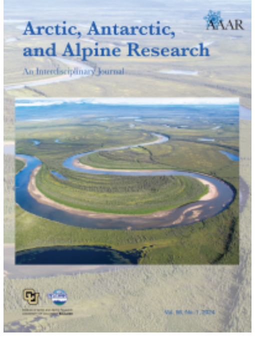

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Arctic, Antarctic, and Alpine Research
An Interdisciplinary Journal

ISSN: (Print) (Online) Journal homepage: www.tandfonline.com/journals/uaar20

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To cite this article: Robyn C. O'Halloran, Jill Kerrigan, Lauren E. O'Connor, Jennifer J. Guerard, Kimberly J. Hageman & Yu-Ping Chin (2024) Photofate of Tetrabromobisphenol-A in the Arctic: Role of photofluence and dissolved organic matter, Arctic, Antarctic, and Alpine Research, 56:1, 2372867, DOI: 10.1080/15230430.2024.2372867

To link to this article: https://doi.org/10.1080/15230430.2024.2372867

ARCTIC, ANTARCTIC, AND ALPINE RESEARCH
2024, VOL. 56, NO. 1, 2372867
https://doi.org/10.1080/15230430.2024.2372867

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Photofate of Tetrabromobisphenol-A in the Arctic: Role of photofluence and dissolved organic matter

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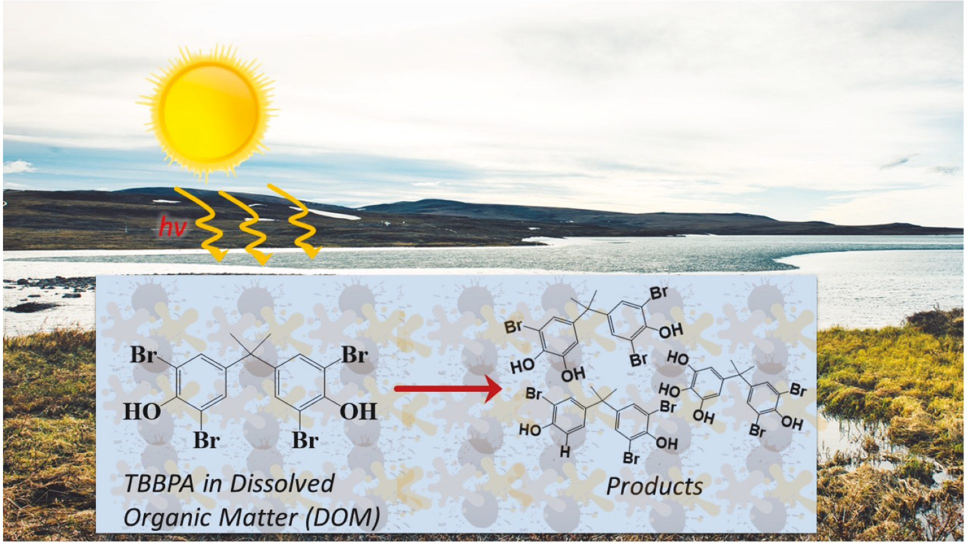
ABSTRACT

Polybrominated diphenyl ethers (PBDEs) used in consumer goods and flame retardants have been replaced by alternatives such as tetrabromobisphenol A (TBBPA). TBBPA does not readily undergo global distal transport, but local sources still threaten aquatic ecosystems. We studied the photofate of TBBPA with a specific focus on how Arctic-derived dissolved organic matter (DOM) affects its reaction kinetics, degradation pathways and formation of photoproducts in artificial and natural sunlight. Our results corroborate earlier studies that reveal a pH-dependent trend in TBBPA's direct photolysis with longer degradation times for its acidic form. DOM either plays no role or it slightly reduces TBBPA's rate of photodegradation via inner-filter effects. Photolysis experiments conducted at our Arctic field site, Toolik Lake Field Station, revealed slower than anticipated degradation, which magnified the half-life significantly during in-lake experiments. Importantly, the composition of DOM was found to influence the type and distribution of TBBPA photoproducts formed, which suggests that different degradation pathways occur in the presence of DOM. These findings provide valuable insights into the intricate interplay of environmental variables that govern the fate of TBBPA in sunlit aquatic ecosystems globally.

ARTICLE HISTORY
Received 30 January 2024
Revised 28 May 2024
Accepted 13 June 2024

KEYWORDS
Tetrabromobisphenol A; photolysis; Arctic; fate; dissolved organic matter



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Supplemental data for this article can be accessed online at https://doi.org/10.1080/15230430.2024.2372867.

Introduction

Tetrabromobisphenol A (TBBPA), a novel brominated flame retardant (BFR), has supplanted polybrominated diphenyl ethers (PBDEs) in global use. This substance is widely employed in the production of printed circuit boards and acrylonitrile butadiene styrene (ABS) plastics, contributing to an estimated global usage of 200 million metric tons (Howard and Muir 2010). While TBBPA can be chemically bound in resins and poses minimal risk to human health, its presence in the environment is a concern. This chemical has been detected in air, surface waters, sediments, and aquatic organisms in lower latitudes with levels elevated near facilities that manufacture and recycle flame retardants (Morris et al. 2004; Yang et al. 2012; Liu et al. 2016, 2017; UNEP 2017; Okeke et al. 2022). TBBPA has also been found to be persistent in a variety of media due to its large, although pH-dependent octanol-water partition coefficient (K_{ow}) (Malkoske et al. 2016, and references therein). For example, Qiao et al. (2023) found TBBPA adsorption to sediments to be well described by Freundlich isotherms, but anionic TBBPA did not sorb as readily and the presence of humic acid also hindered sorption. In addition, several studies have identified endocrine disrupting properties, with mixed results regarding its biomagnification potential and toxicity (Morris et al. 2004; Letcher et al. 2010; Colnot, Kacew, and Dekant 2013; Liu et al. 2015; Vorkamp et al. 2019).

