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Key Points:

- Dissolved organic halogens were quantified in the North Central Atlantic and Pacific
- Dissolved organic bromine and iodine were similar in the surface, but organic bromine was higher and more stable at depth

Supporting Information:

Supporting Information may be found in the online version of this article.

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Halogenated Organic Compounds: A Massive Halogen Reservoir and an Intriguing Component of the Marine Dissolved Organic Matter Pool

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Abstract Biogeochemical reactions produce volatile halocarbons and semi- to nonvolatile dissolved organic halogens (DOX) in marine systems. The former has a large influence on atmospheric chemistry, but little is known about DOX. Here, we present depth profiles of dissolved organic bromine (DOBr) and -iodine (DOI) isolated from the Central North Atlantic and the Central North Pacific. DOX ranged from ∼5 to 11 nM in the surface and decreased to ∼1 to 7 nM below 1,500 m. Relative to DOI, DOBr is elevated and more stable at depth. Moreover, 92 individual DOBr molecular ions were identified by high-resolution mass spectrometry for the first time in seawater using a solid phase extraction/sequential elution technique. Similar DOBr ions with an oxygen-to-carbon ratio of 0.35 and a hydrogen-to-carbon ratio of 1.3 were present throughout the water column. Thus, deep ocean DOBr may be a hitherto overlooked component of marine refractory organic matter.

Plain Language Summary Volatile marine organo-halogens, and the mechanisms that create them, have been well studied due to their role in atmospheric chemistry. The same mechanisms that create volatile halogens also create semi- to nonvolatile halogenated compounds, many of which have been characterized due to their bioactive properties. However, while volatile organo-halogens have been often quantified, little is known about the distribution and reactivity of semi- to nonvolatile halogenated compounds in seawater. In this study we report the first detailed depth profiles of dissolved organic bromine (DOBr) and -iodine (DOI) in the North Atlantic and North Pacific Oceans. Preliminary global inventories are 0.53 petagram (Pg = 10^{15} g) Br in DOBr and 0.27 Pg I in DOI, which does not yet include information for estuarine and coastal systems. Relative to DOI, DOBr is elevated and stable at depth, and therefore DOBr may be an important component of the largely uncharacterized marine refractory organic matter pool. Thus, future work on both the distribution and molecular composition of DOX in the oceans could provide novel insights into how these molecules behave in the oceans as well as their overall role in the biogeochemical cycling of marine dissolved organic matter.

1. Introduction

Marine dissolved organic matter (DOM) is a large and dynamic pool of reduced carbon and associated elements that remains one of the least understood components of the global carbon cycle (Gonsior et al., 2022; Hansell & Carlson, 2001; Wagner et al., 2020). Several clues suggest that halogenation and dehalogenation are critical processes in marine DOM cycling (Atashgahi et al., 2018). Marine organisms produce a complex suite of halogenated organic compounds, which can serve as antibiotics, antifoulants, predation deterrents, pheromones, and more (Gribble, 2004). Moreover, organo-halogens can be synthesized in environments with surprisingly low halide concentrations through diverse and critical carbon-halogen metabolic pathways (Fowden, 1968). Because halides ($X^- = Cl^-$, Br^-, or I^-) are largely unreactive, halogenating enzymes create reactive halogen species (RXS) that react with organic molecules to form halogenated compounds (Blasiak & Drennan, 2009). In addition to biological RXS production, photoreactions can also create RXS in seawater (Parker & Mitch, 2016; Yang & Pignatello, 2017; Zafiriou, 1974) and produce organo-halogens (Méndez-Díaz et al., 2014). The atmosphere may also be an important source of halogenated organic compounds to marine surface waters (Galbán-Malagón et al., 2013; Iwata et al., 1993) through air-to-sea fluxes of both natural (Ofner et al., 2012) and anthropogenic

