrations in humans were found to correlate with PBDE concentrations suggesting metabolic production (31). In addition to PBDE metabolism and subsequent release, OH-PBDEs may also be produced atmospherically by the reaction of hydroxyl radical with PBDEs and thus enter surface waters with precipitation (32). Although Raff et al. found low levels of OH-PBDE production from the reaction of hydroxyl radical with PBDEs, the authors concluded that OH-PBDEs may have been degraded very quickly due to high hydroxyl radical concentrations (32). Additional support for atmospheric generation includes a recent study in Ontario, Canada that took place from 2002 to 2004 which found ΣOH-PBDEs fluxes of 15–170 pg/m²/day in rain and 3.5–190 pg/m²/day in snow (12). The detection of two unidentified tribrominated OH-PBDEs at roughly µg/L and high ng/L levels in wastewater/sewage treatment plant effluent (33) is especially relevant to our

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TABLE 1. Structures of Compounds Studied and Anticipated Dioxin Photoproducts

Parent Compound	Anticipated Dioxin
 6-OH-BDE47	 1,3,7-TBDD
 3-Cl-6-OH-BDE47	 1,3,7-TB-2-CDD
 5-Cl-6-OH-BDE47	 1,3,7-TB-4-CDD
 3,5-Cl-6-OH-BDE47	 1,3,7-TB-2,4-DCDD

work, and may support WWT as an additional source of OH-PBDEs into the environment. In addition to effluent discharge into water bodies, release into the environment from WWT plants may also occur from the land application of sewage sludge. PBDEs largely associate with sludge during WWT (7), and it is anticipated that OH-PBDEs/OH-PBCDEs will sorb to sewage sludge as well.

OH-PBDEs and OH-PBCDEs may be more photolabile and biodegradable than PBDEs. Nevertheless, work by van Boxtel et al. (34) has shown that 6-OH-BDE47 is toxic to zebrafish at nanomolar concentrations, and OH-PBDEs have also been shown to have estrogenic effects (35, 36) and may be endocrine disruptors (37). Furthermore, such compounds that are hydroxylated at an ortho position relative to the ether linkage with a halogen on an ortho position on the adjacent phenyl ring may undergo intramolecular photochemical substitution reactions to form dioxins. Triclosan and chlorinated triclosan derivatives, which fit this criteria, have been shown to form chlorinated dibenzo-*p*-dioxins when exposed to UV light in aqueous solution (38–41). Studies indicate that brominated dioxins have health effects comparable to their heavily regulated chlorinated analogs (42) making them of particular concern.

The aim of this study was to investigate the potential photochemical formation of halogenated dibenzo-*p*-dioxins from four OH-PBDEs/OH-PBCDEs in aqueous solution. PBDE photochemistry has been widely studied and major photoproducts include dibenzo-*p*-furans and lower brominated PBDEs (43–53). To our knowledge OH-PBDE/OH-PBCDE photochemistry has not been reported. Because 2,2',4,4'-tetrabromodiphenyl ether (BDE47) is one of the most ubiquitous PBDE congeners found in environmental samples (1–3), we studied the photochemistry of the ortho-hydroxylated derivative 6-OH-BDE47 (1), and chlorinated derivatives 3-Cl-6-OH-BDE47 (2), 5-Cl-6-OH-BDE47 (3), and 3,5-Cl-6-OH-BDE47 (4) (Table 1). Additionally, 6-OH-BDE47 is a known metabolite of BDE47 (29) and is considered a natural

