

Sunlight-Driven Photochemical Halogenation of Dissolved Organic Matter in Seawater: A Natural Abiotic Source of Organobromine and Organoiodine

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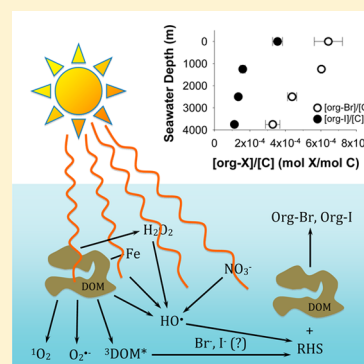
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Supporting Information

ABSTRACT: Reactions of dissolved organic matter (DOM) with photochemically generated reactive halogen species (RHS) may represent an important natural source of organohalogenes within surface seawaters. However, investigation of such processes has been limited by difficulties in quantifying low dissolved organohalogen concentrations in the presence of background inorganic halides. In this work, sequential solid phase extraction (SPE) and silver-form cation exchange filtration were utilized to desalt and preconcentrate seawater DOM prior to nonspecific organohalogen analysis by ICP-MS. Using this approach, native organobromine and organoiodine contents were found to range from $3.2\text{--}6.4 \times 10^{-4}$ mol Br/mol C and $1.1\text{--}3.8 \times 10^{-4}$ mol I/mol C (or $19\text{--}160$ nmol Br L^{-1} and $6\text{--}36$ nmol I L^{-1}) within a wide variety of natural seawater samples, compared with $0.6\text{--}1.2 \times 10^{-4}$ mol Br/mol C and $0.6\text{--}1.1 \times 10^{-5}$ mol I/mol C in terrestrial natural organic matter (NOM) isolates. Together with a chemical probe method specific for RHS, the SPE-ICP-MS approach was also employed to demonstrate formation of nanomolar levels of organobromine and organoiodine during simulated and natural solar irradiation of DOM in artificial and natural seawaters. In a typical experiment, the organobromine content of 2.1×10^{-4} mol C L^{-1} (2.5 mg C L^{-1}) of Suwannee River NOM in artificial seawater increased by 69% (from 5.9×10^{-5} to 1.0×10^{-4} mol Br/mol C) during exposure to 24 h of simulated sunlight. Increasing I^- concentrations (up to 2.0×10^{-7} mol L^{-1}) promoted increases of up to 460% in organoiodine content (from 8.5×10^{-6} to 4.8×10^{-5} mol I/mol C) at the expense of organobromine formation under the same conditions. The results reported herein suggest that sunlight-driven reactions of RHS with DOM may play a significant role in marine bromine and iodine cycling.



INTRODUCTION

More than 4700 natural organohalogen compounds have been identified, most of which are produced in marine environments.^{1,2} The vast majority of these are thought to originate from biological processes.^{1,2} Only a small number of volatile organoiodine and organochlorine compounds, including the important atmospheric ozone-depleting gases CH_3I , CH_2I_2 , CH_2ClI , and CH_3Cl , are presently understood to arise from abiotic processes in marine systems.³⁻⁹ For example, CH_2I_2 , CH_3I , and CHClI_2 may form through reactions of dissolved organic matter (DOM) with HOI and/or I_2 generated via I^- oxidation by O_3 at the ocean surface;⁶ CH_3Cl is believed to arise from nucleophilic substitution of CH_3I and CH_3Br by Cl^- ,¹⁰ as well as from the photosubstitution of aromatic methoxy groups by Cl^- during solar irradiation of DOM in

seawater;^{7,11} and CH_2ClI may form through the photolysis of CH_2I_2 in surface seawater.³

A much wider variety of organohalogenes—including organobromines—may arise from the nonspecific halogenation of DOM by photochemically generated reactive halogen species (RHS) at the ocean surface. Radical and nonradical RHS (e.g., X^\bullet , X_2^\bullet , XY^\bullet , X_2 , XY , and HOX ; where $\text{X} = \text{Br}$ or I , and $\text{Y} = \text{Cl}$) can be produced in sunlit surface seawater from the oxidation of halides by $\bullet\text{OH}$,^{12,13} the DOM-photosensitized reduction of IO_3^- ,¹⁴ and potentially also by photoexcited DOM or chlorophyll.¹⁵⁻¹⁷ Radical RHS may yield organohalogenes via

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addition to unsaturated C–C bonds and/or recombination with carbon-centered radicals,^{18–23} while nonradical RHS (e.g., X₂, HOX) are widely known to halogenate a variety of organic functional groups via electrophilic substitution and/or addition.^{24–26} The formation of CH₃I at the ocean surface is believed to proceed in part through recombination of I[•] and [•]CH₃ arising from photochemical reactions of DOM in the presence of I[–].⁸ Several recent investigations highlight the photoinitiated halogenation of specific organic probe compounds (e.g., bisphenol A, phenol, salicylic acid, and allyl alcohol) during sunlight illumination of natural and simulated seawater,^{27–31} also consistent with a role for RHS. To the authors' knowledge, however, nonspecific photochemical halogenation of DOM under such conditions has not been reported, due in part to difficulties in quantifying the bulk organohalogen (org-X) content of DOM in seawater in the presence of high background levels of inorganic halides.

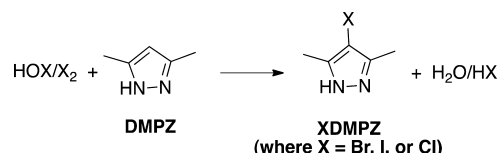
Methods developed for quantification of org-X content in sediments^{32–34} and of total organic halogen, or TOX, levels in drinking water^{35,36} are unsuitable for quantification of org-X in seawater due to interference from high inorganic halide concentrations. Although dissolved organic iodine (DOI) can be quantified in seawater indirectly by measuring iodide concentrations before and after UV photomineralization of DOM,³⁷ the much higher native Br[–] concentrations in seawater prevent the use of such an approach for organobromine quantification. A number of studies have demonstrated that inductively coupled plasma mass spectrometry (ICP-MS) can serve as a sensitive tool for quantification of organobromine and organoiodine in various natural waters (including seawater in the case of organoiodine), provided that separation of organic and inorganic halogen species is assured prior to detection.^{38–42} In these earlier investigations, separations were achieved by online coupling of ICP-MS instrumentation with front-end high performance liquid chromatography (HPLC) systems equipped with ion exchange,^{38,41,42} size-exclusion,^{39,40} or reversed-phase columns.³⁸

In the present work, a novel sample pretreatment method has been developed to enable the offline purification and preconcentration of DOM from seawater prior to quantification of its organobromine and organoiodine content using ICP-MS. In this method, seawater samples are initially passed through solid-phase extraction (SPE) cartridges to achieve both halide removal and DOM preconcentration, followed by filtration of the reconstituted aqueous DOM extracts through a silver-form anion exchange resin to sequester any residual inorganic halides remaining after SPE. Levels of total Br and I in the recovered DOM are then quantified by ICP-MS and the values compared to corresponding measurements of recovered dissolved organic carbon (DOC) to determine the bulk organobromine (org-Br) and organoiodine (org-I) content of the DOM (in mol X/mol C). This org-X method has in turn been utilized here to quantify native org-Br and org-I levels in a wide variety of natural seawater samples, and to demonstrate that nanomolar levels of org-Br and org-I are generated through photochemical processes during the exposure of DOM in natural and artificial seawater to simulated and natural sunlight.

As a complement to the bulk org-X analytical method, an additional technique has been employed that utilizes the synthetic organic compound 3,5-dimethyl-1H-pyrazole (DMPZ) as a selective probe for RHS halogenating activity in sunlight illuminated seawater. DMPZ is highly soluble in water (estimated solubility = 3.8×10^{-1} mol L^{–1}),⁴³ and is

transparent to UV light at wavelengths greater than 250 nm, precluding direct photolysis during exposure to natural sunlight.⁴⁴ Due to the presence of activating methyl groups at its 3 and 5 positions, DMPZ is susceptible to rapid, specific halogenation at the 4 position during exposure to HOX and X₂ species, yielding the respective 4-halo-3,5-dimethyl-1H-pyrazoles (XDMPZs) as products (Scheme 1).^{45,46}

Scheme 1. Formation of XDMPZs in the Reactions of HOX and/or X₂ with DMPZ



Neither DMPZ nor the XDMPZs are likely to be initially present in natural seawater.^{47,48} Consequently, the formation of XDMPZs during solar illumination of natural seawater samples amended with DMPZ can be utilized as a specific indicator of halogenating activity arising from photogenerated RHS, and hence confirmation of RHS formation. This technique has in turn been used to monitor photochemical production of XDMPZs (using HPLC-MS/MS for quantification) during solar illumination of several DMPZ-amended natural estuarine seawater samples, providing additional evidence for the role of RHS in driving bulk org-X formation during solar irradiation of DOM in seawater.