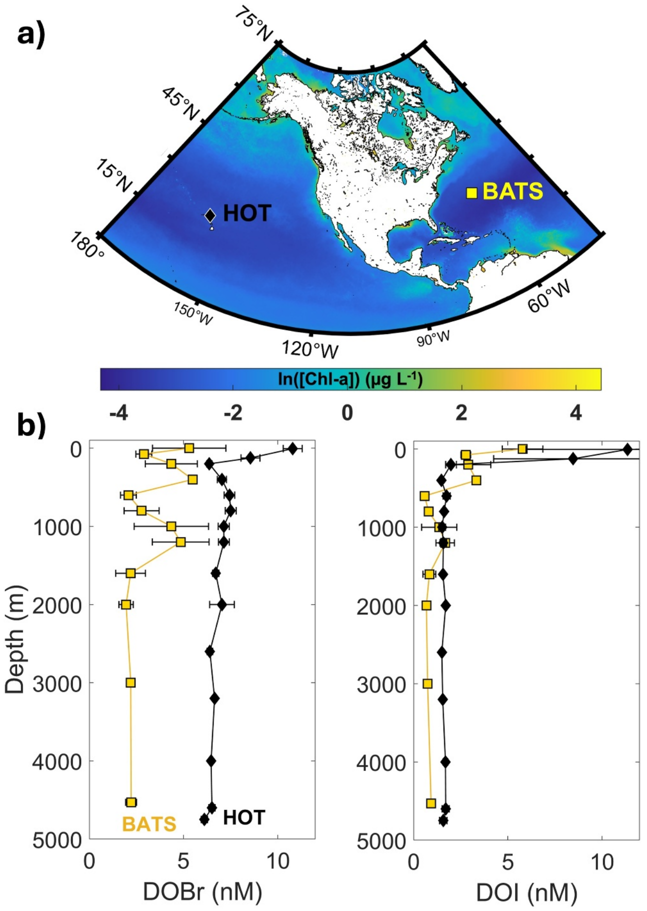

Figure 1. (a) Map of sampling sites: the Hawaii Ocean Time-series (HOT) station and the Bermuda Atlantic Time-series Study (BATS) station plotted against the MODIS July monthly climatology of chlorophyll-a concentrations ([Chl-a]) (μg L^{-1}) obtained from the NASA level-3 browser. (b) Depth profiles of dissolved organic bromine (DOBr, nM) (left) and dissolved organic iodine (DOI, nM) (right) for solid phase extraction samples at BATS (yellow squares, $n = 3$ per depth) and HOT (black diamonds, $n = 3$ per depth).

(Galbán-Malagón et al., 2013) organo-halogens. While these potential sources have been described, links between carbon and halogen biogeochemistry in seawater have not been thoroughly explored.

Over the last 50 years, interest in halogen-containing pollutants has coincidently led to the discovery of over 8,000 naturally occurring halogenated organic compounds (Bidleman et al., 2019; Fowden, 1968; Gribble, 2003, 2010, 2023). The simplest, and perhaps most well-studied pool is volatile halocarbons because of their reactivity in the atmosphere, especially with ozone in the troposphere (Butler et al., 2007; Vogt et al., 1999; Von Glasow et al., 2002). While numerous semi- to nonvolatile halogen-containing compounds have been discovered and characterized in marine systems, the distribution and reactivity of these dissolved organic halogens (DOX) has been rarely studied (Bidleman et al., 2020), except for dissolved organic iodine (DOI). Truesdale (1975) first described evidence for an organically bound iodine fraction in seawater, suggesting that DOI is an active component in iodine cycling. Truesdale and Luther (1995) later demonstrated that hypoiodous acid (HOI) is the main iodine species that reacts with organic compounds in seawater, forming C-I and N-I bonds. New methodology that allowed for the determination of iodine speciation in seawater led to additional reports of the distribution of DOI concentrations in coastal and open ocean seawater, with concentrations ranging from below detection to >100 nM (Table S1) (Campos, 1997; Luther et al., 1991; Schwehr & Santschi, 2003; Schwehr et al., 2005; Truesdale et al., 2001; Wong & Cheng, 1998, 2008). It is now established that biological and abiotic processes can reduce iodate (IO_3^-) to iodide (I^-) as well as oxidize I^- back to IO_3^- and the intermediates between them (e.g., I_2/I_3^- and HOI) can form iodinated organic compounds (Luther, 2023). However, even when sampled at high temporal resolution in coastal systems, DOI concentrations are variable and do not correlate with dissolved organic carbon (DOC) concentrations (Jones et al., 2024; Satoh et al., 2019) so that the overall distribution and reactivity of DOI remain poorly understood.

Compared to DOI, less is known about dissolved organic bromine (DOBr) distributions in seawater, likely due to low concentrations compared to a much higher bromide background. Ratios of organically bound bromine to total organic carbon (TOC) in continental margin sediments have been used to distinguish terrigenous from marine organic matter sources with Br:TOC ratios increasing from river end members to continental slopes (Malcolm & Price, 1984; Mayer et al., 1981, 2007). Data on DOBr in the water column are sparse, but Méndez-Díaz et al. (2014) overcame analytical limitations in DOX analysis by utilizing solid phase extraction (SPE) to concentrate and desalt samples followed by residual halide removal with cartridges containing silver. Using this approach, they determined DOI and DOBr in coastal waters and at four depths in the North Pacific, but there have been no further attempts to use this approach to quantify DOX in seawater. Therefore, in the present work, SPE-methanolic extracts were collected at the Bermuda Atlantic Time-series Study (BATS) station in the western North Atlantic subtropical gyre and at the Hawaii Ocean Time-series (HOT) station ALOHA in the central North Pacific subtropical gyre (Figure 1a). DOBr and DOI were then detected by inductively coupled plasma-mass spectrometry (ICP-MS). To better understand DOX composition, select samples were extracted and fractionated by polarity. These polarity fractions were then analyzed by both ICP-MS and Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS), as detailed below (*Materials and Methods*).