product as well (20, 54). Detection in rain and snow also suggest atmospheric generation (12). The chlorinated derivatives chosen could result from the exposure of 6-OH-BDE47 to wastewater disinfection with chlorine. 3-Cl-6-OH-BDE47 has been found in marine sponge (23, 55), and 5-Cl-6-OH-BDE47 has been found in Baltic Sea salmon (22). The pK_a values of 1–4 were determined so that the reactant speciation could be calculated at any pH. From the sunlight photolysis of 1–4 reactant quantum yields (Φ_r) in buffered solutions, Mississippi River water (MRW), Lake Josephine water (LJW), and ultrapure water adjusted to LJW/MRW pH were determined, along with product yields for the expected dioxins 1,3,7-tribromodibenzo-*p*-dioxin (1,3,7-TBDD (5)), 1,3,7-tribromo-2-chlorodibenzo-*p*-dioxin (1,3,7-TB-2-CDD (6)), 1,3,7-tribromo-4-chlorodibenzo-*p*-dioxin (1,3,7-TB-4-CDD (7)), and 1,3,7-tribromo-2,4-dichlorodibenzo-*p*-dioxin (1,3,7-TB-2,4-DCDD (8)). A solar simulator was used to rapidly produce sufficient amounts of photoproducts for characterization purposes.

Materials and Methods

Chemicals. Compounds 1–4 were synthesized as described in the Supporting Information and purified to >98% by preparatory high-performance liquid chromatography (HPLC). *p*-Nitroacetophenone (PNAP; 97%) and *p*-nitroanisole (PNA; >99%) were purchased from Acros Organics, and pyridine ($\geq 99\%$) was purchased from Sigma Aldrich. 1,3,7-Tribromodibenzo-*p*-dioxin (5) (26 $\mu\text{g/mL}$ in toluene; 96%) was purchased from AccuStandard, Inc. Natural waters (MRW pH 8.2, dissolved organic carbon (DOC) = 11.5 mg/L, nitrate = 0.99 mg/L; and LJW pH 8.2, DOC = 12.4 mg/L, nitrate <0.01 mg/L) were collected in Minneapolis, MN and Roseville, MN, respectively, and 0.2 μm -filtered prior to use in photolysis experiments. pH measurements were made using a Thermo-Orion Ross Ultra Semi-Micro pH meter, DOC measurements were made with a Sievers 900 portable TOC analyzer, and nitrate was measured by ion chromatography with a Metrohm 761 Compact IC. Ultrapure water (18 M Ω) was obtained from a Millipore Simplicity UV purification system. All other solvents were of HPLC grade except *n*-hexane, which was of high-resolution gas chromatography grade.

pK_a Determinations. The pK_a values of 1–4 were determined spectrophotometrically using an Ocean Optics USB2000 spectrophotometer with a 1 cm quartz cell. 1–4 were dissolved in 60% methanolic solutions (v:v with water), adjusted to pH 11 with sodium hydroxide, and titrated with 0.1 and 1.0 M hydrochloric acid solutions. UV–vis absorbance spectra of the solutions were obtained at approximately 0.2 pH unit increments. By plotting the absorbance at the λ_{max} of the phenolate species versus pH, the pK_a values and respective 95% confidence intervals were determined using a nonlinear regression (KaleidaGraph v. 3.5).

Molar Absorptivity Determinations. Molar absorptivity values (ϵ) for 1–4 were calculated from absorbance data collected with an Ocean Optics USB2000 spectrophotometer for pH 10 borate and pH 4 acetate solutions. Due to low solubility 60% methanol was used as a cosolvent under acidic conditions. Molar absorptivity values under pH 8.2 conditions were calculated by determining the compound speciation at pH 8.2, and then computing the absorptivity from the phenol and phenolate absorptivities.

Photolysis Experiments. Photolysis samples were prepared by dissolving reactants 1–4 in 0.01 M pH 10 borate buffer, MRW, LJW, ultrapure water adjusted to pH 8.2, and 0.01 M pH 4 acetate buffer with 20% methanol by volume. The effect of the cosolvent under pH 4 conditions on Φ_r values was investigated under basic conditions due to greater reactant solubility. Comparing pH 10.1 Φ_r values against values obtained in methanol/borate buffer (20:80, v:v, final pH 10.1) the average difference in Φ_r values for 1–4 was

found to be 13%, and the cosolvent effect was deemed negligible. All sample solutions were sonicated and then filtered through 0.2 μm PTFE filters. Aliquots of the filtered samples were analyzed by HPLC to determine reactant concentrations. As necessary, samples were diluted to less than 10 μM to minimize light screening by the reactant. All photolysis experiments used quartz test tubes (OD = 13 mm, ID = 11 mm, $V = 10\text{ mL}$).