While concentrations of TBBPA are low in both surface waters (undetectable to approximately 20 ng/L; Liu et al. 2016) and sediments (detection near or below detection limits; Bakke et al. 2008) globally, there is some evidence of long-range transport of TBBPA to high latitudes. These include the Arctic (De Wit, Alaee, and Muir 2006; Xie et al. 2007; Vorkamp et al. 2019) and the Antarctic (Wild et al. 2022). It has been detected on Arctic vegetation, as well as in predatory birds in Greenland, and cod liver, showing some potential for bioaccumulation/biomagnification (de Wit, Herzke, and Vorkamp 2010). Further, TBBPA has been detected in Nunavut children (Gibson et al. 2016), and shown to affect a major regulator of adipogenesis in polar bears (Routti et al. 2016).

In terms of persistence, it is largely believed that photodegradation is a prominent attenuation mechanism. TBBPA readily undergoes direct photolysis, with a half-life slightly over an hour in simulated sunlight (Wang et al. 2015; Bao and Niu 2015; Xiong et al. 2020). Like sorption, photolysis of TBBPA is also pH-dependent. The more soluble conjugate base ($TBBPA^{-}$) has a significantly higher molar absorptivity, resulting in 6x faster photoreactivity than the protonated form. Given its pK_a values of 7.5 and 8.5, a substantial fraction of TBBPA is thus highly reactive in natural waters.

The production of reactive transient species in aquatic environments is dependent upon dissolved organic matter (DOM) composition (Chin et al. 2004; Guerard et al. 2009; Sharpless et al. 2012; Porras et al. 2014; McNeill and Canonica 2016). Thus, it is worth studying TBBPA in the presence of DOM derived from specific environments over humic acid analogs (Malcolm and MacCarthy, 1986; Chin, Aiken, and O'Loughlin 1994; Bokare and Choi 2015). Given the large degree of indirect enhancement observed for other contaminants in previous studies, the mechanisms by which TBBPA photodegrades may differ considerably in different surface waters.

Previous research attributes TBBPA direct photolysis to the existence of reactive oxygen species (ROS), e.g., $\bullet OH$, $^1O_2$, and $O_2^{\bullet -}$ (Bao and Niu 2015) formed from the photo-excited state of the analyte itself. Photo self-sensitization has been observed for many compounds that undergo observed "direct photolysis" since the photon energy present in sunlight in many cases is insufficient to result in homolytic cleavage of the compound (Fasnacht and Blough 2002; Xie, Hu, and Cheng 2016). TBBPA may also be photochemically dehalogenated to bisphenol A (Bao and Niu 2015), which could further react in the presence of DOM, which generates additional ROS as well as excited triplets (Chin et al. 2004). Furthermore, under anoxic conditions, debromination products stemming from TBBPA photolysis have been observed, though the source of the hydrogen donor remains unidentified (Wang et al. 2015). However, despite DOM's ability to generate ROS and other reactive species in sunlight, previous studies show that DOM predominantly hinders TBBPA degradation via light screening (Han et al. 2009; Xiong et al. 2020; Feng et al. 2022).

TBBPA's short photodegradation kinetics lends itself as an ideal model for applying a fluence-based approach to compare degradation conducted outdoors vs. under simulated sunlight, as well as at different latitudes and light regimes (such as under water). Despite these short half-lives, TBBPA occurrence has nevertheless been observed in Arctic organisms, but not water or sediments. Thus, studying its degradation in high-latitude systems may help us better understand why this bias occurs, despite its photo-lability. To our knowledge, no study of the photochemical transformation mechanisms has been conducted on TBBPA that specifically examines the role of organic matter composition, especially DOM derived from Arctic surface waters.

We investigated TBBPA's photofate under both artificial and natural sunlight conditions, and in the presence of Arctic DOM from diverse surface waters and also reference end-members. To assess the effects of photon flux, we conducted natural sunlight experiments at a temperate latitude (Newark, DE, USA, 39.68° N) and above the Arctic Circle (Toolik Field Station, Alaska, USA, 68.64° N). Finally, we performed photolysis experiments under water in Toolik Lake, investigating whether disparities in photolysis kinetics between near-surface and 5 cm depth could be fully explained by light attenuation alone.

Experimental

Dissolved Organic Matter (DOM)

The solid phase extracted DOM isolates included in this study were from: Toolik Lake (TL), Sagavanirktok Seep (SAG), Oksrukuyik Seep (OKS), and International Humic Substance Society Pony Lake (PL; IHSS 1R109F), and Suwannee River (SR; IHSS 2R101N) (Table 1). Concentrated DOM stock solutions were prepared by redissolving DOM isolate into ultrapure Milli-Q treated and total organic carbon (TOC)-free water (18 MΩ, Millipore). The Arctic DOMs: SAG, TL, and OKS were previously collected from the Alaskan Arctic and characterized (Wei-Haas, Hageman, and Chin 2014; O'Connor et al. 2023). PL (Cawley et al. 2013) comes from the Antarctic and has also been thoroughly characterized, though no longer commercially available. Although the commercially available SR DOM is not derive from a polar latitude, it was included because it has been extensively studied (Chin et al. 2023).

The concentrated DOM stock solutions were vacuum filtered through 0.7 µm, 47 mm glass fiber filters (Whatman GF/F 1825–047). The organic carbon (OC) content of the filtered DOM concentrates was determined on a Shimadzu TOC-L (Shimadzu, Kyoto, Japan) against potassium hydrogen phthalate standards and ultrapure (water 18 MΩ) blanks. Filtered DOM concentrates were stored in the dark at 4° C until use. We and others (Sugimura and Suzuki 1988; Gulliver et al. 2010; Spencer, Butler, and Aiken 2012) have found that DOM does not appreciably change in quantity or composition when stored in this manner. There was no evidence of particulate formation during storage.

Whole waters were collected from Toolik Lake, Oksrukuyik Seep, and Fog Lakes 1 and 2 in June of 2019. These were also filtered through 0.7 µm 47 mm GF/F filters and stored in the dark at 4°C before pH adjustment for use in Arctic sunlight experiments (Table 2).