MATERIALS AND METHODS

Chemicals and Materials. All solutions were prepared using Milli-Q grade (≥ 18.2 M Ω ·cm) deionized water. Artificial seawater (ASW) was prepared according to the formula of Dickson and Goyet⁴⁹ (Supporting Information (SI) Table S1), and amended with additional reagents (e.g., NaI) as needed. Natural estuarine, coastal, and oceanic seawater samples were collected from a variety of geographic locations (SI Figures S2–S7) and stored under refrigeration at 4 °C until processing. Additional details on chemicals and materials are provided in SI Text S1.

Bulk Organohalogen Analytical Method. Prior to extractions, natural seawater samples were filtered through 400 °C baked, 0.7 μ m nominal pore size glass fiber filters (Whatman GF/F, GE Healthcare Life Sciences) to remove suspended solids, and treated with 0.1 units/mL of catalase (Sigma-Aldrich C30, from bovine liver) for >30 min to destroy any hydrogen peroxide that could oxidize halides under the acidic extraction conditions.⁵⁰ Artificial seawater samples subjected to irradiation with natural or simulated sunlight were also treated with catalase as above, but only after irradiations were completed and samples had been removed from the light sources. Control extractions conducted with and without catalase confirmed that it had no influence on organohalogen or DOC concentration measurements in recovered DOM extracts. After acidification to pH \sim 2 by dropwise HCl addition, a typical 2-L seawater sample was split into 1000, 700, and 300 mL fractions. The DOM of each fraction was then concentrated and desalted according to the general approach depicted in Figure 1a, with essential aspects of SPE procedures adapted from Dittmar et al.⁵¹ A portion of the recovered Ba/Ag/H cartridge filtrate was analyzed for DOC while the rest was brought to 5% NH₄OH and analyzed for

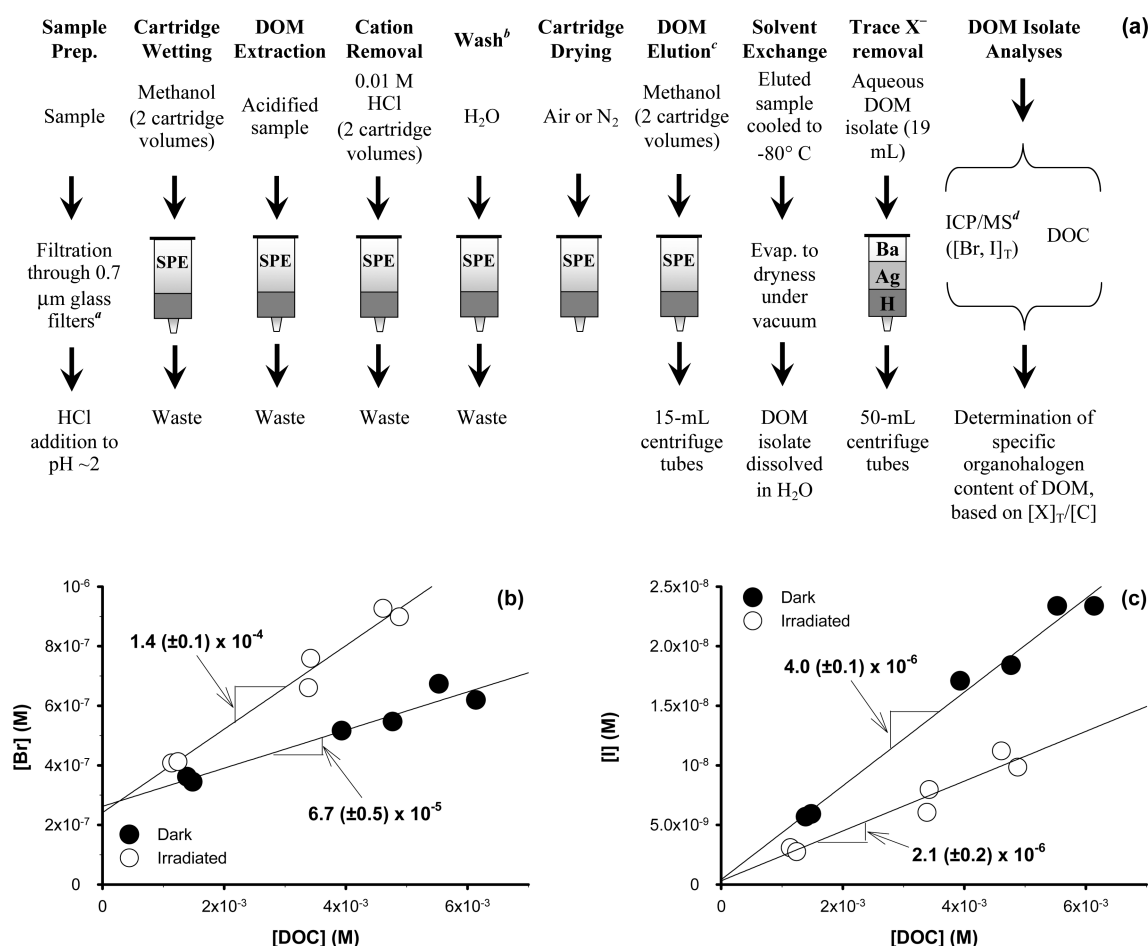


Figure 1. Bulk organohalogen analytical method. (a) Organic matter isolation, preconcentration, desalting, and analytical procedures. Notes: ^aAs necessary (for natural samples), ^bOptional—used only for extractions of samples collected in 2009 (see SI Text S6), ^cSPE manifold and casing rinsed thoroughly with DI H₂O prior to elution to remove halides from surfaces in contact with samples, ^dSeveral samples also analyzed by ion chromatography + ICP-MS, to enable selective quantification of Br⁻ and I⁻. (b) Example analysis for org-Br content of 2.1×10^{-4} mol C L⁻¹ (2.5 mg C L⁻¹) SRNOM in artificial seawater during duplicate exposure to natural sunlight over the course of 4 days (for an in situ fluence of 543 J cm⁻² between 290 and 400 nm) at ambient temperature (293 (±4) K) on a rooftop at the University of Washington in Seattle, WA. (c) Example analysis for org-I content under the same conditions. Dark controls were subject to the same conditions as irradiated samples, except for coverage of glass bottles with aluminum foil. Uncertainties are reported as ±1 SE.

total Br and I by ICP-MS,⁵² or in certain cases for Br⁻ and I⁻ by ICP-MS coupled with ion chromatography (IC+ICP-MS).⁵³ Additional details on SPE and Ba/Ag/H filtration procedures, ICP-MS and DOC instrumentation and methods, and validation of DOC recovery and halide removal are provided in SI Texts S2, S3, S6, and S7. Due to the extensive processing of water samples in this method, it is unlikely that the org-Br and org-I thus quantified consist of significant proportions of volatile halogenated compounds. Quantification of organochlorine (org-Cl) was not pursued due to the low sensitivity of ICP-MS to Cl.

Photochemical Experiments. General Irradiation Conditions. With the exception of some samples irradiated under direct natural sunlight, most irradiation experiments were carried out in an Atlas Suntest XLS+ solar simulator equipped with a 1700 W air-cooled Xe lamp. Lamp output was passed through a daylight filter for attenuation of lamp emission wavelengths below 290 nm and an infrared filter for attenuation of lamp emission wavelengths above 800 nm, resulting in a nominal irradiance of 765 W m⁻² between these wavelengths. Simulated and natural solar spectral irradiance measurements were recorded with an Ocean Optics USB2000+XR spectro-

radiometer. Simulated and natural solar fluence rates were measured from 290 to 400 nm (under the same conditions as for sample irradiations), using chemical actinometry with aqueous solutions containing 10⁻⁵ M *para*-nitroanisole and 10⁻⁴ M pyridine.⁵⁴ Additional details on actinometric measurements are included in SI Text S2.