Duplicate or triplicate samples were photolyzed side-by-side with duplicate or triplicate actinometer solutions under natural sunlight in Minneapolis, MN (45° N latitude) during summer 2008. PNA (10.0 μM)/pyridine (10.0 mM) and PNAP (10.0 μM)/pyridine (20 or 70 mM) actinometer solutions were used for the basic and acidic photolysis experiments, respectively, as described by Leifer (56). Control samples were prepared by wrapping solution-containing test tubes with aluminum foil. Samples were oriented facing the sun at a 45° angle. At periodic intervals during the irradiation, 100 μL subsamples were taken for HPLC analysis. Reactant quantum yields were calculated using eq 1 (56):

$$\Phi_r = \frac{k_r \sum \epsilon_{a,\lambda} I_\lambda}{k_a \sum \epsilon_{r,\lambda} I_\lambda S_\lambda} \Phi_a \quad (1)$$

For experiments under basic conditions the observed first-order rate constants for the reactant and actinometer (k_r and k_a) were determined from the slopes of $\ln(C_t/C_0)$ vs photolysis time, where C_t is the concentration of the reactant or actinometer at a given time, and C_0 is the concentration of the initial subsample ($t = 0$). Under acidic conditions, reactant and actinometer rate constants could not be determined in this manner because of the variation in light intensity over the longer irradiance time. Instead, the ratio k_r/k_a was determined from the slope of $\ln(C_{r,t}/C_{r,0})$ vs $\ln(C_{a,t}/C_{a,0})$, and then used in eq 1. Solar irradiance values (I_λ) were calculated using the Simple Model of Atmospheric Radiative Transfer of Sunshine (SMARTS v. 2.9.5) (57, 58). Irradiance values were corrected for experiments performed in the natural waters to account for light screening (S_λ) by dissolved organic matter using eq 2 (56):

$$S_\lambda = \frac{1 - 10^{(-\alpha_\lambda z)}}{2.303\alpha_\lambda z} \quad (2)$$

where z is the path length, and α_λ is the beam attenuation coefficient (obtained from the UV-vis absorbance spectrum of the natural water). Actinometer quantum yield values (Φ_a) were calculated from pyridine concentrations as described elsewhere (56). Once Φ_r values were determined, maximum reaction rate constants were predicted using eq 3 (56):

$$k_{\text{max}} = 2.303\Phi_r \sum_\lambda \epsilon_{r,\lambda} I_\lambda S_\lambda \quad (3)$$

Photolysis experiments aimed at identifying OH-PBDE/OH-PBCDE photoproducts used an Atlas Suntest CPS+ solar simulator equipped with a Xe-arc lamp and a UV special glass filter to irradiate samples. Use of the solar simulator was justified by the observance of identical HPLC photoproduct peaks from sunlight and solar simulator photolysis of the reactants. HPLC analysis of photolyzed samples took place either by direct injection or extraction of the photolysis solutions with *n*-hexanes, followed by concentration, solvent exchange into methanol, and final injection of the concentrated methanol sample onto the HPLC. This method allowed for the preparative chromatographic isolation of individual photoproducts which were analyzed by GC/MS after photoproduct extraction and concentration. Photoproduct retention times and spectra were compared with standard material as available.

Analytical Methods. Photolysis solutions were analyzed using an 1100 Series Agilent HPLC equipped with UV-vis absorbance detection to determine rates of reactant loss and product growth. Analysis of photolyzed solutions used a Supelco Discovery RP-Amide C₁₆, 150 \times 4.6 mm, 5 μm particle size analytical column. The method for the analysis of photolyzed reactant samples consisted of a 85:15 A:B mobile phase, where A is methanol, and B is 90:10 pH 3 phosphate buffer/acetonitrile, 35 μL injections, 1.0 mL/min flow rate, and 230 nm detection. PNA actinometer samples were analyzed using 55:45 acetonitrile/pH 3 phosphate buffer as the mobile phase, 50 μL injections, 1.0 mL/min as the flow rate, and 280 nm detection, whereas PNAP samples were analyzed using a mobile phase of 56:44 acetonitrile/pH 5 acetate buffer, 100 μL injections, a flow rate of 1.0 mL/min, and 300 nm detection. Product identification by HPLC used an Agilent 1200 Series instrument equipped with photodiode array detection. The method and column for reactant analysis was also used for the analysis of OH-PBDE/OH-PBCDE photoproducts.