Photolysis experiments

Photolysis experiments were conducted in simulated sunlight, natural sunlight, and outdoors underwater. For both direct and indirect photolysis, experiments were conducted at varying pH (5.5, 8, 10.5) to bracket the $\mathrm{p}K_a$ of TBBPA. Indirect photolysis experiments were conducted with DOM (1, 2.5, 5, 10, and 20 mg C/L) solutions from each isolate (Table 1). Simulated sunlight experiments were conducted using a Suntest CPS+ with a 500 W filter Xe Arc Lamp (Atlas instruments, Mount Prospect, IL) with internal temperature maintained near

Table 1. Origin and properties of DOM isolates used in this study.

Source	Toolik Lake[a]	Sagavanirktok Seep[a]	Oksrukuyik Seep[a]	Suwannee River[c]	Pony Lake[c]
Abbr.	TL	SAG	OKS	SR	PL
Collected	Jul-13	Jun-13	Jul-13	IHSS (2R101N)	IHSS (1R109F)
Location	AK, USA	AK, USA	AK, USA	GA, USA	Antarctica
Extraction	PPL	PPL	PPL	RO	XAD-8
SUVA_{254} (L/mg/m)[b]	3.6	4.6	4.2	5.0	2.8
FI[b]	1.49	1.44	1.37	1.35	1.48

[a]Toolik Lake, Saganavirktok, and Oksrukuyik Seep isolates from Wei-Haas, Hageman, and Chin (2014); [b]Specific UV absorbance at 254 nm and fluorescence index (FI) from (O'Connor et al. 2023); [c]Obtained from the International Humic Substance Society (IHSS).

Table 2. Sampled Alaskan Arctic waters filtered to 0.7 µm and used in this study. Data from (O'Connor et al. 2023).

Source	Toolik Lake	Fog 1 Lake	Fog 2 Lake	Oksrukuyik Seep
Abbr.	TL	Fog1	Fog2	OKS
Collected	Jul-19	Jul-19	Jul-19	Jul-19
Latitude	68°38' N	68°40' N	68°41' N	68°41' N
Longitude	149°36′ W	149°5′ W	149°5′ W	149°7′ W
DOC (mg/L)	5	3	3	15
pH	7.28	7.85	7.82	6.75
Sp. Cond. (µs/cm)	12.1	100.5	97.6	61.4

20°C. Outdoor experiments were either conducted at the University of Delaware (Newark, DE 39.680967°N, −75.751658°W) using DOM isolates described in Table 1 or at Toolik Lake Field Station (TFS), AK, USA (68.628103°N, −149.594320°W) using filtered whole water samples described in Table 2. The underwater experiments were conducted in Toolik Lake, an oligotrophic lake. Analyte controls and blanks were run concurrently.

For all experiments, TBBPA was dissolved in hexane to create a 1 mM stock solution. This stock solution was plated on the inside of a glass amber reactor and the solvent allowed to evaporate. Ultrapure Milli-Q water, Millipore) or DOM stock diluted to working concentrations, or filtered whole water were added and stirred overnight to achieve equilibration, the time of which was evaluated in previous experiments (data not shown). Initial concentrations were measured for all experiments at time zero, as this was required to elucidate the pseudo-first order apparent rate constant. Initial peak areas were consistent across treatments for all direct and indirect photolysis experiments. This process resulted in an approximate aqueous concentration of 0.3 μM TBBPA, which enabled us to detect TBBPA to approximately three half-lives of degradation.

One hour prior to photolysis, the TBBPA reaction solution was pH adjusted using HCl or NaOH in ultrapure Milli-Q water in the absence of buffers to avoid any possible radical scavenging side reactions. pH was adjusted to the target pH described above, or pH 8 for comparison between DOM type. Solutions were transferred into 14-mL quartz photolysis tubes laid flat (leveled) and run in triplicate in artificial or natural sunlight (near mid-day) at our two sites as stated previously. Keeping the tubes at the same angle in all experiments allowed for photon-fluence determinations to compare between sites, described below. For in-lake experiments, quartz tubes were secured 5 cm below the surface on a leveled black rack. Dark controls wrapped in aluminum foil were run concurrently in all photolysis experiments. Aliquots were taken at various time points and transferred to 2-mL amber HPLC vials and analyzed directly after collection. Sampling time points were chosen as such that seven time points covered at least three half-lives.

With respect to photoproduct analyses we conducted photo experiments to completion in 0.3 μM TBBPA solutions in the presence and absence of our DOM samples. All solutions were composited, and the analytes concentrated using Oasis HLB solid phase extraction (SPE) cartridges on a vacuum manifold, and eluted with methanol.

A radiometer measuring 239–500 nm was used to monitor the stability of the light source irradiance throughout photolysis experiments, while 10 μM p-nitroanisole with 26 mM pyridine chemical actinometry (Dulin and Mill, 1982) was used to correlate photon flux between artificial and natural sunlight light sources (Wei-Haas and Chin 2015). Due to the rapid photolytic rates, we observed little variation in photon flux over the course of the experiments in both natural and artificial sunlight. We normalized all kinetics data with accumulated light fluence from the actinometry data (see SI for more detail), utilizing the methods reported in Wei-Haas and Chin (2015). These were also conducted for our underwater experiments at the same depth to compensate for changes in light pathlength, refraction, and reflection.