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2. Materials and Methods

2.1. Sample Handling and Processing

Seawater samples were collected on two separate research cruises: the BATS cruise in August 2019 aboard the R/V *Atlantic Explorer* and the HOT cruise in July 2021 aboard the R/V *Kilo Moana*, as described previously (Gonsior et al., 2024). Briefly, 10-L samples were collected at selected depths from the surface to the seafloor using Niskin bottles mounted on a CTD rosette. These samples were acidified to pH 2 with ultrapure HCl (puriss. p.a., ≥32%, Sigma Aldrich) and filtered through combusted 0.7 μm GF/F filters in-line above the SPE columns (1 g Agilent Bond Elut Priority PolLutant (PPL) cartridges). Prior to extraction by gravity, PPL cartridges were activated with 10 mL methanol (LC-MS Chromasolv, Sigma Aldrich) and rinsed with 10 mL 0.1% formic acid in water (LC-MS Chromasolv Sigma Aldrich). Post-extraction, all cartridges were rinsed with 30 mL of 0.1% formic acid in water. Cartridges were then completely dried using vacuum manifolds in the hood and eluted with 10 mL methanol. All extracts were stored at −20°C prior to analysis. Statistically significant differences in DOBr and DOI between stations and depths were determined using a two-tailed unpaired Student's *t*-test in Excel and p-values < 0.05.

To examine DOX composition along a polarity gradient, samples at HOT (deep chlorophyll maximum (DCM, 125 m), 1,000 m, and bottom at 4,750 m) were extracted in duplicate as described above but were instead eluted sequentially with 10 mL methanol/water mixtures. These mixtures were prepared using ultrapure methanol and water at methanol percentages (v/v) of 7.4, 15.2, 23.4, 32.3, 40, 50, 60, 70, 80, 90, and 100, for a total of 11 fractions. For all fractions containing water (7.4%–90% methanol), extracts were completely dried in the hood under a gentle stream of N_2 gas. Fractions were then redissolved in 10 mL methanol and stored at −20°C.

2.2. DOBr and DOI Quantification

Extracts were dried under N_2 and redissolved in ultrapure water for a 25× dilution for whole water extracts and a 50× dilution for polarity fraction extracts. As done in previous work (Méndez-Díaz et al., 2014; Powers et al., 2024), these aqueous SPE samples were passed through Dionex™ OnGuard™ II Ba/Ag/H cartridges to remove any remaining inorganic halides. Ba/Ag/H cartridges were tested to ensure that bromide was completely removed from NaBr solutions with concentrations ranging from 10 to 10,000 μg Br L^{-1} and that organic bromine and iodine were not affected using a 10 μg Br L^{-1} solution of 5-bromo-3-iodobenzoic acid (Sigma-Aldrich). Ba/Ag/H-treated samples were then added in a 50:50 ratio to ultrapure water containing 1% NH_4OH and 1.0 μg Co L^{-1} (Agilent) in polycarbonate tubes and loaded into the ICP-MS autosampler. Blanks were prepared in the same manner using ultrapure water and standards were prepared using 5-bromo-3-iodobenzoic acid containing 0.5% NH_4OH and 0.5 μg Co L^{-1}. DOBr and DOI were determined using a triple-quadrupole inductively coupled plasma mass spectrometer (ICP-MS/MS, Agilent 8900 ICP-QQQ) with no gas in the Octopole Reaction System, as described previously (Powers et al., 2024). Briefly, Br was determined using m/z 79 (MS1) and m/z 79 (MS2) and I was determined using m/z 127 (MS1) and m/z 127 (MS2) with an integration time of 0.5 ms, 1 point per peak, 3 replicates, and 50 sweeps per replicate. The ICP was tuned weekly using a 1 ppb multi-element tuning solution containing Li, Co, Y, Tl, and Ce (Agilent) and ^{59}Co served as the internal standard in all samples, blanks, and standards. After analysis, DOBr and DOI concentrations were scaled for final dilution and for extraction and elution volume.