Bulk Organohalogen Formation Experiments. For experiments evaluating variations in org-X levels during irradiation under simulated sunlight, samples were loaded into 2 L borosilicate glass bottles containing approximately 100 mL of headspace, sealed with threaded caps (to preclude interference from ambient gas species such as O₃), and placed on top of a multiposition magnetic stir plate submerged in a 20 L Plexiglas water bath within the test chamber of the Atlas solar simulator for irradiation. Each experiment involved duplicate irradiated samples and duplicate dark controls (2 L bottles wrapped in aluminum foil) treated in parallel, and each sample was continuously mixed with Teflon-coated magnetic stir bars. Temperature was maintained at 298 (±1) K using an external recirculating constant temperature bath connected to the water bath located within the Atlas test chamber. Control experiments in which the headspace in each bottle was continuously

Table 1. Characteristics of Dissolved Organic Matter Isolated from Natural and Artificial Seawater Matrixes^a

name	sample month	sample information				isolated DOM properties ^c			
		sample location	map code ^b	character	salinity (ppt)	pH	[DOC] (mol C L ⁻¹)	DOC recovery (%)	$\frac{[\text{org-Br}]/[\text{C}]}{[\text{Br}/\text{mol C}]} (\times 10^{-4} \text{ mol I/mol C})$
SRNOM in ASW	NA	Okefenokee Swamp (GA)	NA	IHSS NOM isolate in ASW	35.0	8.1	2.1×10^{-4}	58 (± 3)	0.59 (± 0.03)
NRNOM in ASW	NA	Vallsjoen Reservoir, (Skarnes, Norway)	NA	IHSS NOM isolate in ASW	35.0	8.1	2.1×10^{-4}	61 (± 1)	1.1 (± 0.1)
Magerholm (Norway)	05/09	62° 25' 56" N, 6° 29' 46" E	E1	Estuarine	29.9	7.9	0.92×10^{-4}	53 (± 2)	ND ^d
Spurwink River (ME)	06/09	43° 34' 55" N, 70° 15' 29" W	E2	Estuarine, low tide	13.8	ND	3.9×10^{-4}	42 (± 10)	ND ^d
Higgins Beach (ME)	06/09	43° 33' 40" N, 70° 16' 29" W	E3	Estuarine, low tide	27.9	ND	1.1×10^{-4}	48 (± 9)	ND ^d
Great Kills Harbor (NY)	07/09	40° 32' 7" N, 74° 8' 28" W	E4	Estuarine	25.0	ND	2.2×10^{-4}	43 (± 5)	ND ^d
Hood Canal - Union (WA)	07/09	47° 22' 27" N, 123° 6' 36" W	E5	Estuarine	22.5	7.8	0.83×10^{-4}	49 (± 2)	ND ^d
Hood Canal - Hansville (WA)	07/09	47° 55' 34" N, 122° 36' 60" W	E6	Estuarine	28.7	ND	0.58×10^{-4}	48 (± 4)	ND ^d
Golden Gardens (WA)	12/12	47° 41' 38" N, 122° 24' 21" W	E7	Estuarine, high tide	21.5	ND	0.75×10^{-4}	58 (± 3)	25 (± 1)
Golden Gardens (WA)	12/12	47° 41' 38" N, 122° 24' 21" W	E7	Estuarine, low tide	23.6	ND	0.83×10^{-4}	54 (± 3)	32 (± 2)
Deception Pass (WA)	12/12	48° 24' 5" N, 122° 39' 22" W	E8	Estuarine, high tide	29.2	ND	0.75×10^{-4}	43 (± 1)	37 (± 2)
Deception Pass (WA)	12/12	48° 24' 5" N, 122° 39' 22" W	E8	Estuarine, low tide	28.7	ND	0.83×10^{-4}	38 (± 2)	38 (± 2)
Ocean Beach (CA)	06/09	37° 45' 34" N, 122° 30' 58" W	C1	Coastal	29.8	ND	1.0×10^{-4}	28 (± 1)	ND ^d
Sargasso Sea - Surface	07/09	28° N, 66° W	O1	Oceanic	37.1	7.8	0.92×10^{-4}	48 (± 5)	ND ^d
Pacific Ocean, Station Papa - Surface	10/12	50° N, 145° W	O2	Oceanic	33.1	8.1	1.0×10^{-4}	21 (± 1)	36 (± 3)
Pacific Ocean, Station Papa -1250 m	10/12	50° N, 145° W	O2	Oceanic	35.2	ND	0.58×10^{-4}	25 (± 1)	16 (± 1)
Pacific Ocean, Station Papa -2500 m	10/12	50° N, 145° W	O2	Oceanic	35.3	ND	0.58×10^{-4}	30 (± 1)	14 (± 1)
Pacific Ocean, Station Papa -3750 m	10/12	50° N, 145° W	O2	Oceanic	34.8	ND	0.58×10^{-4}	29 (± 3)	11 (± 1)

^aNA, not applicable, ND, not determined. ^bMaps of sample locations are provided in SI Figures S2–S7. ^cUncertainties reported as ± 1 SD for carbon recoveries, and ± 1 SE for [org-X]/[C] values. Each extraction series comprised three sample volumes, ranging from 100 to 1000 mL, and was performed at least in duplicate. DOC recoveries represent average values across all extracted sample volumes. [org-X]/[C] values were calculated from ICP-MS measurements as depicted in Figure 1. ^dQuantification of org-I was only undertaken in samples collected after 2009, following expansion of the investigation's scope to encompass both org-Br and org-I.

replenished with a stream of compressed air during irradiation confirmed that oxygen supply in irradiated solutions was not limiting. Natural sunlight experiments were undertaken according to similar procedures, except that samples were exposed to sunlight without thermostating (at an ambient temperature of $293 (\pm 4)$ K), over the course of four full days in early September, on the roof of the More Hall Civil and Environmental Engineering building (University of Washington).

RHS Probe Experiments. Aqueous solutions (25 mL) containing 1×10^{-5} M of DMPZ were added into 30 mL, 18 mm \times 150 mm quartz tubes with glass stoppers. Two illuminated samples and one aluminum foil-wrapped dark control per experimental condition were inclined at 45° within the Atlas solar simulator. Experiments were undertaken without thermostating, resulting in operational temperatures of $308 (\pm 2)$ K. Samples were periodically withdrawn from each tube after inverting the tube several times to ensure sample homogeneity, and spiked with 4-chloro-1H-pyrazole (CPZ) as an internal standard. Concentrations of DMPZ, 4-chloro-DMPZ (CDMPZ), 4-bromo-DMPZ (BDMPZ), 4-iodo-DMPZ (IDMPZ), and CPZ were then determined by HPLC-MS/MS (SI Text S4).

RESULTS AND DISCUSSION

Quantification of org-Br and org-I in Seawater Samples. The org-X content of organic matter recovered and analyzed according to Figure 1a was determined from the slope of plots of [X] vs [DOC] for the three different volume fractions extracted from each seawater sample. Figures 1b and 1c provide representative plots of [Br] and [I] vs [DOC] for 2.1×10^{-4} mol C L^{-1} (2.5 mg C L^{-1}) Suwannee River NOM (SRNOM) in ASW with and without exposure to natural sunlight. The nonzero y-intercept of Figure 1b, which was characteristic of org-Br plots, originated from an impurity in the SPE cartridges used for DOM extraction, and was confirmed to have no influence on accurate determination of org-Br (SI Text S8, Figure S1).