Quantitative analysis

TBBPA and its photoproducts identified in solar simulator and Delaware outdoor experiments were quantified using a Waters ACQUITY Ultra High-Pressure Liquid Chromatography (UHPLC) coupled to an Asentis RP Amide (100 × 2.1 mm, 3 μm) analytical and matching guard columns. An ACQUITY QDa single quadrupole mass selective detector with an electrospray ionization (ESI) interface was used to detect our analytes in negative ionization mode. An Agilent 1220 High-Pressure Liquid Chromatography (HPLC) with a Pinnacle II C18 column (150 × 4.6 mm, 5 μm) and UV detector was used to measure TBBPA in Arctic outdoor photolysis experiments conducted at Toolik Field Station. Because of the lack of instrument sensitivity in scanning mode, we conducted separate large batch kinetic experiments (comprised of the combination of many phototubes) and concentrated the analytes by solid phase extraction (SPE using a Waters Oasis HLB cartridge), which was subsequently eluted with methanol and blown down to 500 μL for the identification of the photo-derivatives. As such we were only able to identify three photoproducts from our photolysis experiments, which were evaluated by comparison of fragment patterns conducted at a higher ESI orifice potential (further described in the SI) to those reported by Wang et al. (2015). TBBPA calibration curves were prepared from standards ranging from 0.05 to 1 μM; however, photoproduct standards are not available commercially and are reported herein as chromatographic peak area counts. Finally, matrix blanks were run for all quantitative analyses. Details regarding both UHPLC and mass spectrometer parameters can be found in the SI.

Data and statistical analysis

Rate constants were determined by fitting the triplicate degradation data to a pseudo-first-order kinetics model using a least-squares approach. For photolysis experiments, apparent rate coefficients (k_{obs}) were corrected (k_{corr}) for aggregate light screening factors ($S_{\Sigma\ \lambda}$) (Miller and Chin 2002). Light screening factors and quantum yield were determined from photon flux and chemical actinometry. A fluence-based pseudo-first-order rate constant was calculated following the methods and calculations outlined by Wei-Haas and Chin (2015) and described further in the SI. Briefly, fluence-based rate constants (k_F) were determined as the log-linearized loss of concentration compared to initial (ln (C/C_0) vs. accumulated dose of light (J/cm^2) and equivalent (based on fluence) time (min).

Linear regression from replicate data across sample points was assessed using analysis of variance (ANOVA), to test for non-zero slope to a significance threshold set a $p < .05$. An analysis of covariance (ANCOVA) was used to test for difference between slopes from linear regressions to a significance threshold set a $p < .05$ in order to compare fitted rate constants across experiments. Statistics analysis was run in Prism 10.2.3 (GraphPad).

Results

pH dependence of TBBPA photolysis in simulated and natural sunlight

All kinetics experiments performed in the solar simulator had log linearized first order regression fits with $R^2 > 0.99$ and no evidence of thermal degradation in dark controls (Figure S2). We observed rapid degradation of TBBPA by direct photolysis in the presence of artificial sunlight (Table 3). The kinetics of photodegradation correlated to pH due to the red shift that occurs for the conjugate base relative to the acid form of TBBPA making the former substantially more photoreactive (Figure S1). The pseudo-first order rate constants of the TBBPA conjugate base species were roughly a factor of two higher than those associated with the acidic form; however, there was little difference between partially and fully deprotonated forms (Figure S1). This occurred even after normalizing for differences in photon fluence between natural sunlight and our solar simulator (Table 3).

We observed a small statistical difference in the rate constants between direct and indirect photolysis of TBBPA at pH 10.5 (fully deprotonated) and none at pH 8 (partially deprotonated) in the presence of SR DOM, while a consistent higher half-life as a function of DOM concentration was observed for the indirect photolysis rate constant at pH 5.5 (fully protonated) (Figure S1). We observe little to no difference in DOM source, however, influencing the rate in which TBBPA photodegrades, as the observed first-order fitted rate constants for TBBPA did not change very much (less than a factor of 2; Figure 2) and revealed no discernable pattern.

Solar simulator vs. outdoor direct and indirect photolysis

In natural sunlight, all outdoor experiments had log linearized first-order regression fits with $R^2 > 0.98$ except for the underwater experiment, which had an $R^2 = 0.842$ (Figure S3, S4). Solar simulator rate constants were fluence corrected and are presented as both time (min^{-1}) and fluence based (cm^2/J) in Table 3. For the outdoor experiments, they were measured both by time and fluence, but because fluence was measured, we were also able to convert to equivalent solar simulator time (Table 3). Thus, comparing both equivalent solar simulator times and rate constants (designated superscript “ss”), it was observed that the TBBPA direct photolysis experiments conducted at pH 8.0

Table 3. DOM isolate specific TBBPA photodegradation rate constants with associated standard errors.

	Indoor Solar Simulator (SS)				Outdoor Natural Sunlight (NS), 40°N				
DOM	SF	k^{SS} *exp*	$t_{1/2}^{SS}$	k_F^{SS}	k_F^{NS} *exp*	k^{NS} *exp*	$t_{1/2}^{NS}$	k^{SS} *calc*	$t_{1/2}^{SS}$
		(min^{-1})	(min)	(cm^2/J)	(cm^2/J)	(min^{-1})	(min)	(min^{-1})	(min)
Water	1.00	0.233 ± 0.011	3.0	0.447	0.375 ± 0.044	0.092 ± 0.011	7.5	0.146 ± 0.017	4.7
SR	0.90	0.176 ± 0.007	3.9	0.342	0.315 ± 0.037	0.075 ± 0.004	9.3	0.147 ± 0.008	4.7
TL	0.90	0.156 ± 0.012	4.5	0.307	0.377 ± 0.022	0.075 ± 0.009	9.2	0.123 ± 0.014	5.7
OKS	0.90	0.184 ± 0.011	3.8	0.356	0.376 ± 0.042	0.102 ± 0.011	6.8	0.147 ± 0.017	4.7
PL	0.93	0.194 ± 0.009	3.6	0.378	0.496 ± 0.047	0.139 ± 0.008	5.0	0.194 ± 0.018	3.6
SAG	0.90	0.173 ± 0.013	4.0	0.339	0.356 ± 0.020	0.083 ± 0.018	8.3	0.182 ± 0.010	3.8

Screening factors (SF) are listed next to each DOM isolate: Suwannee River (SR), Toolik Lake (TL), Oksrukuyik (OKS), Pony Lake (PL), and Sagavanirktok (SAG). Left: solar simulator rate constants (k^{SS} exp) with half-life ($t_{1/2}^{SS}$) and equivalent photofluence determined rate constants (k_F^{SS}). Right: 40°N (Delaware) photofluence and time-measured outdoor photodegradation rate constants (k_F^{NS} exp, k_F^{NS} exp) with calculated half-lives for natural sunlight ($t_{1/2}^{NS}$), and converted to equivalent solar simulated light (k_F^{SS}, $t_{1/2}^{SS}$).