Product identification by GC/MS was performed using a HP 5890 Series GC system equipped with a HP 5972 Series electron impact mass spectrometer. The instrument was operated with helium as the carrier gas in splitless mode with a 30 m Restek Rtx-5 capillary column, 0.25 mm i.d. and 0.25 μm film thickness. The following conditions were used for the analysis: 1 μL injections, source temperature 280 °C, inlet temperature 270 °C, initial column temperature 40 °C (2.0 min), initial rate 10 °C/min to 180 °C and then 15 °C/min to 280 °C (7 min). The detector was operated in scan mode. Initial experiments indicated that **1–4** underwent thermal reactions in the injector to form both Smiles rearrangement products and dioxins via cyclization. To eliminate the possibility of thermal transformation of parent compounds into dioxins and Smiles rearrangement products, individual photoproducts were isolated by preparative HPLC before GC/MS analysis.

Results and Discussion

pK_a and Molar Absorptivity Determinations. The pK_a values of **1–4** were determined to be 8.28 ± 0.02 , 7.94 ± 0.03 , 7.20 ± 0.02 , and 6.29 ± 0.02 respectively (Figure S1). The chlorinated derivatives (**2–4**) are more acidic than **1** because of the electron-withdrawing nature of the chlorine atoms. Chlorination also leads to greater light absorbance in the solar region due to increased electron density of the phenol ring. The phenolate forms of **1–4** show enhanced light absorbance in the solar region compared to the phenol forms (Figure 1). Although this is primarily due to electron delocalization, enhanced solvation of the compounds may also lead to increased light absorbance. Because natural water pH is typically 6.5–8.5, a significant fraction of **1–4** will be in the phenolate forms (which have greater spectral overlap with sunlight) in aquatic environments.

Reactant Quantum Yields. Φ_r values of **1–4** over a range of conditions are shown in Table 2. Values range between 0.03 and 0.21, with the highest Φ_r values for **1** under all conditions. Although significant fractions of **1–4** are in both phenol and phenolate forms at pH 8.2 conditions, the phenolate fraction is responsible for >98% of the light absorbance (Table 2). Observed Φ_r values, therefore, are expected to be relatively independent of pH insofar as the phenolate is the major light absorber. With the exception of **1**, Φ_r values under the four basic conditions for the compounds were very similar. In pH 4.3 buffer Φ_r values were generally lower than under basic conditions indicating that the phenol forms more readily undergo deactivation back down to the ground state. Indirect photochemical degradation of **1–4** by dissolved organic matter (DOM)-produced reactive oxygen species does not appear to be