Method detection limits for org-X, defined as the minimum slopes of [X] vs [DOC] plots significantly different from 0 ($P < 0.05$) – were estimated as 4.9×10^{-5} mol Br/mol C and 1.6×10^{-6} mol I/mol C (SI Text S9). To evaluate method accuracy, org-Br and org-I contents of SRNOM and Nordic Reservoir NOM (NRNOM) were determined before and after extraction. Samples of each NOM isolate dissolved at concentrations of 8.3×10^{-4} to 5.0×10^{-3} mol C L^{-1} (10–60 mg C L^{-1}) in Milli-Q water were analyzed directly by ICP-MS. In addition, samples of each NOM isolate dissolved at 2.1×10^{-4} mol C L^{-1} in ASW were carried through the extraction procedure prior to analysis by ICP-MS. No significant differences in org-Br were observed between extracted and nonextracted samples (SI Table S2), indicating the stability of org-Br content during the extraction procedure and confirming the insignificance of background bromine species. However, the org-I content of NOM extracts was 50–60% lower than for the Milli-Q water samples (SI Table S2), indicating that org-I measurements obtained by this approach should be taken as lower limits. Research is continuing to determine whether certain org-I species are inefficiently retained by the SPE cartridges, or are labile toward decomposition during the extraction procedure.

Levels of org-Br and org-I in Simulated and Natural Seawater Samples. The org-X analytical method was validated by application to (a) ASW amended with terrestrial

NOM isolates and (b) natural seawater samples collected from a variety of geographic locations (Table 1, SI Figures S2–S7). Carbon recoveries ranged from ~40–60% for estuarine samples and NOM isolates spiked into ASW, and from ~20–50% for open ocean samples. Recoveries were highly repeatable, featuring relative standard deviations of <10% across extraction aliquots.

The org-Br contents of SRNOM and NRNOM isolates spiked into and recovered from ASW were 5.9×10^{-5} and 1.2×10^{-4} mol Br/mol C, respectively; comparable to levels previously measured in freshwater sediments.³² By comparison, the org-Br contents of natural estuarine and coastal surface seawater samples ranged from 3.2 to 6.1×10^{-4} mol Br/mol C, similar to levels previously measured in marine sediments.^{32,33} The org-Br levels measured in the estuarine and coastal seawater samples equate to dissolved organic bromine (DOBr) concentrations of approximately 0.3 – 1.6×10^{-7} mol Br L^{-1} , based on measured pre-extraction DOC concentrations (Table 1). The 2.7- to 10.3-fold higher org-Br content of marine DOM compared to the terrestrial SRNOM and NRNOM isolates is consistent with incorporation of Br into terrestrial DOM during export into marine environments.

The org-I contents of SRNOM and NRNOM isolates recovered from ASW were 5.7×10^{-6} and 1.1×10^{-5} mol I/mol C, an order of magnitude lower than their org-Br contents. In contrast, the org-I content of estuarine and coastal samples ranged from 2.5 to 3.8×10^{-4} mol I/mol C (equating to DOI concentrations of 1.9 – 3.2×10^{-8} mol I L^{-1}), comparable to the org-Br contents of the same samples, and more than ten times the org-I contents in the terrestrial NOM isolates.

The org-X levels measured over a depth profile collected in October, 2012, at Ocean Station Papa (located on the southeast edge of the Alaska Gyre in the northeastern Pacific Ocean) are summarized in Table 1. The org-Br and org-I contents of DOM in the surface sample were 6.4×10^{-4} mol Br/mol C and 3.6×10^{-4} mol I/mol C (equating to DOBr and DOI levels of 6.4×10^{-8} mol Br L^{-1} and 3.6×10^{-8} mol I L^{-1}), respectively; comparable to org-X levels within the other surface seawater samples analyzed in this investigation (Table 1). However, as illustrated in SI Figure S8, org-Br and org-I contents declined by a factor of 2 or more with depth, to minima of 3.3×10^{-4} mol Br/mol C and 1.1×10^{-4} mol I/mol C (equating to DOBr and DOI levels of 1.9×10^{-8} mol Br L^{-1} and 6.4×10^{-9} mol I L^{-1}) in the deepest samples, with the org-I content decreasing at a steeper rate. These trends are consistent with prior reports for organoiodine,^{28,35} and indicative of DOM halogenation by biotic and/or abiotic processes at the ocean surface, coupled with depletion of org-Br and org-I (e.g., by nucleophilic substitution of Br or I by $Cl^{-5,10}$) as seawaters become sequestered from halogenation pathways prevailing at the surface. Despite the apparent negative bias in measured org-I levels mentioned above, the magnitudes of the DOI and org-I values reported here are also in good agreement with DOI levels previously observed for various seawater samples,^{37,55} as well as org-I contents reported for marine foams⁵⁶ and estimated for particulate organic carbon in surface seawater.⁵⁷

Sunlight-Driven Halogenation of DOM in Artificial Seawater. Experiments to quantify nonspecific sunlight-driven halogenation of DOM in seawater were performed on solutions of SRNOM or NRNOM in ASW irradiated with simulated or natural solar light. Terrestrial NOM isolates were chosen for these experiments in order to represent riverine DOM exported through estuaries and into the open ocean, and because they

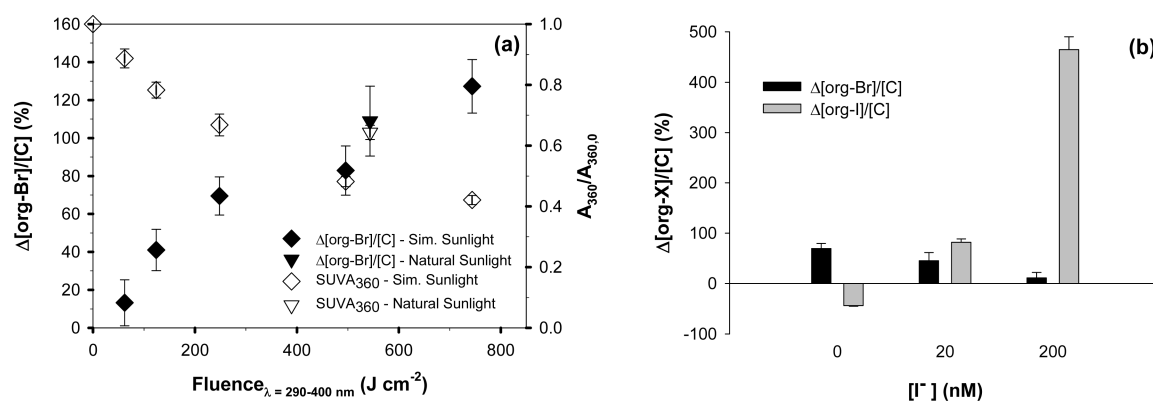


Figure 2. Dependence of org-X formation in irradiated DOM-containing ASW on fluence and iodide concentrations. (a) Percentage increase in $[\text{org-Br}]/[\text{C}]$ ratios (relative to dark controls) and corresponding decrease in $A_{360}/A_{360,0}$ within iodide-free ASW containing $2.1 \times 10^{-4} \text{ mol C L}^{-1}$ (2.5 mg C L^{-1}) of SRNOM during simulated and natural solar irradiation at $T = 298 (\pm 1) \text{ K}$ (simulated sunlight) and $293 (\pm 4) \text{ K}$ (natural sunlight). (b) Percentage change in org-Br and org-I content of $2.1 \times 10^{-4} \text{ mol C L}^{-1}$ SRNOM in artificial seawater exposed to 248 J cm^{-2} of simulated sunlight as a function of $[\text{I}^-]$. Uncertainties are reported as ± 1 SD for absorbance measurements, and ± 1 SE for $[\text{org-X}]/[\text{C}]$ values, from duplicate experiments.

are initially low in org-X levels compared to DOM in natural seawaters. DOC concentrations were selected on the basis of levels anticipated within the nearshore region of the Suwannee River estuarine plume (SI Text S5).

The changes in org-X content, $\Delta[\text{org-X}]/[\text{C}]$, observed in these experiments—reported as percent difference of $[\text{org-X}]/[\text{C}]$ within irradiated samples relative to dark controls—are summarized in SI Table S3. Exposure to sunlight consistently yielded increases in the org-Br content of terrestrial NOM isolates in ASW, as typified by the results depicted in Figure 1b. No significant difference in $\Delta[\text{org-Br}]/[\text{C}]$ was observed between nonsterile and filter sterilized samples, and no increase in org-Br was observed in dark controls, confirming the abiotic, photochemical nature of the measured changes in org-Br within irradiated samples (SI Table S3).