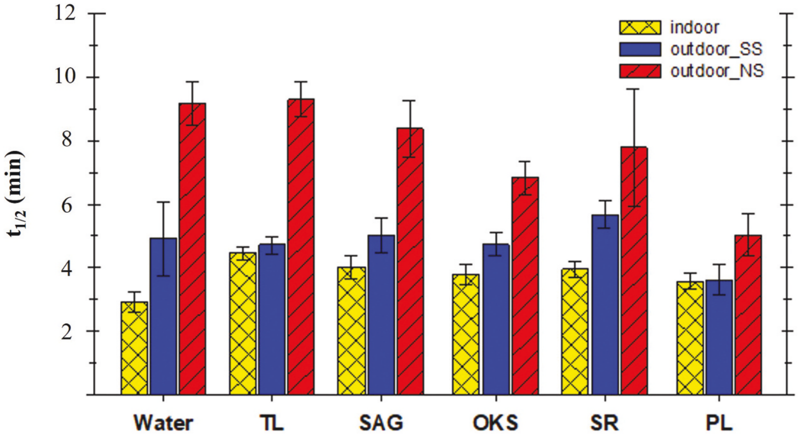

Figure 1. Photofluence corrected first order half-lives at pH = 8 in either solar simulator or 40°N sunlight equivalent time units, with error bars representing standard deviation. Yellow (Solar simulator): Solar simulator (SS) experimental half-life; Blue (40°N_SS): 40°N photofluence corrected half-lives for irradiance conducted in natural sunlight but converted to equivalent half-life in the solar simulator; Red (40°N_NS): 40°N photofluence corrected half-lives for irradiance at 40°N in natural sunlight (NS).

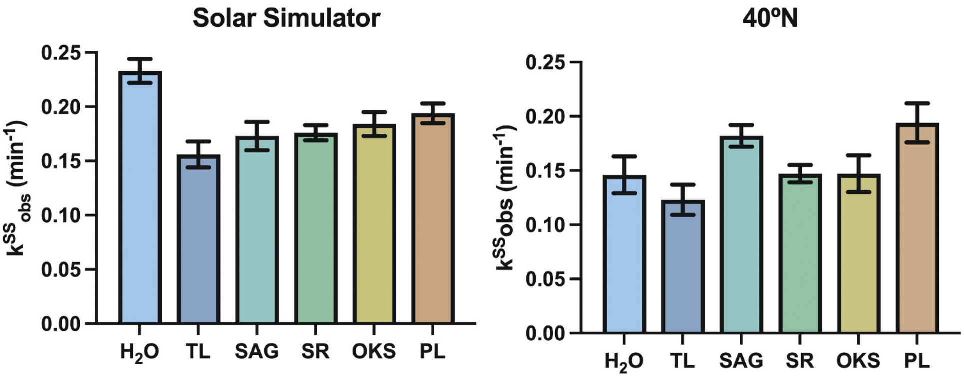

Figure 2. Photofluence corrected solar simulator time-based equivalent rate constant for TBBPA degradation at pH = 8 for solar simulator and Delaware outdoor (40°N), with error bars displaying standard deviation.

under natural sunlight (Newark, DE 39° 40' N in June 2018 at noon) were slightly slower (1.7 x) than comparable rates measured in the solar simulator ($t_{1/2}^{SS}$ 3 min in solar simulator vs. 4.7 min outdoors after converting to solar simulator photofluence) (Figure 1; Table 3). Similar differences are also observed for outdoor vs. solar simulator indirect photolysis experiments with different DOM isolates at the same pH.

Overall, the presence of DOM slowed the rate of TBBPA photodegradation in the solar simulator compared to direct photolysis, by as much as 33 percent (TL), whereas PL had the least effect at a decrease of 17 percent relative to direct photolysis. While the effect of these DOMs does differ ($p < .0001$, Table S1), overall, this range of effect on TBBPA rate constant from DOM is not that large (less than a factor of 2). Thus, while some differences may be significant with respect to DOM source (Table S1), those impacts are small (Figure 2, Table S3).

Photolysis of TBBPA in natural sunlight at Toolik Lake (68°N)

As with the experiments above, rate constants and half-lives were normalized using chemical actinometry and radiometry data based upon photo-fluence and converted to time-based units while including corrections for sun angle differences between the two sites (Wei-Haas and Chin 2015). Direct photolysis rate constants for TBBPA in Arctic natural sunlight (Table 4) were approximately 65 percent lower than those observed at 40°N (Table 3) after these conversions could be compared between the two outdoor sites. While we attempted to maintain consistent experimental conditions, differences in air temperature (~ 20°C) may have played a role that

Table 4. Arctic outdoor whole water photolysis rate constant (k_F *exp*) and photofluence calculated rate constants and half-lives for calculated natural sunlight (k_F^{NS}, $t_{1/2}^{NS}$) and solar simulator light (k_F^{SS}, $t_{1/2}^{SS}$).