2.3. DOBr Molecular Characterization by FT-ICR MS

We used FT-ICR MS to identify DOBr molecular ions in SPE-DOM polarity fractions. These methanolic extracts were diluted 1:20 in ultrapure methanol and analyzed using a Bruker Solarix 12 Tesla FT-ICR mass spectrometer housed at Helmholtz Munich, Germany. The flow rate was held constant at 2 μL min^{-1} and samples were directly infused into the instrument using an autosampler that was washed with 600 μL of 80:20 MeOH:water between samples to prevent carryover. Samples were ionized using negative mode electrospray ionization at 3,600 V and 500 scans were averaged. The FT-ICR mass spectrometer was initially calibrated using known arginine clusters and post-calibrated using previously identified known molecular ions within DOM (Timko et al., 2015). Unambiguous molecular formulas were assigned with a mass error <0.2 ppm using a network approach (Tziotis et al., 2011), which is based on combinations of the elements $^{12}C_{1-\infty}$, $^{1}H_{1-\infty}$, $^{16}O_{1-\infty}$, $^{14}N_{0-10}$, $^{32}S_{0-2}$, $^{35}Cl_{0-5}$, $^{79}Br_{0-5}$, $^{127}I_{0-5}$, as well as the ^{13}C, ^{34}S, ^{37}Cl, and ^{81}Br isotopologues (Herzsprung et al., 2014, 2016). Molecular formula assignments with Br were confirmed manually using isotope simulation in the Bruker data analysis

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software (Gonsior et al., 2015), which confirms the ^{81}Br isotopologue at 49.31% natural abundance. Additional FT-ICR MS data analysis and visualization details are described in Text S1 in Supporting Information S1.

3. Results and Discussion

3.1. DOBr and DOI Distributions

Depth profiles obtained from BATS in August 2019 and HOT in July 2021 exhibit elevated DOX concentrations above 200 m followed by lower and somewhat stable concentrations at depth (Figure 1b). A similar trend was observed in samples collected beyond the shelf break of the Mid-Atlantic Bight, USA (Text S2 in Supporting Information S1, Table S1) and in select samples collected in the Northeast Pacific (Méndez-Díaz et al., 2014). DOBr concentrations were also significantly higher in surface waters at HOT (10.8 ± 0.6 nM, $n = 3$) than at BATS (5.3 ± 2.1 nM, $n = 3$) (p-value = 0.03). While not significantly different (p-value = 0.56), DOI concentrations were higher and more variable in surface samples at HOT (11.4 ± 5.4 nM, $n = 3$) than at BATS (5.8 ± 1.1 nM, $n = 3$). These values were approximately 3 orders of magnitude larger than those reported for various volatile halocarbons (Butler et al., 2007; Chuck et al., 2005; Liu et al., 2024; Liu, Yvon-Lewis, Thornton, Butler, et al., 2013; Liu, Yvon-Lewis, Thornton, Campbell, & Bianchi, 2013). Previous estimates of DOI based on the difference between total iodine and inorganic iodine in the open ocean are somewhat higher (~40–100 nM) (Tian & Nicolas, 1995; Wong & Cheng, 1998). However, given that DOI may be 10% or less of total iodine in the open ocean, estimations of DOI in both surface and deep water have been often analytically uncertain using this difference method (Tian & Nicolas, 1995; Wong & Cheng, 1998). While SPE allows for sample concentration and well-resolved DOI and DOBr depth profiles, we could underestimate DOX by a factor of 2 based on average DOC SPE recoveries of ~50% in seawater (Dittmar et al., 2008). On the other hand, if extracted compounds form adducts with halides, which has been demonstrated for sugars with chloride (Boutegrabet et al., 2012), SPE DOX may be overestimated. It is not yet known whether adducted halides are removed when passed through silver cartridges, but sugars are not likely retained using our SPE approach. Therefore, both DOBr and DOI in this study should be considered low end estimates of total DOX or, more specifically, measurements of extractable DOX concentrations.