The $\Delta[\text{org-Br}]/[\text{C}]$ for $2.1 \times 10^{-4} \text{ mol C L}^{-1}$ SRNOM in ASW (absent I^-) was found to increase nonlinearly with solar fluence, reaching 130% at 744 J cm^{-2} , or 72 h of simulated sunlight (Figure 2a). Mirroring the upward trend in org-Br versus fluence was a decrease in the measured 360 nm absorbance (A_{360}) of SRNOM in these samples (Figure 2a). Samples illuminated with natural sunlight also generated org-Br (Figures 1b and 2a), and their data coincide reasonably well with the data for simulated sunlight samples with respect to $\Delta[\text{org-Br}]/[\text{C}]$ and A_{360} versus fluence (Figure 2a). Together, these results suggest that formation of org-Br is linked to a subset of reactive DOM chromophores that become progressively photobleached at higher fluences.

The org-Br content of $2.1 \times 10^{-4} \text{ mol C L}^{-1}$ NRNOM in ASW also increased during exposure to 248 J cm^{-2} (24 h) of simulated sunlight, but to a lesser degree than SRNOM (i.e., 17% for NRNOM versus 69% for SRNOM, SI Table S3). This result is likely due to a combination of lower aromaticity⁵⁸ and higher initial org-Br content of NRNOM. The absolute values of $\Delta[\text{org-Br}]/[\text{C}]$ measured for SRNOM and NRNOM under these conditions (equal to 4.1×10^{-5} and $2.0 \times 10^{-5} \text{ mol Br/mol C}$, SI Table S3) correspond to production of 8.5×10^{-9} and $4.2 \times 10^{-9} \text{ mol Br L}^{-1}$ of org-Br, respectively, in pre-extracted samples.

Org-I content of irradiated SRNOM in ASW increased by up to 460% with the addition of increasing I^- concentrations during exposure to a simulated sunlight fluence of 248 J cm^{-2} ;

reaching $4.8 \times 10^{-5} \text{ mol I/mol C}$ at $[\text{I}^-] = 2 \times 10^{-7} \text{ mol L}^{-1}$ (Figure 2b, SI Table S3). Conversely, the addition of I^- resulted in decreased org-Br formation, indicating a competitive effect between the two halide ions. The absolute values of $\Delta[\text{org-Br}]/[\text{C}]$ and $\Delta[\text{org-I}]/[\text{C}]$ measured for SRNOM in the presence of $[\text{I}^-] = 2 \times 10^{-7} \text{ mol L}^{-1}$ (equal to $7.0 \times 10^{-6} \text{ mol Br/mol C}$ and $4.0 \times 10^{-5} \text{ mol I/mol C}$, SI Table S3) correspond to production of $1.5 \times 10^{-9} \text{ mol Br L}^{-1}$ and $8.3 \times 10^{-9} \text{ mol I L}^{-1}$ of org-X in pre-extracted samples.

In solutions of ASW absent I^- , the org-I contents of irradiated SRNOM and NRNOM declined by 44% and 53%, respectively, during exposure to 248 J cm^{-2} of simulated sunlight. This indicates that a substantial portion of the pre-existing org-I in each NOM isolate is photolabile, consistent with previous findings pertain to DOI,⁵⁹ and in accord with the relatively high photolability of C–I bonds.^{3,60,61} In solutions of ASW absent both Br^- and I^- , the org-Br and org-I contents of SRNOM declined by 26% and 35%, respectively, during exposure to 248 J cm^{-2} of simulated sunlight, indicating that a portion of the pre-existing org-Br in SRNOM is also photolabile. These observations confirm that increases in org-Br and org-I contents of SRNOM during irradiation in the presence of Br^- and I^- are due to sunlight-driven DOM halogenation, as opposed to enrichment of pre-existing org-Br and org-I due to photomineralization of nonhalogen containing DOC. Furthermore, the observation that portions of the org-Br and org-I contents in SRNOM are photolabile suggests that in sunlight irradiated seawater, the prevailing levels of org-X likely reflect a balance between organohalogen formation and decomposition.

Interestingly, org-Br formation from $2.1 \times 10^{-4} \text{ mol C L}^{-1}$ SRNOM was not observed in 1 mM phosphate buffered solutions (pH 8.1) containing 0.84 mM NaBr only (no other salts), whereas substantial increases in org-Br were measured when such solutions also contained 0.54 M NaCl (SI Table S3). This result indicates that seawater levels of Cl^- facilitate org-Br formation, suggesting a possible role for mixed halogen species such as $\text{BrCl}^{\bullet-}$ and/or BrCl . It is also notable that org-Br yields during irradiation of phosphate buffered solutions containing 0.84 mM NaBr and 0.54 M NaCl were similar in magnitude to those observed in ASW (absent I^-) (SI Table

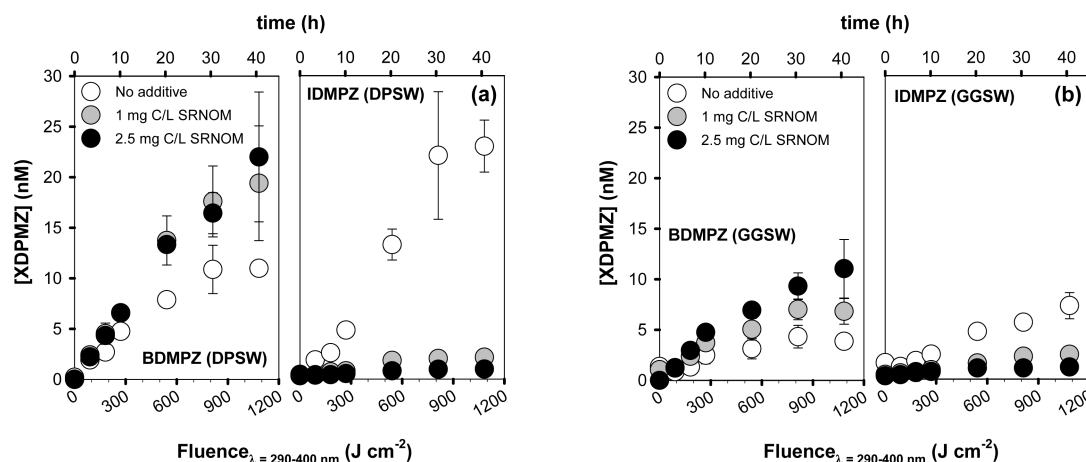


Figure 3. Formation of BDMPZ and IDMPZ during simulated solar irradiation of natural estuarine seawater amended with DMPZ. XDMPZ formation in (a) Deception Pass seawater (DPSW) and (b) Golden Gardens (GGSW) seawater (each collected at low tide, in 12/11 and 8/11, respectively), in the presence and absence of added SRNOM. Experiments were conducted at $[DMPZ]_0 = 1.0 \times 10^{-5}$ M and $T = 308 (\pm 2)$ K. XDMPZ formation was not observed in the absence of light. Uncertainties are reported as ± 1 SD from duplicate experiments.

S3), indicating that seawater ions other than halides do not play significant roles in driving photohalogenation.

Additional experiments with 2.1×10^{-4} mol C L⁻¹ SRNOM in ASW were conducted to evaluate the potential roles of reactive oxygen species (SI Table S3). Compared to the control case in which irradiation led to a 69% increase in org-Br, org-Br formation was, (a) suppressed (25% increase) by prior deaeration; (b) suppressed (50% increase) by 100 mM of the \bullet OH scavenger methanol; (c) enhanced (120% increase) by 1 μ M Fe³⁺, a generator of \bullet OH via photoreduction of iron or the photo-Fenton reaction;⁶² but (d) suppressed by addition of 0.5 μ M nitrite (28% increase) or 5 μ M nitrate (41% increase)—each of which are also known to be \bullet OH photoprecursors.^{13,63} These results suggest a role for O₂, but are ambiguous with respect to a role for \bullet OH in driving RHS formation, signifying the possible involvement of photooxidants other than \bullet OH in generating RHS. This is consistent with prior observations that enhancement of DOM photobleaching in the presence of seawater halide concentrations could not be explained solely on the basis of reactions driven by \bullet OH.⁶⁴

Sunlight-Driven Halogenation of RHS Probe in Natural Seawater. As a consequence of the high native levels of org-X in natural seawater samples, it was not possible to directly quantify sunlight-driven formation of org-X in such samples. Instead, DMPZ was utilized as a selective probe for nonradical RHS production in irradiated natural samples. DMPZ is known to react rapidly with Br₂ in the dark ($k = 1.4 \times 10^9$ M⁻¹ s⁻¹) to form the halogenated product BDMPZ quantitatively.^{45,46} In the present work, DMPZ was also found to react rapidly and quantitatively with HOBr and HOI in the dark to give BDMPZ and IDMPZ, respectively, with apparent second-order rate constants of 2.7×10^5 M⁻¹ s⁻¹ and 7.9×10^2 M⁻¹ s⁻¹ at pH 8.1 (SI Text S10, Figure S9). In contrast, the reaction of DMPZ with HOCl (with $k_{app} = 4.8 \times 10^2$ M⁻¹ s⁻¹), was found to result in <50% yield of CDMPZ under the same conditions (SI Text S10). Based on observations reported for structurally similar imidazoles, it is anticipated that DMPZ reacts with X₂ \bullet /XY \bullet by one-electron oxidation,⁶⁵ rather than 4-halogenation, and therefore does not serve as a probe for radical RHS.

