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Key Points:

- Novel method developed to continuously measure chemical uptake of ozone by seawater
- Surface ocean ozone uptake dominated by reactions with iodide and marine organics
- Substantial ozone uptake capacity also observed in deep seawater

Supporting Information:

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

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Marine Biogeochemical Control on Ozone Deposition Over the Ocean

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Abstract The ocean is a large but uncertain sink of tropospheric ozone. Ozone deposition is controlled partly by its reactions with marine substances, but in situ evidence of this marine biogeochemical control remains sparse. Here we report a novel measurement of ozone uptake efficiency (OUE) from a trans-Atlantic cruise (50°N to 45°S). Observed OUE for surface waters varied two-fold and the implied chemical deposition velocity varied from 0.012 to 0.034 cm s^{-1}. Iodide accounted for on average 2/3 of total OUE, with generally higher contributions in tropical waters. The residual OUE, generally higher in temperate waters and positively correlated with biological proxies, was likely due to marine organics. OUE was also measured for 1,000 m waters, which were likely devoid of iodide but contained biologically refractory organics. Unexpectedly, these waters were rather reactive toward ozone, suggesting that surface organics that affect ozone uptake are not all freshly produced by marine biota.

Plain Language Summary Ozone in the lower atmosphere is a key air pollutant and a strong greenhouse gas. Deposition to the ocean represents a large removal mechanism for ozone but the processes driving this removal remain poorly understood. The rate of ozone deposition to the ocean is thought to be controlled by its reactions with marine substances and by surface ocean turbulence. However, in situ evidence of marine biogeochemical control on ozone deposition is sparse, hampering the mechanistic description of this process. Here we employ a novel technique to measure the chemical uptake of ozone on a research cruise in the Atlantic Ocean that spans 95° latitude. We found that iodide and organics in surface seawater are both important reactants toward ozone deposition, with different relative contributions at different latitudes. Surprisingly, we found that deep waters also have substantial reactivity toward ozone, suggesting that when these waters are mixed to the surface, the nominally biologically inert organics are oxidized by reactions with ozone.

1. Introduction

Ozone in the troposphere is a key oxidant, pollutant, and greenhouse gas (e.g., Monks et al., 2015). Deposition to the ocean surface is a large but poorly quantified sink for tropospheric ozone, accounting for approximately a third of the global ozone deposition (100–600 Tg ozone yr^{-1}; Ganzeveld et al., 2009; Hardacre et al., 2015; Luhar et al., 2018; Pound et al., 2020). The ozone deposition flux is parametrized as $-V_d$ [ozone], where V_d is the deposition velocity and typically assumed to be constant (e.g., 0.05 cm s^{-1}) in most chemistry and climate models (Ganzeveld & Lelieveld, 1995). However, theory suggests that ozone deposition velocity is governed by both its reactions with marine substances as well as by surface ocean turbulence (e.g., Fairall et al., 2007). Direct V_d measurements of ozone to the ocean vary by more than an order of magnitude and show marked regional variability, with typically higher V_d in coastal or warmer waters (Bariteau et al., 2010; Helmig et al., 2012; Loades et al., 2020). A large part of the variability in V_d is postulated to be due to the variability of biogeochemical reactants in seawater.

Marine iodide reacts rapidly with ozone and exists at sufficiently high concentrations to be a key reactant (Garland et al., 1980). Organics in seawater may be another important reactant (e.g., Ganzeveld et al., 2009; Sarwar et al., 2016), as ozone is known to react with a range of functional groups including carbon-carbon double bonds, activated aromatic rings (e.g., phenols), amines and thiols (Lim et al., 2022). However, due to the complexity in organic composition it remains unclear which fraction of marine organics are most important toward ozone

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reactivity. In laboratory experiments, Martino et al. (2012) showed that NOM (natural organic material, Suwannee River standard) and iodide are of similar importance toward ozone deposition velocity. Given the fact that Suwannee River NOM is considerably more unsaturated and possibly reacts with ozone faster than marine dissolved organic carbon (DOC), the representativeness of their results for the real ocean is unclear. Marine Chlorophyll *a* (Clifford et al., 2008) and dimethyl sulfide (DMS, Gershenzon et al., 2001) may also contribute to enhanced ozone deposition, but these are only small fractions of marine organics. Clearly, understanding the distributions of the key reactants will help to improve the mechanistic understanding and parameterization of ozone deposition to the ocean.