Our profiles indicate that both DOBr and DOI exhibit significantly higher concentrations below 1,500 m at HOT (6.6 ± 0.3 nM DOBr and 1.6 ± 0.08 nM DOI, $n = 8$) than at BATS (2.2 ± 0.09 nM DOBr and 0.79 ± 0.12 nM DOI, $n = 5$) (p-values < 0.01). Prior work at both HOT and BATS has demonstrated that I^- concentrations measured over several sampling campaigns are approximately two times higher in the top 100 m at HOT (215 ± 52 nM) versus BATS (102 ± 16 nM) (Campos et al., 1996). Because IO_3^- is thermodynamically stable in oxygenated seawater (Luther, 2023), higher I^- concentrations at HOT were explained using a function that related I^- formation to primary production and loss to mixing and oxidation (Campos et al., 1996). While iodine cycling also depends on additional factors (e.g., freshwater flux, mixed layer depth) (Wadley et al., 2020), higher primary production at HOT relative to BATS (Karl et al., 2001) may explain overall higher DOI concentrations at HOT compared to BATS. Higher halogenation activity, perhaps due to biotic and abiotic (i.e., photochemical) processes, and export of refractory DOX at HOT could also explain the much higher DOBr concentrations throughout the water column at HOT since bromide is not redox active and is lower at HOT than at BATS (Figure S1 in Supporting Information S1). Moreover, DOX distributions at depth may be explained by the influence of North Atlantic Deep Water at BATS and DOBr accumulation during deep water circulation. Dissolved lignin phenol concentrations, proxies for terrestrial DOM, decrease progressively from the deep Atlantic to the deep Pacific (Hernes & Benner, 2006) and terrestrial DOM has very low DOX concentrations relative to marine DOM (Méndez-Díaz et al., 2014). Another possibility may be that there is some hydrothermal influence from the Kama'ehuakanaloa (Lō'ihi) Seamount in the deep waters at HOT, which has been studied extensively for iron geochemistry (Boyle et al., 2005; Rouxel et al., 2018). Reductive dehalogenation activity was found in cold seeps (Han et al., 2025), and halogenated compounds have been detected in vent fluids (Grandy et al., 2020) and volcanic gases (Schwandner et al., 2013), suggesting that hydrothermal features may be a source of organohalogens in seawater. Without more information on DOX distributions globally, it is difficult to explain differences in DOX profiles between these two oceanographic locations. However, given that DOBr and DOI concentrations reported previously in the deep waters of the North Pacific (5.6 ± 0.9 and 1.9 ± 0.3 nM, respectively) (Méndez-Díaz et al., 2014) are similar to those at HOT, this preliminary evidence suggests that deep ocean DOX concentrations may be higher in the Pacific than in the Atlantic.

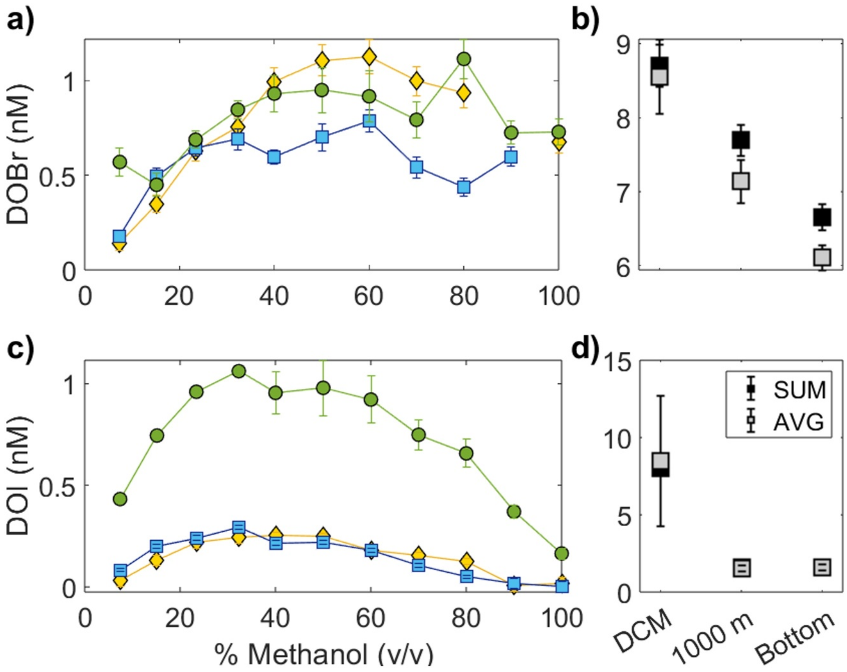

Figure 2. (a) DOBr (nM) and (c) DOI (nM) versus methanol content in fractions sequentially eluted from solid phase extraction cartridges, reported in %methanol (v/v), for a deep chlorophyll maximum (DCM, 125 m) sample (green circles), a 1,000 m sample (yellow diamonds), and a bottom (4,750 m) sample (light blue squares) collected at the Hawaii Ocean Time-series station. Total (b) DOBr (nM) and (d) total DOI (nM) (black squares), calculated as the sum of that in each fraction in panels (a, c), respectively, compared with average concentrations at each depth (gray squares) in unfractionated samples (Figure 1).