Results obtained during simulated solar irradiation of two natural estuarine samples (each collected from the Puget

Sound) amended with 1.0×10^{-5} mol L⁻¹ DMPZ are depicted in Figure 3. Measured water quality parameters for each sample are provided in SI Table S4. Experiments were undertaken with and without supplementation of the samples' native DOM by addition of SRNOM. Formation of BDMPZ and IDMPZ was observed in both seawaters during irradiation, but not in the dark. Yields of both BDMPZ and IDMPZ increased with fluence (Figure 3), up to levels ranging from 0.5 to 2.5×10^{-8} mol L⁻¹ in the absence of added SRNOM, consistent with the nanomolar concentrations of bulk org-Br and org-I produced during irradiation of SRNOM and NRNOM in ASW. Although chlorination of specific organic compounds has been reported to occur during solar irradiation of seawater,^{28,30,31} CDMPZ was not observed here. The failure to detect CDMPZ suggests that a sunlight-driven pathway to org-Cl is less significant than for org-Br and org-I.

Addition of 8.3×10^{-5} or 2.1×10^{-4} mol C L⁻¹ (1 or 2.5 mg C L⁻¹) SRNOM to either seawater sample increased BDMPZ yields (Figure 3), indicating that terrestrial DOM contains substances that induce or photosensitize bromination. In contrast, the rates of IDMPZ formation decreased substantially with increasing amount of SRNOM added. Competition experiments conducted in ASW showed that SRNOM reacts with HOI nearly as rapidly ($k_{app} = 9.4 \times 10^3$ (mol C)⁻¹ L s⁻¹) as with HOBr ($k_{app} = 2.0 \times 10^4$ (mol C)⁻¹ L s⁻¹) (SI Text S11). It is therefore anticipated that DOM scavenging of photoproducted RHS should suppress IDMPZ formation to a much greater extent than BDMPZ formation, as the rate constant for reaction of DMPZ with HOI under these conditions is more than 2 orders of magnitude lower than for its reaction with HOBr. These observations in turn suggest that the rate of XDMPZ formation in the Deception Pass and Golden Gardens samples is a balance between (i) stimulation of RHS production by DOM and (ii) RHS scavenging by DOM, with the former effect prevailing for BDMPZ and the latter for IDMPZ.

These experiments provide strong evidence that nonradical RHS play a role in driving org-X formation, as XDMPZ is expected to form exclusively through halogenation by nonradical RHS (i.e., HOX, X₂, and XY). However, the XDMPZ data do not distinguish between nonradical RHS arising from \bullet OH-initiated or alternative halide oxidation pathways. Addi-

tional work is needed to elucidate the relative importance of various photosensitized pathways in driving RHS production.

Potential Global Implications. Prior modeling of DOM behavior within the estuarine plume of the Suwannee River indicates that roughly 59% of chromophoric DOM (CDOM) absorbance at 443 nm may be lost to photolysis during transport into the Gulf of Mexico,⁶⁶ consistent with measurements of CDOM photobleaching at 350–360 nm in Suwannee River water⁶⁷ and in a variety of other estuarine and coastal waters subjected to extended solar irradiation.^{68–70} Considering SRNOM to be representative of bulk DOM in the Suwannee River and taking ~60% as a conservative measure of anticipated SRNOM chromophore photobleaching at 360 nm (the wavelength of maximal sunlight-driven SRNOM photobleaching⁶⁴), one can estimate from the data shown in Figure 2a that solar irradiation would lead to an enrichment of ~130% in the org-Br content of DOM discharged from the Suwannee River in the absence of iodide, from 5.9×10^{-5} to 1.4×10^{-4} mol Br/mol C (i.e., $\Delta[\text{org-Br}]/[\text{C}] = 8.1 \times 10^{-5}$ mol Br/mol C). In the presence of a representative estuarine surface seawater iodide concentration of 2×10^{-7} mol $\text{I}^- \text{L}^{-1}$,^{37,55} one would expect org-Br formation to be suppressed by ~80% (Figure 2b, SI Table S3), limiting $\Delta[\text{org-Br}]/[\text{C}]$ to roughly 1.6×10^{-5} mol Br/mol C. At the same time, one would expect the presence of I^- to lead to a roughly 500% (or greater) increase in org-I, from 5.7×10^{-6} to at least 3.4×10^{-5} mol I/mol C (i.e., $\Delta[\text{org-I}]/[\text{C}] = 2.8 \times 10^{-5}$ mol I/mol C).

Further investigation will be necessary to confirm the extent to which the magnitudes of sunlight-driven org-X formation observed for SRNOM can be generalized. However, assuming that the preceding estimates of org-Br and org-I formation at $[\text{I}^-] = 2 \times 10^{-7}$ mol L^{-1} are representative of the behavior of DOM in other estuarine river plumes, and noting that global riverine DOC exports to the ocean total approximately 2.5×10^{14} g per year⁷¹ (nearly 66% of which originates from rivers in tropical regions subject to high annual sunlight exposure⁷²), one can estimate that photochemical halogenation of terrestrial DOM in estuaries alone could generate on the order of 30 Gg of org-Br and 70 Gg of org-I annually. Substantially higher values would be anticipated for annual production of both org-Br and org-I if RHS-driven reactions with marine DOM in the open ocean result in even a small fraction of the increases in org-X observed here.

It is noteworthy that the figure estimated for org-Br photoproduction is similar in magnitude to the well-known deficit in global CH_3Br emissions inventories (~ 32 Gg yr^{-1} ⁷³). Although the measurements reported here presumably capture primarily nonvolatile org-Br content, and so do not provide direct evidence of volatile org-Br production, it seems plausible that photochemical halogenation of terrestrial DOM in estuarine river plumes could represent an unrecognized source of CH_3Br , especially in light of recent measurements indicating elevated CH_3Br sea-air fluxes in coastal seawaters.⁷⁴ Further research will be necessary to evaluate this possibility.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, and figures addressing artificial and natural seawater composition, analytical method details, method validation and control experiments, natural seawater sampling locations, org-X levels in irradiated samples and the Station Papa depth profile, and kinetics and stoichiometries of XDMPZ