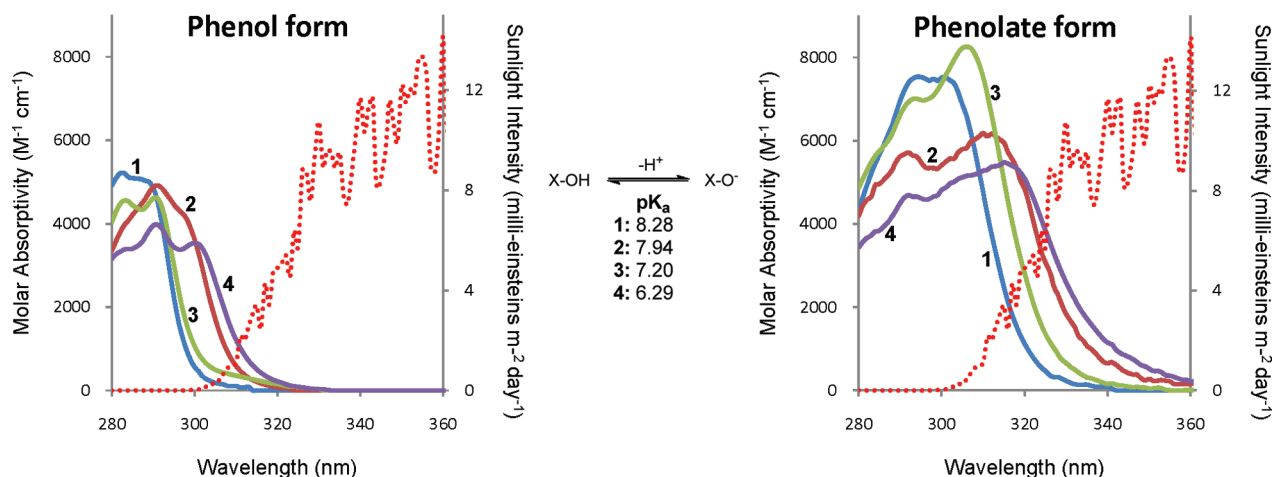


FIGURE 1. Overlap of the molar absorptivity of the phenol and phenolate forms of 6-OH-BDE47 (1), 3-Cl-6-OH-BDE47 (>2), 5-Cl-6-OH-BDE47 (3), and 3,5-Cl-6-OH-BDE47 (4) with the solar spectrum.

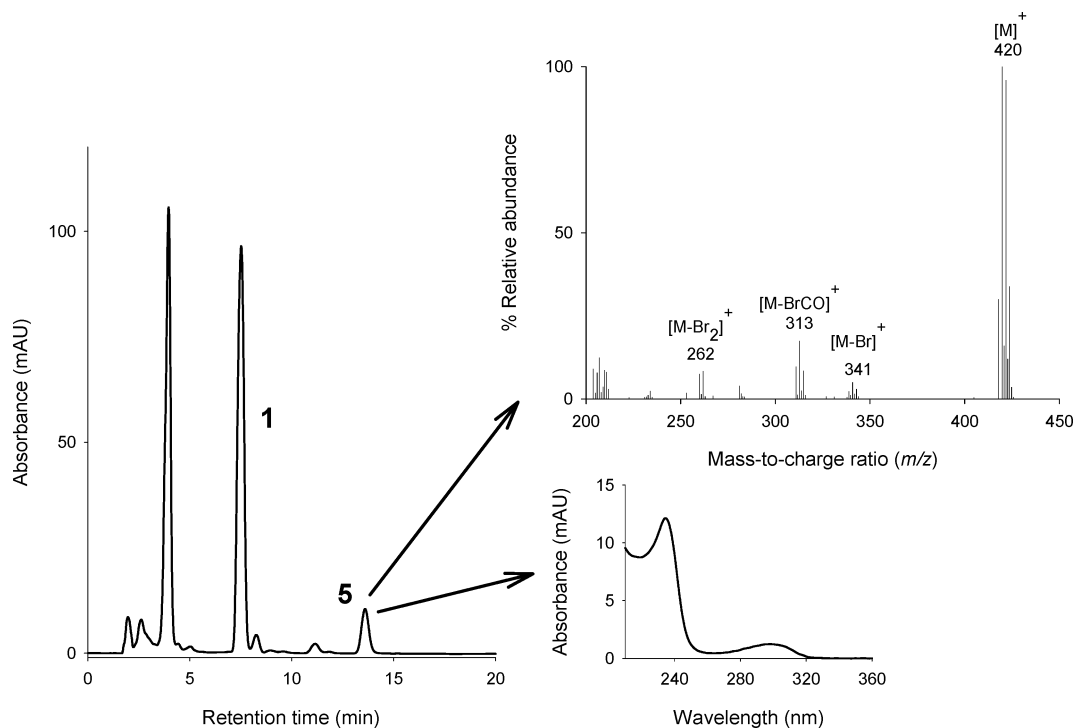


FIGURE 2. Characterization of the dioxin photoproduct of 6-OH-BDE47 photolysis by HPLC retention time, UV-vis absorbance spectrum, and MS fragmentation.

significant as Φ_r values in MRW and LJW are comparable to the values obtained in pH 8.2 ultrapure water. Similarly, hydroxyl radicals produced by nitrate do not appear to be important, but indirect photolysis processes may become important in waters with higher levels of sensitizers.