DOM	pH	SF	k_F *exp* (cm^2/J)	k_F^{NS} *exp* (min^{-1})	$t_{1/2}^{NS}$ (min)	k^{SS} *calc* (min^{-1})	$t_{1/2}^{SS}$ (min)
Water	7.56	1.00	0.351	0.066 ± 0.024	10.5	0.137 ± 0.024	5.1
Water2	7.85	1.00	0.318	0.079 ± 0.007	8.8	0.124 ± 0.007	5.6
OKS	7.50	0.71	0.322	0.085 ± 0.002	8.2	0.176 ± 0.005	3.9
Fog 1	7.70	0.95	0.341	0.101 ± 0.010	6.8	0.133 ± 0.010	5.2
Fog 2	8.00	0.97	0.342	0.102 ± 0.006	6.8	0.133 ± 0.006	5.2
TL	7.83	0.93	0.354	0.050 ± 0.006	13.9	0.138 ± 0.014	5.0
TL Underwater	7.28	0.93	0.044	0.007	100.9	0.017	40.8

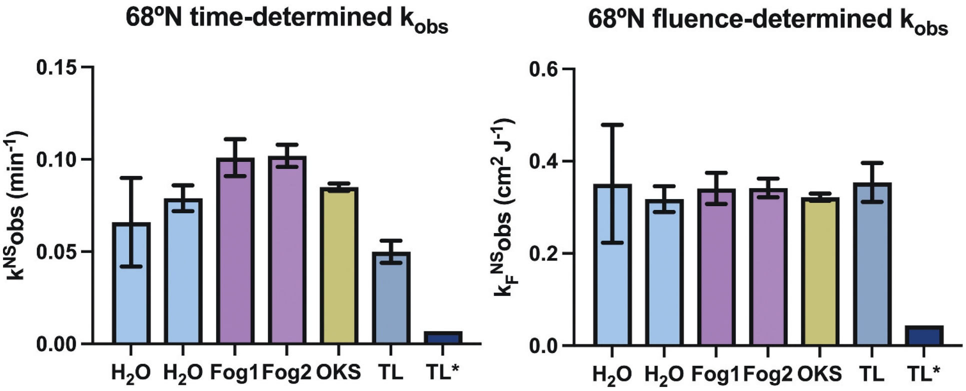

Figure 3. Arctic outdoor TBBPA degradation rate constants, with error bars displaying standard deviations. Blue: milliQ water (H_2O) direct photolysis (left pH = 7.56, right pH = 7.85), Purple: Fog whole water samples (Fog1 ph = 7.7, Fog1 pH = 8.03), Green: OKS whole water samples (pH = 7.5), Light gray: Toolik Lake (TL) whole water samples (pH = 7.83), Dark blue/gray: Toolik Lake (TL*) whole water samples underwater experiment (pH = 7.56). Left: Time based observed rate constant in natural sunlight. Right: Fluence based observed rate constant in natural sunlight.

could not be captured by our fluence-based approach. Regardless, the direct photolysis of TBBPA is rapid (Figure 3) and half-lives occur within a factor of 2 in aqueous solution despite differences in photon flux at these two divergent latitudes. Comparing time-based vs. fluenced-based observed rate constants reveals different trends in the observed photolysis of TBBPA which may be due to differing cloud cover and sunlight conditions during experiments run.

TBPPA photolysis rate constants obtained from experiments conducted underwater in Toolik Lake were significantly lower by almost an order of magnitude (Figure 3, Table 4) than anticipated (based on above water direct photolysis rates) when corrected for inner-filter effects and expected light attenuation based on water depth. We attribute this to differences in the photon flux resulting from light refraction and reflection, which influences pathlength and differences between air and water temperature, which varies by more than 10°C at noon at TFS.

Formation of photoproducts from TBBPA photolysis

We identified three photoproducts in this study: Hydroxyl-tribromobisphenol (HTBBP: *m/z* = 479 Da), dihydroxyl-dibromobisphenol A (DHBP: *m/z* = 417), and tribromobisphenol A (TrBBPA: *m/z* = 463) (Figure S3). Others could not be identified due to sensitivity limitations with our single quadrupole mass spectrometer in scanning mode even after SPE concentration as discussed above. Because we lacked original standards, peaks were determined by matching library mass fragmentation patterns and all photoproduct relative concentrations are reported as peak area.

In direct photolysis, HTBBP was the only photoproduct observed. It was not stable and disappeared over time (Figure 4). In indirect photolysis, HTBBP was also observed in all experiments except for PL, and again, increased and then started to decrease over time. DHBP and TrBBPA are only observed in indirect experiments. DHBP was observed in all DOMs except for PL, but TrBBPA was only observed in experiments with SAG and TL DOM isolates. (Figure 4, S6). Where DHBP and

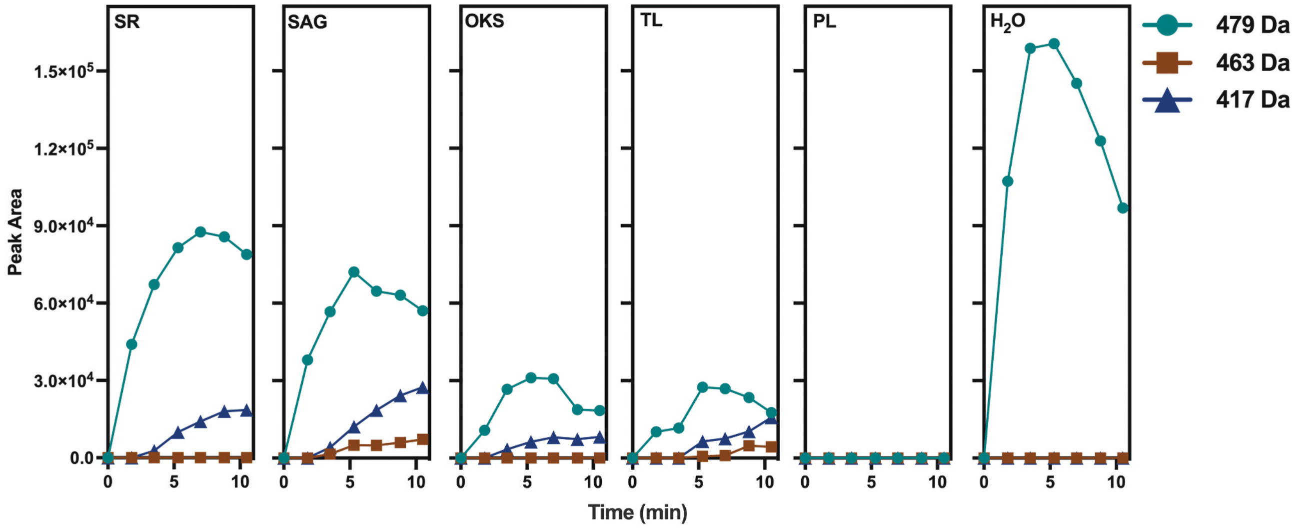

Figure 4. Peak areas of 5 mg C/L DOM isolates of identified photoproducts by indirect photolysis of at pH = 8 over time.