formation in reactions with HOX. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Gribble, G. W. Naturally occurring organohalogen compounds. *Acc. Chem. Res.* **1998**, *31*, 141–152.
- (2) Gribble, G. W. *Naturally Occurring Organohalogen Compounds—A Comprehensive Update*; Springer-Verlag: Vienna, 2010; Vol. 91.
- (3) Jones, C. E.; Carpenter, L. J. Solar photolysis of CH_2I_2 , CH_2ClI , and CH_2IBr in water, saltwater, and seawater. *Environ. Sci. Technol.* **2005**, *39*, 6130–6137.
- (4) Carpenter, L. J.; Archer, S. D.; Beale, R. Ocean-atmosphere trace gas exchange. *Chem. Soc. Rev.* **2012**, *41*, 6473–6506.
- (5) Zafriou, O. C. Reaction of methyl halides with seawater and marine aerosols. *J. Mar. Res.* **1975**, *33*, 75–81.
- (6) Martino, M.; Mills, G. P.; Woeltjen, J.; Liss, P. S. A new source of volatile organoiodine compounds in surface seawater. *Geophys. Res. Lett.* **2009**, *36*.
- (7) Moore, R. M. A photochemical source of methyl chloride in saline waters. *Environ. Sci. Technol.* **2008**, *42*, 1933–1937.
- (8) Moore, R. M.; Zafriou, O. C. Photochemical production of methyl iodide in seawater. *J. Geophys. Res.: Atmos.* **1994**, *99*, 16415–16420.
- (9) Carpenter, L. J.; Hopkins, J. R.; Jones, C. E.; Lewis, A. C.; Parthipan, R.; Wevill, D. J.; Poissant, L.; Pilote, M.; Constant, P. Abiotic source of reactive organic halogens in the sub-arctic atmosphere? *Environ. Sci. Technol.* **2005**, *39*, 8812–8816.
- (10) Moore, R. M.; Groszko, W.; Niven, S. J. Ocean-atmosphere exchange of methyl chloride: Results from NW Atlantic and Pacific Ocean studies. *J. Geophys. Res.: Oceans* **1996**, *101*, 28529–28538.
- (11) Dallin, E.; Wan, P.; Krogh, E.; Gill, C.; Moore, R. M. New pH-dependent photosubstitution pathways of syringic acid in aqueous solution: Relevance in environmental photochemistry. *J. Photochem. Photobiol., A* **2009**, *207*, 297–305.
- (12) Zafriou, O. C. Sources and Reactions of OH and Daughter Radicals in Seawater. *J. Geophys. Res.* **1974**, *79*, 4491–4497.
- (13) Mopper, K.; Zhou, X. L. Hydroxyl radical photoproduction in the sea and its potential impact on marine processes. *Science* **1990**, *250*, 661–664.
- (14) Saunders, R. W.; Kumar, R.; MacDonald, S. M.; Plane, J. M. C. Insights into the photochemical transformation of iodine in aqueous systems: Humic acid photosensitized reduction of iodate. *Environ. Sci. Technol.* **2012**, *46*, 11854–11861.

- (15) Jammoul, A.; Dumas, S.; D'Anna, B.; George, C. Photoinduced oxidation of sea salt halides by aromatic ketones: A source of halogenated radicals. *Atmos. Chem. Phys.* **2009**, *9*, 4229–4237.
- (16) Reeser, D. I.; George, C.; Donaldson, D. J. Photooxidation of halides by chlorophyll at the air-salt water interface. *J. Phys. Chem. A* **2009**, *113*, 8591–8595.
- (17) De Laurentiis, E.; Minella, M.; Maurino, V.; Minero, C.; Mailhot, G.; Sarakha, M.; Brigante, M.; Vione, D. Assessing the occurrence of the dibromide radical ($\text{Br}_2^{\bullet-}$) in natural waters: Measures of triplet-sensitised formation, reactivity, and modelling. *Sci. Total Environ.* **2012**, *439*, 299–306.
- (18) Hasegawa, K.; Neta, P. Rate constants and mechanisms of reaction of $\text{Cl}_2^{\bullet-}$ radicals. *J. Phys. Chem.* **1978**, *82*, 854–857.
- (19) Guha, S. N.; Schoneich, C.; Asmus, K. D. Free-radical reductive degradation of vic-dibromoalkanes and reaction of bromine atoms with polyunsaturated fatty-acids: Possible involvement of Br^{\bullet} in the 1,2-dibromoethane-induced lipid peroxidation. *Arch. Biochem. Biophys.* **1993**, *305*, 132–140.
- (20) Solomons, G.; Fryhle, C. *Organic Chemistry*; 7 ed.; John Wiley and Sons, Inc.: New York, NY, 2000.
- (21) Alegre, M. L.; Gerones, M.; Rosso, J. A.; Bertolotti, S. G.; Braun, A. M.; Martire, D. O.; Gonzalez, M. C. Kinetic study of the reactions of chlorine atoms and $\text{Cl}_2^{\bullet-}$ radical anions in aqueous solutions. I. Reaction with benzene. *J. Phys. Chem. A* **2000**, *104*, 3117–3125.
- (22) Martire, D. O.; Rosso, J. A.; Bertolotti, S.; Le Roux, G. C.; Braun, A. M.; Gonzalez, M. C. Kinetic study of the reactions of chlorine atoms and $\text{Cl}_2^{\bullet-}$ anions in aqueous solutions. II. Toluene, benzoic acid, and chlorobenzene. *J. Phys. Chem. A* **2001**, *105*, 5385–5392.
- (23) Grebel, J. E.; Pignatello, J. J.; Mitch, W. A. Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters. *Environ. Sci. Technol.* **2010**, *44*, 6822–6828.
- (24) Bichsel, Y. *Behavior of Iodine Species in Oxidative Processes During Drinking Water Treatment*; Swiss Federal Institute of Technology Zurich: Zurich, Switzerland, 2000.
- (25) Deborde, M.; von Gunten, U. Reactions of chlorine with inorganic and organic compounds during water treatment—Kinetics and mechanisms: A critical review. *Water Res.* **2008**, *42*, 13–51.
- (26) Heeb, M. B.; Criquet, J.; Zimmermann-Steffens, S. G.; von Gunten, U. Oxidative treatment of bromide-containing waters: Formation of bromine and its reactions with inorganic and organic compounds—A critical review. *Water Res.* **2014**, *48*, 15–42.
- (27) Anastasio, C.; Matthew, B. M. A chemical probe technique for the determination of reactive halogen species in aqueous solution: Part 2—Chloride solutions and mixed bromide/chloride solutions. *Atmos. Chem. Phys.* **2006**, *6*, 2439–2451.
- (28) Calza, P.; Vione, D.; Novelli, A.; Pelizzetti, E.; Minero, C. The role of nitrite and nitrate ions as photosensitizers in the photo-transformation of phenolic compounds in seawater. *Sci. Total Environ.* **2012**, *439*, 67–75.
- (29) Tamam, F.; Chiron, S. New insight into photo-bromination processes in saline surface waters: The case of salicylic acid. *Sci. Total Environ.* **2012**, *435*, 345–350.
- (30) Liu, H.; Zhao, H. M.; Quan, X.; Zhang, Y. B.; Chen, S. Formation of chlorinated intermediate from bisphenol A in surface saline water under simulated solar light irradiation. *Environ. Sci. Technol.* **2009**, *43*, 7712–7717.
- (31) Calza, P.; Massolino, C.; Pelizzetti, E.; Minero, C. Role of iron species in the photo-transformation of phenol in artificial and natural seawater. *Sci. Total Environ.* **2012**, *426*, 281–288.
- (32) Mayer, L. M.; Schick, L. L.; Allison, M. A.; Ruttenberg, K. C.; Bentley, S. J. Marine vs. terrigenous organic matter in Louisiana coastal sediments: The uses of bromine: Organic carbon ratios. *Mar. Chem.* **2007**, *107*, 244–254.
- (33) Leri, A. C.; Hakala, J. A.; Marcus, M. A.; Lanzirrotti, A.; Reddy, C. M.; Myneni, S. C. B. Natural organobromine in marine sediments: New evidence of biogeochemical Br cycling. *Global Biogeochem. Cycles* **2010**, *24*.
- (34) Leri, A. C.; Hay, M. B.; Lanzirrotti, A.; Rao, W.; Myneni, S. C. B. Quantitative determination of absolute organohalogen concentrations in environmental samples by X-ray absorption spectroscopy. *Anal. Chem.* **2006**, *78*, S711–S718.
- (35) Hua, G. H.; Reckhow, D. A. Determination of TOCl , TOBr and TOI in drinking water by pyrolysis and off-line ion chromatography. *Anal. Bioanal. Chem.* **2006**, *384*, 495–504.
- (36) APHA. *Standard Methods for the Examination of Water and Wastewater*; 21 ed.; APHA, AWWA, WPCF, 2005.
- (37) Wong, G. T. F.; Cheng, X. H. Dissolved organic iodine in marine waters: Determination, occurrence and analytical implications. *Mar. Chem.* **1998**, *59*, 271–281.
- (38) Heumann, K. G.; Rottmann, L.; Vogl, J. Elemental speciation with liquid chromatography-inductively coupled plasma isotope dilution mass spectrometry. *J. Anal. At. Spectrom.* **1994**, *9*, 1351–1355.
- (39) Radlinger, G.; Heumann, K. G. Determination of halogen species of humic substances using HPLC/ICP-MS coupling. *Fresenius J. Anal. Chem.* **1997**, *359*, 430–433.
- (40) Radlinger, G.; Heumann, K. G. Transformation of iodide in natural and wastewater systems by fixation on humic substances. *Environ. Sci. Technol.* **2000**, *34*, 3932–3936.
- (41) Gilfedder, B. S.; Petri, M.; Wessels, M.; Biester, H. An iodine mass-balance for Lake Constance, Germany: Insights into iodine speciation changes and fluxes. *Geochim. Cosmochim. Acta* **2010**, *74*, 3090–3111.
- (42) Gilfedder, B. S.; Petri, M.; Wessels, M.; Biester, H. Bromine species fluxes from Lake Constance's catchment, and a preliminary lake mass balance. *Geochim. Cosmochim. Acta* **2011**, *75*, 3385–3401.
- (43) Karickhoff, S.; Carreira, L.; Hilal, S. SPARC: SPARC Performs Automated Reasoning in Chemistry. ARChem: Automated Reasoning in Chemistry: Danielsville, GA. (<http://archemcalc.com/sparc/>).
- (44) Bernarducci, E.; Schwindinger, W. F.; Hughey, J. L.; Kroghjerspersen, K.; Schugar, H. J. Electronic spectra of copper(II)-imidazole and copper(II)-pyrazole chromophores. *J. Am. Chem. Soc.* **1981**, *103*, 1686–1691.
- (45) Boulton, B. E.; Collier, B. A. W. Kinetics, stoichiometry, and mechanism in bromination of aromatic heterocycles: I. Aqueous bromination of pyrazole, 1-methylpyrazole, and 3,5-dimethylpyrazole. *Aust. J. Chem.* **1971**, *24*, 1413.
- (46) Grimmett, M. R. Halogenation of Heterocycles: I. Five-Membered Rings. *Adv. Heterocycl. Chem.* **1993**, *57*, 291.
- (47) Wiley, R. H. *The Chemistry of Heterocyclic Compounds: Pyrazoles and Reduced and Condensed Pyrazoles*; John Wiley & Sons, 2009; Vol. 22.
- (48) Kumar, V.; Kaur, K.; Gupta, G. K.; Sharma, A. K. Pyrazole containing natural products: Synthetic preview and biological significance. *Eur. J. Med. Chem.* **2013**, *69*, 735–753.
- (49) Dickson, A. G.; Goyet, C. E. *Handbook of Methods for the Analysis of Various Parameters of the Carbon Dioxide System in Seawater*, ORNL/CDIAC-74; Department of Energy, (<http://cdiac.ornl.gov/ftp/cdiac74/>).
- (50) Bray, W. C.; Livingston, R. S. The catalytic decomposition of hydrogen peroxide in a bromine-bromide solution, and a study of the steady state. *J. Am. Chem. Soc.* **1923**, *45*, 1251–1271.
- (51) Dittmar, T.; Koch, B.; Hertkorn, N.; Kattner, G. A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. *Limnol. Oceanogr.: Methods* **2008**, *6*, 230–235.
- (52) Bu, X. D.; Wang, T. B.; Hall, G. Determination of halogens in organic compounds by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). *J. Anal. At. Spectrom.* **2003**, *18*, 1443–1451.
- (53) Shi, H. L.; Adams, C. Rapid IC-ICP/MS method for simultaneous analysis of iodoacetic acids, bromoacetic acids, bromate, and other related halogenated compounds in water. *Talanta* **2009**, *79*, 523–527.