Rate Constants. Photolysis of pH 10.1 solutions occurred on June 18, 2008, pH 8.2 on July 4, 2008, and pH 4.3 experiments September 3–18, 2008. To compare the photoreactivity of 1–4 under the same solar conditions, rate constants were calculated for a surface of a water body under maximal sunlight intensity conditions (noon on June 20 at 45° N latitude with clear skies). Table 2 shows these calculated first-order rate constants (k_{\max}). Under the four basic conditions, 1–4 have rate constants that correspond to half-lives of 2–21 min, whereas under acidic conditions the half-lives are 3–28 h. Rate constants are driven by both quantum yields and light absorbance. Although quantum yields for the phenol forms of 1–4 are generally lower than the phenolate forms it can be concluded that the large difference in reaction rates is primarily driven by the much greater light

absorbance of the phenolates (Figure 1). Given their pK_a values, the rate of photochemical degradation of 1–4 in natural waters will be determined primarily by the speciation.

Dioxin Characterization. HPLC analysis of photolyzed solutions of 1 showed several product peaks (Figure 2). The UV-vis absorbance spectrum and MS fragmentation and isotope pattern of the late-eluting peak at 14 min are also shown in Figure 2. Comparison of this characterization data along with HPLC and GC retention times to that of an authentic standard of 5 confirmed that the late-eluting peak was the anticipated dioxin. Production of 5 was confirmed under all experimental conditions. Authentic standards of 6–8 were unavailable. As with the late-eluting peak from the photolysis of 1, the late-eluting peaks from the photolysis of 2–4 in all solutions were analyzed by GC/MS and HPLC. The MS fragmentation patterns, UV-vis absorbance spectra, and HPLC and GC/MS retention times supported that dioxins 6–8 are produced upon the photolysis of 2–4. Characterization data are shown in the Supporting Information. Although non-dioxin photoproducts were not characterized, we expect

TABLE 2. Solar Quantum Yields, Rate Constants, and Dioxin Yields for 6-OH-BDE47 (1), 3-Cl-6-OH-BDE47 (2), 5-Cl-6-OH-BDE47 (3), and 3,5-Cl-6-OH-BDE47 (4)

compound	conditions	pH	$\chi_{\text{phenolate}}^a$	phenolate contribution to light absorbance ^b	Φ_r	k_{max} (s ⁻¹) ^c	% dioxin yield
1	0.01 M borate buffer	10.1	0.985	100%	0.09	7.2×10^{-4}	3.5%
	Mississippi River water	8.2	0.448	99%	0.21	6.4×10^{-4}	3.2%
	Lake Josephine water	8.2	0.437	99%	0.21	6.7×10^{-4}	3.6%
	pH-adjusted water	8.2	0.443	99%	0.16	5.6×10^{-4}	-
	0.01 M acetate buffer	4.3	0.000	1%	0.07	6.8×10^{-6}	-
2	0.01 M borate buffer	10.1	0.993	100%	0.07	1.9×10^{-3}	1.3%
	Mississippi River water	8.2	0.640	98%	0.09	1.4×10^{-3}	1.2%
	Lake Josephine water	8.2	0.629	98%	0.10	1.8×10^{-3}	1.6%
	pH-adjusted water	8.2	0.635	98%	0.08	1.4×10^{-3}	-
	0.01 M acetate buffer	4.3	0.000	1%	0.04	3.4×10^{-5}	-
3	0.01 M borate buffer	10.1	0.999	100%	0.05	8.2×10^{-4}	2.1%
	Mississippi River water	8.2	0.907	99%	0.06	7.0×10^{-4}	0.9%
	Lake Josephine water	8.2	0.903	99%	0.06	8.2×10^{-4}	0.7%
	pH-adjusted water	8.2	0.905	99%	0.06	8.8×10^{-4}	1.2%
	0.01 M acetate buffer	4.3	0.001	2%	0.03	2.5×10^{-5}	-
4	0.01 M borate buffer	10.1	1.000	100%	0.04	1.3×10^{-3}	1.1%
	Mississippi River water	8.2	0.988	100%	0.03	9.8×10^{-4}	1.3%
	Lake Josephine water	8.2	0.987	100%	0.04	1.2×10^{-3}	1.2%
	pH-adjusted water	8.2	0.987	100%	0.03	1.2×10^{-3}	1.2%
	0.01 M acetate buffer	4.3	0.009	17%	0.04	7.6×10^{-5}	-