TrBBPA were detected, their peak areas only increased over time; no decrease was noted over the course of the experiments.

Discussion

Fluence-based observations of TBBPA photodegradation: Impacts of light regime and water depth

In the solar simulator experiments, photolysis rates are significantly higher than those reported previously for TBBPA in some studies (Wang et al. 2015; Bao and Niu 2015), but more closely aligned with others (Xiong et al. 2020). These differences in rate constants could be caused by the various light sources used in these previous studies (such as Xe lamps of varying wattage), and differences in starting concentrations or media; however, a direct comparison cannot be made to these earlier studies as chemical actinometry was not reported by these investigators and it is required to account for differences in light fluence (Wei-Haas and Chin 2015).

Our natural sunlight experiments at 40°N also did not exactly match our solar simulator rate constants after fluence corrections and conversion to equivalent solar simulator time. Because of the exceptionally fast kinetics observed under both simulated and natural sunlight (half-lives of 3 to 4 minutes), we attribute part of the discrepancy to the delay between radiometer measurements and the sampling sequence for both the TBBPA experiments and the concurrently run actinometers, as mere seconds can have a large impact on these rates. This issue is likely further exacerbated by the presence of some itinerant cloud cover that occurred as the experiment progressed, i.e., a radiometer measurement that is higher or lower than expected between sampling and the actual reading.

TBPPA photolysis rate constants obtained from experiments conducted underwater in Toolik Lake were significantly slower, by almost an order of magnitude (Figure 3), than anticipated based above water direct photolysis rates when corrected for inner-filter effects and water depth. This observation was surprising given the highly oligotrophic nature of the lake. We can partially attribute this phenomenon to light refraction and scattering. With respect to the former, the *actual pathlength* is longer than the distance between the sample and the lake surface, while the latter could influence the number of photons impinging the reactor. Thus, simple corrections for inner-filter effects and pathlength to estimate the photofate of compounds undergoing both direct and indirect photolysis would overestimate the photodegradation rates of TBBPA and other photoreactive contaminants.

Influence of DOM on TBBPA photodegradation

As stated previously, the rapid kinetics observed for the conjugate base species resulted in some inconsistencies between experiments, but our results corroborated previous studies (Wang et al. 2015; Bao and Niu 2015) that observed overall *no enhancement* of the photolytic degradation of TBBPA by dissolved organic matter. Despite this, there were differences between DOMs, albeit small, on TBBPA degradation rates (Figure 2). Of the DOMs in simulated sunlight, PL had the fastest TBBPA degradation rates, and TL had the slowest. It is interesting to note that SR, a terrestrial end-member reference material (Chin et al. 2023), was *not* an end-member for TBBPA photolysis behavior. This is different from cases where for example triplet excited state processes have been able to be bracketed by terrestrial (SR) vs. microbial (PL) DOMs (Guerard et al. 2009), but the fact that this is not the case with a suite of Arctic DOMs is not unprecedented in our studies (O'Connor et al. 2023).

When looking simply at the time-based kinetics of TBBPA in different media in Arctic sunlight, none of the impacts of DOM on indirect photolysis rates appear to align with those trends observed at 40°N or in the solar simulator (Figure 3, left). It is noted that these experiments were run on different days with different meteorological cloud cover conditions, though we did aim for full sunlight near mid-day as best as logistically feasible. However, when rate constants are determined from photon fluence instead of time, we again see the same trends in influence of DOM relative to direct photolysis for TBBPA photodegradation, showing that the results in the Arctic are in fact completely consistent with the results of the experiments done at lower latitudes.

Formation of photoproducts by indirect photolysis

Even though the fluence-corrected rate constants in the presence of DOM isolates are all very similar to each other, it is interesting that there are marked differences in the relative proportions of photoproducts. This suggests that the TBBPA transformation mechanism varies with DOM source, and we posit that the observed pseudo-first order reactions are comprised of the sum of the unique second order reactions that represents the individual mechanisms through which each photoproduct is formed. Further, the second order rate constants when summed surprisingly resulted in similar overall observed pseudo-first order rate constants regardless of DOM type.

HTBBP, the only photoproduct observed during direct photolysis, has been reported by others (Wang et al. 2015; Bao and Niu 2015; Xiong et al. 2020). In contrast to previous studies (Wang et al. 2015; Xiong et al. 2020), we did not observe HTBBP's photoproduct, DHBP, in direct photolysis, but did in indirect photolysis experiments with DOM, apart from PL (Figure S11). PL is a DOM extracted from a hyper-eutrophic pond in Antarctica and is derived solely from microbial precursors (Cawley et al. 2013). Further, PL did not affect the photodegradation rate of TBBPA, but surprisingly *none* of the major photo products were observed for this DOM. We lack an explanation for this phenomenon and speculate that other unknown TBBPA photolysis pathways occur and photoproducts formed in the presence of PL.