This work presents novel observations of the ozone uptake by seawater during a transect of the Atlantic Ocean in October–November 2019 from Southampton, UK to Punta Arenas, Chile on the Atlantic Meridional Transect (AMT) 29 cruise. A new measurement method was developed to continuously measure the ozone uptake efficiency (OUE) by seawater. Observations of seawater iodide concentration, coupled with laboratory rate experiments using iodide standards, were used to determine the contribution of iodide toward ozone uptake. We assess how the residual OUE varies with widely observed organic proxies including Chlorophyll *a* and colored dissolved organic matter (CDOM). Measurements of OUE on seawater from 1,000 m depth are further used to explore the reactivity of deep water toward ozone.

2. Experimental

2.1. Description of the OUE Method

OUE is a relative measure of the fraction of ozone taken up by a water sample. In the OUE system, ozone produced by an ozone generator was diluted by zero air, resulting in a total gas flow rate of 200 standard $cm^3\ min^{-1}$ (controlled by two mass flow controllers, Bronkhorst EL-FLOW Select). This flow of diluted ozone was mixed with a flow of water driven by a peristaltic pump (Watson Marlow 120S/DV) at a flow of 100 mL min^{-1} in a segmented flow coil equilibrator (SFCE, as described by Wohl et al., 2019). This naturally leads to the formation of many cm-scale, alternating water/air segments that transit through the SFCE coil (2 m long, 4 mm inner diameter Teflon tube). Gas exchange and ozone reactions occur at the interfaces of water/air segments as well as on the wetted tubing wall within a transit time of 4.8 s. Gas and water phases separate after passing through the SFCE coil, with the gas phase measured continuously for the ozone mixing ratio using an ozone monitor (2B Technologies model 205, output every 10 s) and the sampled water drained away. A schematic of the OUE system is provided in the Supplement (Figure S1 in Supporting Information S1), where further details about the method can also be found.

During the AMT29 cruise, fresh, unfiltered seawater from ∼5.5 m below the surface and at the bow of the ship was continuously pumped into the ship. This underway seawater was flushed into an overflowing, narrow-necked glass sample bottle. Occasional discrete water samples from 1,000 m depth were also collected into 2 L glass bottles from the polypropylene Niskins attached to a conductivity, temperature, and depth rosette (CTD). The choice of sampling the underway water or discrete water was achieved by manually moving the Teflon water inlet tube for the peristaltic pump. In this paper, we refer to the underway water as "surface," with the implicit understanding that this is distinct from the <1 mm thick skin of the ocean (surface microlayer, SML). Underway water sampling is much easier logistically than SML sampling, especially for continuous measurements. Recent observations also suggest a high correlation in DOC concentration between the SML and underlying water (e.g., Mustaffa et al., 2018). Possible biases from using underway water to infer ozone deposition to the ocean surface are discussed in Section 4.

A bypass in the OUE system enabled the periodic monitoring of the ozone input mixing ratio. A three-way solenoid valve (Takasago Electric, Inc. MLV-3T-1/8NG) was used to alternate the sampling of ozone through or bypassing the SFCE every 5 min. OUE is determined from adjacent periods of SFCE and bypass:

$$\mathrm{OUE} = 1 - (\mathrm{ozone}_{\mathrm{SFCE}}/\mathrm{ozone}_{\mathrm{bypass}}) \quad (1)$$

Here $\mathrm{ozone}_{\mathrm{SFCE}}$ and $\mathrm{ozone}_{\mathrm{bypass}}$ represent the averages of the last 2.5 min of respective periods, where the signals were stable. The length and the inner diameter of the SFCE coil were chosen such that roughly half of the ozone remains after passing through the SFCE for a typical seawater sample (i.e., OUE ≈ 0.5). Underway OUE measurements every 10 min were averaged into 1 hr bins to reduce noise. The hourly standard deviation (σ) was 0.01 or ~2% of the mean OUE. Compared to previous discrete methods of measuring ozone uptake such as stirred-flask (Martino et al., 2012) and wetted-wall flow tube (Barcellos da Rosa et al., 2003; Clifford et al., 2008), this system can be operated continuously and is thus suitable for measurements over a large spatial/temporal scale at a high resolution. In addition, the turbulent conditions within the SFCE (generated by passing air/water segments) means that the system is insensitive to platform motion, which is a clear advantage for shipboard deployments relative to more quiescent methods.