^a $\chi_{\text{phenolate}}$ = fraction of reactant in phenolate form. ^b Phenolate contribution to light absorbance = $(\chi_A \Sigma \epsilon_{A,i} I_i) / (\chi_A \Sigma \epsilon_{A,i} I_i + \chi_{\text{HA}} \Sigma \epsilon_{\text{HA},i} I_i) \times 100\%$; A⁻ = phenolate, HA = phenol. ^c Calculated rate constant for the surface of a water body on June 20 at noon at 45° N with clear skies. Irradiance calculated with SMARTS to be 583 W/m² (300–800 nm) under these conditions.

dibenzo-*p*-furans, bromo- and bromo/chloro-phenols, and debromination products to be produced from the photolysis of OH-PBDEs/OH-PBCDEs.

Dioxin Yields. The rates of dioxin production and reactant degradation were fit to a set of first-order differential equations (using Scientist for Windows, v. 2.01, Micromath Scientific) to determine the rate constants of dioxin production (k_{dioxin}) and formation of all other photoproducts (k_{other}). Dioxin yields were determined from the ratio $(k_{\text{dioxin}})/(k_{\text{dioxin}} + k_{\text{other}})$. The determination of dioxin rates of formation required quantification of dioxin peaks. Because standards for 6–8 were unavailable, HPLC response factors were approximated by applying the relative response factors of 1–4 to 5–8 using the response factor of 5 to determine the relative response factor between parent and dioxin compounds. Dioxin yields are shown in Table 2 (although not shown, quantum yields of dioxin formation can be calculated from the product: $\Phi_r \times \text{dioxin yield}$). Dioxin yields were not determined for 1–2 in pH 8.2 water due to low solubility, and 1–4 in pH 4.3 acetate (20% methanol) because of potential cosolvent effects. Calculated yields ranged between 0.7 and 3.6% which are comparable to values found for triclosan and its chlorinated derivatives under various conditions (38, 41). The yields for 1–4 were generally unaffected by the presence of DOM. 1 was found to have higher yields than 2–4 under all conditions. Lower yields for 2–4 are likely owing to the increased halogenation of the phenol ring, which leads to greater relative light absorbance by the phenol ring compared to the nonphenolic ring. Support for the idea that the two phenyl rings act as separate chromophores is found in the discussion of UV–vis absorbance spectra of PBDEs (59). Dioxin production from 1–4 likely proceeds by the nonphenolic ring first absorbing a photon, which can lead to cleavage of the C–Br bond in the ortho position. The resulting ion or radical can then undergo cyclization to form the dioxin. It is therefore anticipated that ortho-hydroxylated PBDEs/PBCDEs with more halogens on the non-phenolic ring will have higher dioxin yields than their lesser halogenated counterparts. Similarly, those with

high degrees of halogenation on the phenolic ring will lead to lower yields.