HTBBP and DHBP both are produced via oxidative dehalogenation, i.e., loss of Br and a gain of an OH group. Han et al. (2009) found that sensitization of the TBBPA anion occurs by singlet oxygen through a radical process and may explain the increased rates of transformation at higher pH. One might thus expect this most abundant product to occur in the presence of DOM, which is known to generate singlet oxygen when photolyzed. However, in our study, the highest abundance of product occurred during direct photolysis in the absence of DOM. As stated previously, PL did not produce *any* HTBBP despite its much higher $^1O_2$ quantum yield relative to SR DOM (Wenk, Von Gunten, and Canonica 2011; Partanen et al. 2020). Finally, the presence of the bromines on TBBPA would be expected to severely deactivate the aromatic rings and inhibit electron transfer via triplet excited reactions compared to bisphenol A, which lacks halogens (Chin et al. 2004). All of this suggests that the oxidative dehalogenation of TBBPA giving rise to HTBBP and DHBP products may *not* solely occur via triplet-mediated and $^1O_2$ processes. Despite its lack of formation of HTBBP and DHBP photoproducts, the rate of TBBPA photodegradation is on par with that of the other DOMs (Figure 2). Unfortunately, because PL inventories are currently exhausted at the IHSS, we will be unable to conduct experiments to elucidate this pathway(s).

While TrBBPA was *not observed* during previous studies (Wang et al. 2015; Bao and Niu 2015; Xiong et al. 2020), we observed it in the presence of two DOM isolates: SAG and TL. Unlike the other two photoproducts formed presumably through reaction with reactive oxygen species (Wang et al. 2015), TrBBPA is only formed through a photoreduction. Even though photo-oxidation and/or energy transfer (from excited triplet species) are the principal degradation mechanisms, photoreduction can occur under certain circumstances (McNeill and Canonica 2016). For example, Porras et al. (2014) reported the photoreduction of the fungicide chlorothalonil in the presence of DOM (as humic substances) via a combination of energy transfer from the triplet state coupled with the humic substrate as a hydrogen donor. Photolytic debromination reactions have also been reported for PBDEs in water/methanol mixtures (Eriksson et al. 2004) as well as in organic solvents and soils (Soderstrom et al. 2004). With regard to all these studies, an effective hydrogen donor is needed to facilitate the photoreduction process. Further, the degree to which this occurs is dependent upon the range of DOM triplet energies in addition to its ability to act as a hydrogen donor. The alternative pathway occurs when certain excited state DOM moieties act as both electron and hydrogen donors. Porras et al. (2014) was able to demonstrate the energy transfer/hydrogen donor pathway through competitive reaction kinetic experiments by the addition of a probe compound (2,4,6 trimethylphenol or TMP) since it only reacts via an energy transfer pathway that leads only to oxidation products (Chin et al. 2004). The presence of TMP inhibited the formation of reduced chlorothalonil as both species initially rely upon energy transfer from the excited state triplet DOM. The energy transfer pathway results in the formation of triplet state chlorothalonil that can accept a hydrogen atom from DOM resulting in the reduced derivative as opposed to being oxidized. Finally, these investigators showed that the diversity of DOM composition, i.e., from different sources and precursors, influences whether reduced analyte species are formed. We believe that this process also occurs for TBBPA for specific types of DOMs that have triplet energies high enough to form the triplet TBBPA coupled with its ability to act as a hydrogen donor. From the DOMs used in this study, only SAG and TL possess these two qualities based upon the existence of TrBBPA, which was not detected in our other experiments. We were unable to conduct further studies using selective scavengers to elucidate pathways, however, due to the limited quantities of SAG and TL DOM in our inventory.

Conclusion

This work corroborates conclusions from past studies about the fate of TBBPA in sunlit waters, and demonstrated that fast direct photolysis occurs, especially for the conjugate base. Given that most natural waters have pH ranges that bracket the pK_a values of TBBPA, this is an important pathway for the transformation of TBBPA and may help to suggest why many measurements in the Arctic report "no detects." Regardless, we observed *much slower than anticipated* kinetics in Arctic water bodies relative to estimates based upon natural sunlight studies, even after correcting for depth below surface, and "inner filter" effects. We believe that light scattering coupled with longer than expected pathlengths due to refraction and sun angle at this latitude likely play an important role. Even though the photolytic TBBPA kinetics are roughly an order of magnitude slower than anticipated, half lives in the water column are still high enough to enable other processes such as bioaccumulation to occur. This slower than anticipated photodegradation process could explain why TBBPA is detected (albeit sporadically) in some marine organisms in the polar regions (Vorkamp et al. 2019; Wild et al. 2022). Importantly, we have shown that fluence-based methods are key for comparisons between different light regimes and show that trends with DOM source only are reproduced relative to simulator experiment if fluence-based kinetics are compared. Finally, we have shown that DOM composition plays an important role in the type and quantity of photoproducts formed. Given that little is known about the toxicity of these substances, further investigation is warranted.

Environmental significance

Tetrabromobisphenol-A is used as flame retardant and is detected in environmental matrices from predominantly local/regional sources. In sunlit waters, TBBPA readily undergoes direct photolysis to form a number of oxidized products; however, the presence of dissolved organic matter produces other products and/or suppresses those formed by direct photolysis. DOM composition also influences the abundance, distribution, and types of photoproducts formed. Understanding the types and abundances of TBBPA photoproducts produced helps us understand the environmental fate of this flame retardant in natural waters.

Acknowledgments

We extend our gratitude to Jeffrey Perala Dewey, Ginna Quesada, and the Toolik Lake Field Station staff for helping us conduct field work and setting up experiments. We would like to convey our appreciation to the Editors of the journal and the anonymous reviewers for their constructive and insightful feedback on the manuscript.

Disclosure statement

The authors have no relevant financial or non-financial interests to disclose. The views expressed in this manuscript are those of the authors and do not reflect the official policy or position of the Department of Defense or the U.S. Government.

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Funding

This work was supported by the National Science Foundation under Grant CBET [1804611] (Chin) and CBET [18004271] (Guerard, Hageman).

Author contributions

YC and JK contributed to the studies conception and design. Material preparation and data collection was performed by RO, JK, and JG. All authors contributed to the analysis of data. The first draft of the manuscript was written by RO, and all authors commented on previous versions of the manuscript.

Data availability

The data that support the findings of this study are openly available in the NSF Arctic Data Center at https://arcticdata.io/ reference number *fd53dd87-967e-4c34-b2a1-9e7523b6c0bb*.

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