3.2. DOX Physicochemical Properties and Molecular Composition

It is likely that DOBr and DOI exhibit differences in reactivity driven by differences in their composition. Thus, we examined DOX physical distribution along a polarity gradient for three samples: DCM (125 m), 1,000 m, and bottom (4,750 m) at HOT. Summed DOX concentrations were in good agreement with total DOBr and DOI concentrations discussed above that were eluted with one volume of methanol (Figures 2b and 2d). In general, DOBr was lowest in the low methanol high polarity fractions and increased to somewhat stable concentrations in the mid polarity (~40% methanol) to low polarity (100% methanol) range (Figure 2a). DOI was also low in the high polarity fractions and increased to its highest concentrations around 33% methanol. Unlike DOBr, DOI concentrations then decreased from 60% to 100% methanol (Figure 2c). DOI was always higher in the DCM fractions compared to those from 1,000 m and the bottom sample whereas DOBr concentrations were similar in each fraction at all three depths. This result is not surprising, as DOBr only decreases by 17% and 28% between the DCM and 1,000 m and the bottom, respectively, whereas DOI decreases by ~82% below the DCM (Figure 1b). While the production of both DOBr and DOI may be linked to primary production (Cabrita et al., 2010; Paul & Pohnert, 2011), these variations between DOBr and DOI along a polarity gradient point to fundamental differences in DOBr and DOI composition. Early work that subjected marine sediments to a variety of chemical tests suggested that organic iodine mainly exists as N-iodoamides but organic bromine may be composed of aliphatic compounds, neutral compounds, non- to semi-polar organic acids, amines, and phenolic compounds (Harvey, 1980). Organic bromine was found to be ubiquitous in a variety of marine sediments, which was linked to organic bromine content in sinking particles (Leri et al., 2010). There is some variation in bromine speciation with depth in the sediment (Leri et al., 2010), suggesting some cycling between inorganic and organic forms, but given the high organic bromine content observed in sinking particles, the authors suggest that a portion of the stable organic bromine found in sediments was produced in surface waters (Leri et al., 2010). On the other hand, sedimentary organic iodine appears to be more labile. Iodine enrichment in surface sediments was explained by active iodine cycling near the water sediment surface followed by I^- release at depth during the decomposition of organic iodine (Kennedy & Elderfleld, 1987). Thus, if DOM degradation results in stable

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organic bromine that contributes to DOBr, it may partly explain why DOBr concentrations are higher at depth when compared to DOI concentrations.

We further investigated DOBr molecular composition in each polarity fraction for the DCM, 1,000 m, and deep sample using FT-ICR MS (Text S1, Figures S2 and S3 in Supporting Information S1, Figure 3). In general, intensities for ions containing carbon, hydrogen, oxygen, and bromine (CHOBr) were low, which explains why these ions have not been identified by direct-infusion FT-ICR MS in previous studies. In total, 92 CHOBr ions were found across all sample depths and all polarity fractions, with some ions found in two (*n* = 24), three (*n* = 10), four (*n* = 8), or five (*n* = 4) fractions (Figures S2 and S3 in Supporting Information S1). Inclusive of this repetition, a total of 82 CHOBr ions were found in DCM fractions, 120 were found in 1,000 m fractions, and 81 were found in bottom fractions. Of these, 33 CHOBr ions were common between the DCM, 1,000 m, and deep samples, which were centered around an *m*/*z* of 425, an O/C ratio of 0.35, a H/C ratio of 1.3, and an average carbon oxidation state (COS) of −0.5 (Figure S2 in Supporting Information S1). While ions unique to DCM were the most diverse (Figures S2 and S3 in Supporting Information S1), most ions unique to a particular depth displayed similar oxygenation and saturation to common ions, clustered around an *m*/*z* of 400 to 550, an O/C ratio of ~0.3 to 0.5, a H/C ratio of ~1.2 to 1.5, and a COS of ~−0.8 to −0.2 (Figure 3 and Figure S4 in Supporting Information S1). Moreover, these somewhat oxygenated and unsaturated ions are similar in composition to ions attributed to carboxyl-rich alicyclic molecules (CRAM) (Figures S4 and S5 in Supporting Information S1), a proposed major component of refractory DOM (Hertkorn et al., 2006). While CHO ions attributed to CRAM by Hertkorn et al. (2006) are generally more oxidized with higher mass (*m*/*z* 537 ± 70), higher O/C ratios (0.42 ± 0.10), lower H/C ratios (1.15 ± 0.16), and higher COS (−0.30 ± 0.32), standard deviations of intensity-weighted averages overlap for the CHOBr ions in this study (Figures S4 and S5 in Supporting Information S1). While FT-ICR MS data alone cannot be used to provide structural information, a few homologous series containing 4–6 CHOBr ions were also observed in modified Kendrick plots (Figure 3b), suggesting that some ions are related. Because carboxyl groups are a major component of CRAM (Hertkorn et al., 2006), we also determined CO_2-based (44 Da) Kendrick mass defect for CHOBr ions (Figure 3c), which resulted in 15 series containing two ions and 7 series containing three ions. Again, these analyses cannot provide structural information, but they do suggest that the CHOBr ions characterized here, while more reduced, display similarities to CRAM. Intriguingly, recent work suggests that high polarity CRAM signatures are more refractory than low polarity CRAM signatures identified by FT-ICR MS after a 90-day incubation experiment (Cai et al., 2025). Thus, similar approaches could be applied in future work to better understand the composition and reactivity of DOX.