Environmental Implications. Based on our observed results, when exposed to sunlight in aquatic environments all ortho-hydroxylated PBDEs/PBCDEs that are halogenated in at least one ortho position on the adjacent phenyl ring are expected to photodegrade to form halogenated dioxins, among other photoproducts. Photochemistry is one of several processes that would lead to the transformation and/or removal of OH-PBDEs/OH-PBCDEs from aquatic environments. Other loss processes include sorption to organic matter/particles and settling, biological uptake and degradation, and volatilization. The significance of photochemical removal and hence extent of dioxin production will depend on many factors including water clarity, sunlight intensity, and water body pH. Because the phenolate forms are much more photolabile, knowledge of the reactant pK_a and natural water pH will be important in predicting the potential of photochemical transformation into dioxins. Under conditions where OH-PBDEs/OH-PBCDEs are primarily protonated, loss due to sorption would increase and photochemical degradation decrease.

Once produced, halogenated dioxins are not expected to be long-lived in the water column. Sorption/settling would likely be the major loss process in most water bodies. Few studies have investigated the aquatic photochemistry of halogenated dibenzo-*p*-dioxins, but work by Kim et al. (60) determined 1,2,7,8-tetrachlorodibenzo-*p*-dioxin and octachlorodibenzo-*p*-dioxin to have half-lives of 6.4 and 23 h respectively, in pure water under sunlight at 42° N in July. Photochemical degradation of brominated and bromo/chloro dioxins could therefore be significant in their removal from water bodies.

Because OH-PBDEs/OH-PBCDEs have been detected in numerous samples from aquatic environments, it is expected that photochemically generated halogenated dioxins are also ubiquitous in aquatic environments. 2'-OH-BDE68 and 6-OH-BDE47 are the two most commonly detected tetra-brominated OH-PBDEs in samples from the Baltic Sea, including

red alga and cyanobacteria (54), and algae, mussels, and salmon (20). As shown in our work, 6-OH-BDE47 photodegrades to form 1,3,7-TBDD, and 2'-OH-BDE68 is expected to form 1,3,8-TBDD upon exposure to sunlight in water. Malmvärn et al. (61) analyzed blue mussels from the Baltic Sea for PBDDs and found 1,3,7-TBDD and 1,3,8-TBDD to account for >90% of the di- through tetra-brominated congeners detected. Similarly, Haglund et al. (62) detected 1,3,7-TBDD and 1,3,8-TBDD as the major PBDDs in marine fish, mussels, and shellfish from the Baltic Sea. We propose that the photochemical transformation of OH-PBDE natural products is at least in part leading to the detection of brominated dioxins in samples from the Baltic Sea. This transformation could be occurring within OH-PBDE producing aquatic organisms in addition to surface waters containing OH-PBDEs. A recent study found ΣOH-tetraBDE concentrations of 39 ng/g dry weight and estimated ΣtriBDDs at 0.45 ng/g dry weight in the red alga *Ceramium tenuicorne* from the Baltic Sea (54). These findings may be explainable by the photochemical degradation of OH-PBDEs into brominated dioxins. Photochemistry could be the link that similarly helps to explain the occurrence of halogenated dioxins in other aquatic environments where OH-PBDEs/OH-PBCDEs are present.

WWT plants may be an additional source of dioxin precursors in aquatic environments. This will depend on the degree of PBDE hydroxylation during WWT. The chlorinated derivatives 2–4 are more acidic than 1, and therefore potentially more water-soluble and available to undergo photochemical transformations into dioxins. Chlorination of the phenol ring would be beneficial as it is expected to decrease dioxin yields and favor the production of other products, which would probably be less toxic. On the other hand, the dioxins that do form from these halogenated compounds would likely be more toxic given their higher degree of halogenation. Incomplete removal of PBDE metabolites during WWT, excretion of PBDE metabolites by wildlife, and precipitation may also be sources of dioxin precursors into aquatic environments. Further studies are warranted to investigate the presence of OH-PBDEs/OH-PBCDEs and halogenated dioxins in aquatic environments and organisms.

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Supporting Information Available

Synthesis and purification of 1–4, titration curves of 1–4 for spectrophotometric pK_a determinations, kinetic plots of 1–4 in borate buffer, MRW, LJW, ultrapure water adjusted to pH 8.2, and pH 4 acetate buffer/methanol, and UV–vis absorbance and mass spectra of 5–8. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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