- (54) Dulin, D.; Mill, T. Development and evaluation of sunlight actinometers. *Environ. Sci. Technol.* **1982**, *16*, 815–820.
- (55) Wong, G. T. F.; Cheng, X.-H. Dissolved inorganic and organic iodine in the Chesapeake Bay and adjacent Atlantic waters: Speciation changes through an estuarine system. *Mar. Chem.* **2008**, *111*, 221–232.
- (56) Truesdale, V. W.; Zic, V.; Garnier, C.; Cukrov, N. Circumstantial evidence in support of org-I as a component of the marine aerosol arising from a study of marine foams. *Estuarine, Coastal Shelf Sci.* **2012**, *115*, 388–398.
- (57) Wong, G. T. F.; Brewer, P. G.; Spencer, D. W. The distribution of particulate iodine in the Atlantic Ocean. *Earth. Planet. Sci. Lett.* **1976**, *32*, 441–450.
- (58) International Humic Substances Society Home Page, 2014. <http://www.humicsubstances.org/>.
- (59) Wong, G. T. F.; Cheng, X. H. The formation of iodide in inshore waters from the photochemical decomposition of dissolved organic iodine. *Mar. Chem.* **2001**, *74*, 53–64.
- (60) Carpenter, L. J. Iodine in the marine boundary layer. *Chem. Rev.* **2003**, *103*, 4953–4962.
- (61) Martino, M.; Liss, P. S.; Plane, J. M. C. Wavelength-dependence of the photolysis of diiodomethane in seawater. *Geophys. Res. Lett.* **2006**, *33*.
- (62) Pignatello, J. J.; Oliveros, E.; MacKay, A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 1–84.
- (63) Mack, J.; Bolton, J. R. Photochemistry of nitrite and nitrate in aqueous solution: A review. *J. Photochem. Photobiol., A* **1999**, *128*, 1–13.
- (64) Grebel, J. E.; Pignatello, J. J.; Song, W. H.; Cooper, W. J.; Mitch, W. A. Impact of halides on the photobleaching of dissolved organic matter. *Mar. Chem.* **2009**, *115*, 134–144.
- (65) Parsons, B. J.; Navaratnam, S.; Zhao, Z.; Chen, L. One-electron oxidation of iron(II) imidazole and iron(II) bis[imidazol-2-yl]methane complexes: A pulse-radiolysis study. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2467–2474.
- (66) Jolliff, J. K.; Walsh, J. J.; He, R. Y.; Weisberg, R.; Stovall-Leonard, A.; Coble, P. G.; Conmy, R.; Heil, C.; Nababan, B.; Zhang, H. Y.; Hu, C. M.; Muller-Karger, F. E. Dispersal of the Suwannee River plume over the West Florida shelf: Simulation and observation of the optical and biochemical consequences of a flushing event. *Geophys. Res. Lett.* **2003**, *30*.
- (67) Miller, W. L.; Zepp, R. G. Photochemical production of dissolved inorganic carbon from terrestrial organic-matter: Significance to the oceanic organic carbon cycle. *Geophys. Res. Lett.* **1995**, *22*, 417–420.
- (68) Vodacek, A.; Blough, N. V.; DeGrandpre, M. D.; Peltzer, E. T.; Nelson, R. K. Seasonal variation of CDOM and DOC in the Middle Atlantic Bight: Terrestrial inputs and photooxidation. *Limnol. Oceanogr.* **1997**, *42*, 674–686.
- (69) Moran, M. A.; Sheldon, W. M.; Zepp, R. G. Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. *Limnol. Oceanogr.* **2000**, *45*, 1254–1264.
- (70) Shank, G. C.; Evans, A. Distribution and photoreactivity of chromophoric dissolved organic matter in northern Gulf of Mexico shelf waters. *Cont. Shelf Res.* **2011**, *31*, 1128–1139.
- (71) Hedges, J. I.; Keil, R. G.; Benner, R. What happens to terrestrial organic matter in the ocean? *Org. Geochem.* **1997**, *27*, 195–212.
- (72) Spitzy, A.; Leenheer, L. In *SCOPE 42: Biogeochemistry of Major World Rivers*; Degens, E. T., Kempe, S., Richey, J. E., Eds.; Wiley: UK, 1991; pp 214–232.
- (73) Yvon-Lewis, S. A.; Saltzman, E. S.; Montzka, S. A. Recent trends in atmospheric methyl bromide: Analysis of post-Montreal Protocol variability. *Atmos. Chem. Phys.* **2009**, *9*, 5963–5974.
- (74) Hu, L.; Yvon-Lewis, S. A.; Liu, Y.; Salisbury, J. E.; O'Hern, J. E. Coastal emissions of methyl bromide and methyl chloride along the eastern Gulf of Mexico and the east coast of the United States. *Global Biogeochem. Cycles* **2010**, *24*.