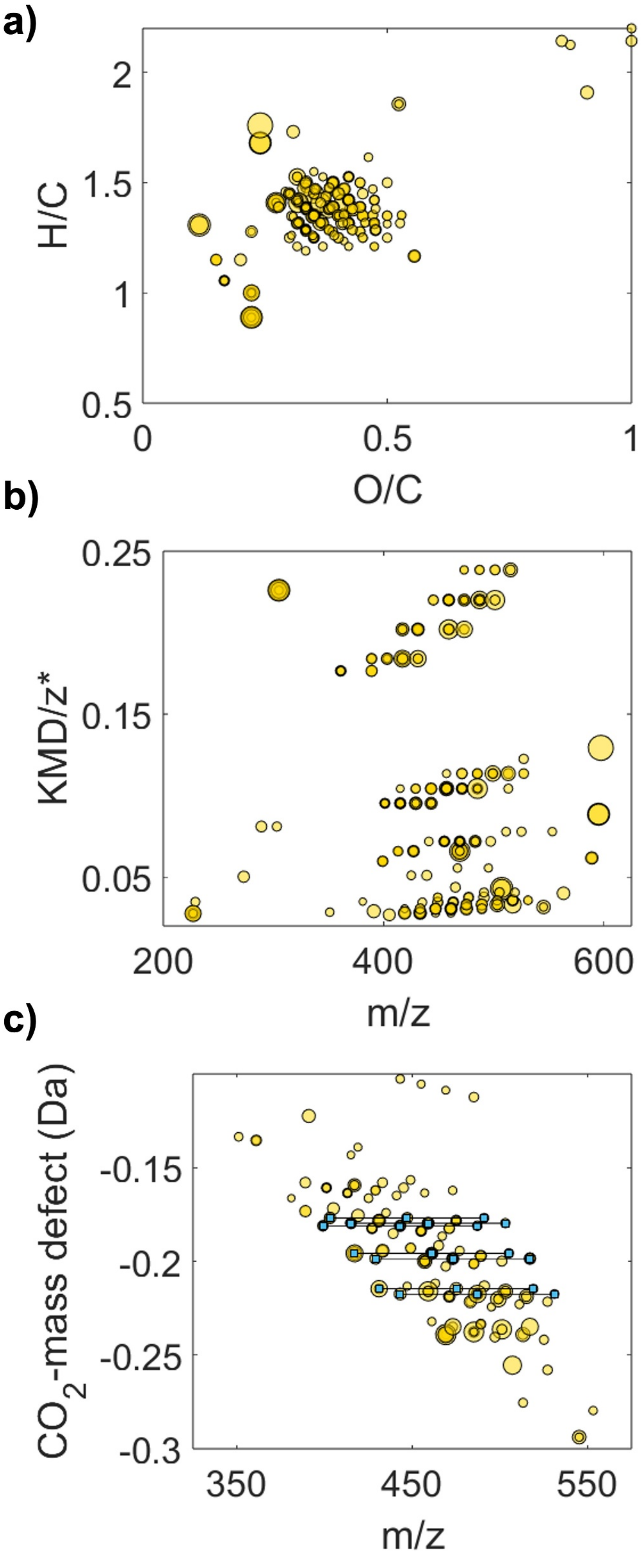

Figure 3.

Figure 3. (a) Oxygen-to-carbon (O/C) versus hydrogen-to-carbon (H/C) ratios, (b) modified Kendrick mass defect (KMD/z*) versus *m*/*z*, and (c) CO_2-based Kendrick mass defect versus *m*/*z* for molecular ions containing carbon, hydrogen, oxygen, and bromine (CHOBr) in polarity fractions isolated from the deep chlorophyll maximum, 1,000 m, and bottom (4,725 m) at Hawaii Ocean Time-series. Individual CHOBr molecular ions are represented by yellow circles whose size indicates average ion intensity. Connected blue squares in panel (c) are CO_2-mass defect series containing 3 ions.