2.2. Calibration of the OUE Measurement

OUE in the SFCE is measured at a fixed level of turbulence and thus represents the combined contribution from chemical reactivity and physical uptake. Repeated measurements of high purity water (18.2 MΩ; MilliPore Milli-Q) yielded a blank (OUE_{blank}) of 0.15 (±0.01), which was found to be independent of the ozone input mixing ratio. This blank was likely due to a combination of physical uptake of ozone via air–water exchange, aerodynamic resistance, and any wall losses within the SFCE. Assuming the physical and chemical contributions to ozone exchange are parallel and additive (e.g., Helmig et al., 2012), in Section 3 we subtract OUE_{blank} from the measured OUE. The blank-corrected OUE should approximate chemically mediated ozone uptake, with a higher OUE indicating greater chemical reactivity.

A rather high ozone input mixing ratio (1.2 ± 0.4 ppmv) was used in the SFCE system during AMT29 to ensure a high signal:noise ratio. This equates to a theoretical equilibrium dissolved ozone concentration (in the absence of any chemical reactions) of ~12 nM, which is still several times less than the typical iodide concentration in surface water across the majority of the ocean surface (Chance et al., 2014, 2019). Post-cruise laboratory experiments show that OUE varies linearly with the ozone input mixing ratio, with higher OUE at a lower input (Figure S2 in Supporting Information S1). Based on this empirical relationship, we adjust field OUE data to the mean input of 1.2 ppmv in this section to account for variations in the ozone input from the generator.

Surface iodide concentration was measured using cathodic stripping square wave voltammetry (following Campos, 1997; Chance, Tinel, et al., 2020). The analysis was performed post-cruise on discrete daily water samples (50 mL) taken from the ship's underway system, filtered (through GF/F filter paper using a glass syringe), and frozen (−20°C) during the cruise. The sensitivity of OUE toward iodide was determined in post-cruise experiments by measuring iodide standards at different concentrations (Figure S3 in Supporting Information S1). The iodide contribution to observed OUE on the cruise was then estimated by combining this empirical relationship with the ambient iodide concentrations. Laboratory OUE measurements using Milli-Q water, 100 nM iodide standard, and the same batch of seawater samples at different temperatures (5–35°C) did not reveal any clear temperature dependency. The lack of temperature sensitivity in the iodide measurements is consistent with recent, independent laboratory results from Brown et al. (2024). DOC concentration was not measured during AMT29, and so we make use of modeled DOC from Roshan and DeVries (2017) for the surface and previous measurements (Hansell et al., 2021; Ogawa & Tanoue, 2003; Romera-Castillo et al., 2016) for the deep ocean for interpretation. The cruise track for the AMT29 cruise is shown Figure S4 in Supporting Information S1.

3. Spatial Distributions in Surface OUE and Relationships With Biogeochemical Proxies

As shown in Figure 1, surface OUE during AMT29 varied from about 0.30 to 0.60 during the cruise, with a mean (standard deviation) of 0.44 (0.06). Higher OUE values were broadly observed in the tropics, especially the tropical North Atlantic, where surface iodide concentrations were elevated. Some spikes in OUE were also observed in temperate waters at around 50°N and 45°S, which broadly corresponded to elevated Chlorophyll *a* concentration (measured from underway water by absorption following Dall'Olmo et al., 2012) and CDOM absorption (extracted from MODIS satellite data and measured underway following Dall'Olmo et al., 2017).

Surface seawater iodide concentration ranged from 26 to 174 nM (mean of 98 nM), in good agreement with previous measurements (Chance et al., 2014). OUE clearly shows correspondence with iodide concentration, but the modest correlation ($r^2 = 0.28$; Figure 2a) suggests that iodide is not the only control for OUE. The estimated contribution from iodide toward OUE follows the distributions of iodide concentration, amounting to on average two thirds of the surface OUE for the entire transect and over 80% for the tropics (Figure 1b). In contrast, the