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3.3. Preliminary DOX Inventories

To estimate DOX inventories, we first calculated DOC:DOBr and DOC:DOI molar ratios for our SPE samples (Table S2 in Supporting Information S1). Details of these calculations are provided in Text S3 in Supporting Information S1. DOC:DOBr ratios were stable with depth, averaging ∼7,900 ± 2,400 at BATS and ∼2,800 ± 440 at HOT for the entire water column. DOC:DOBr ratios at HOT were like those reported in the North Pacific, which averaged 2,130 ± 680 for four stations sampled between the surface and 3,750 m (Méndez-Díaz et al., 2014). These stable ratios with depth further support a link between refractory DOC and DOBr as well as differences between the production and/or degradation rates of DOBr and DOI. DOC:DOI ratios behaved differently from DOC:DOBr (Table S1), being significantly lower in the upper 125 m (3,240 ± 270) than at depths ≥1,200 m (10,900 ± 800) (p-value = 0.02) at HOT. DOC:DOI ratios were higher at BATS than at HOT, but also significantly lower in the upper 125 m (8,270 ± 3,790) than at depths ≥1,200 m (23,500 ± 7,340) (p-value = 0.02). Increases in DOC:DOI and DOBr:DOI with depth could be explained by the preferential remineralization of DOI relative to both DOC and DOBr in the surface ocean, as C-I bonds are generally thought to be labile (Campos et al., 1996). DOC:DOI ratio for Suwannee River Natural Organic Matter (SRNOM) increased when irradiated in artificial seawater (Méndez-Díaz et al., 2014), suggesting some DOI removal due to photochemistry. While SRNOM in artificial seawater is very different from the natural marine waters studied here, these results may suggest that DOI in surface waters is susceptible to both biological and photochemical degradation, whereas DOBr may be more stable.

Despite the differences in DOX between HOT and BATS, we utilized average DOC:DOBr and DOC:DOI ratios (Table S2 in Supporting Information S1) and estimated SPE extractable DOC from reported global DOC inventories (Hansell et al., 2009) to calculate preliminary global DOX inventories (Text S3 in Supporting Information S1) of 532 ± 173 Tg Br and 265 ± 62 Tg I, amounting to a combined DOX inventory of ∼0.75 Pg. DOX is likely very similar in size to other heteroatoms within DOM, such as dissolved organic sulfur (6.7 Pg) (Ksionzek et al., 2016) and dissolved organic phosphorus (2.1 Pg) (Letscher & Moore, 2015), especially because this study only focused on DOBr and DOI and dissolved organic chlorine (DOCl) may also represent a substantial portion of the DOX pool. Organic chlorine in POM ranged from 180 to 694 mg Cl kg^{-1} for material collected in sediment traps deployed in the Arabian sea (Leri et al., 2015) and was comparable to the organic bromine content of the POM in these samples (Leri et al., 2014). Like the formation of DOBr and DOI, Leri et al. (2015) demonstrate that both enzymatic and abiotic processes can produce chlorinated organic matter. Therefore, it is likely that DOCl together with DOBr and DOI represent major organic halogen reservoirs within the oceans.

4. Conclusions

In this study we provide new information on DOX quantities and composition in the Central North Atlantic at BATS and in the Central North Pacific at HOT. While DOX concentrations are elevated in surface waters and decrease with depth, DOX was always higher at depths >1,000 m at HOT than at BATS. Moreover, DOBr concentrations were higher and more stable throughout the water column when compared to DOI concentrations, perhaps reflecting their contribution to the refractory DOM pool. The molecular composition of DOBr further displays similarities to CRAM, a proposed component of refractory DOM, but DOBr structural information is not available at this time. Thus, future work on both the distribution and molecular composition of DOX in the oceans could provide novel insights into how these molecules behave in the oceans as well as their overall role in the biogeochemical cycling of marine DOM.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

For this study we used DOC data from repeat hydrography cruises at BATS (Bates et al., 2025), available at https://www.bco-dmo.org/dataset/3782 (doi: 10.26008/1912/bco-dmo.3782.8). DOC data from repeat hydrography cruises at HOT was obtained via Hawaii Ocean Time-series HOT-DOGS application (2022) (https://hahana.soest.hawaii.edu/hot/hot-dogs/interface.html). Data described in this manuscript may be found at https://www.bco-dmo.org/dataset/986596 (doi: 10.26008/1912/bco-dmo.986596.1) (Powers & Gonsior, 2025).

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