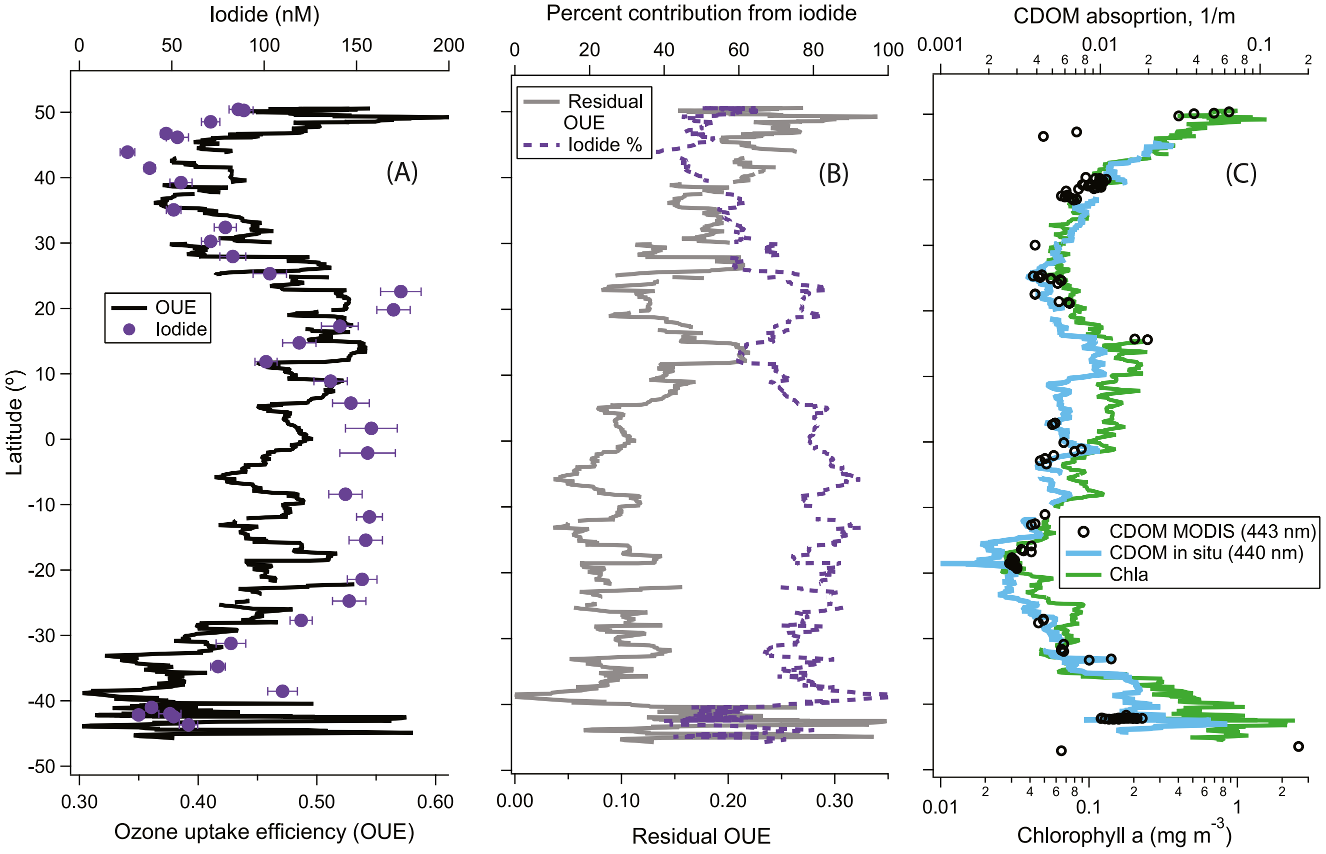

Figure 1. Latitudinal distributions of (a) surface ozone uptake efficiency (OUE) and iodide (b) residual OUE and percent contribution from iodide toward total OUE; and (c) Chlorophyll *a* concentration and CDOM absorption (from both MODIS satellite and from in situ). Observed OUE contains contributions from both iodide (which dominate in the tropics) and organics (which becomes more important in temperate waters).

residual OUE (total OUE minus iodide contribution) mostly peaks in temperate waters (e.g., 50°N and 45°S), and is broadly higher in the North Atlantic than the South Atlantic.

The relationship between OUE and underway sea surface temperature (SST) clearly shows two distinct groupings (Figure 2b) between cooler temperate waters and warmer tropical waters. Consistent with post-cruise laboratory experiments, at a constant iodide concentration (e.g., 80 nM), OUE during AMT29 does not obviously vary with SST (Figure 2a). Thus, the apparent relationship between OUE and SST in warm waters is likely due to the higher iodide concentration in the tropics, rather than due to a temperature dependence in the ozone reaction kinetics. Once the iodide contribution has been subtracted, the residual OUE correlates positively with CDOM and Chlorophyll *a* (Figures 2c and 2d), two proxies of biological activity. This strongly implies that the residual OUE is in part due to biologically derived organic reactivity. The slope in the CDOM spectra between 420 and 490 nm is indicative of the extent of photodegradation of organic matter (e.g., Helms et al., 2008). There is a subtle hint from Figure 2c that at a constant CDOM absorption, a higher CDOM slope (i.e., more photodegraded, or smaller organic molecules) corresponds to a lower residual OUE, implying that photodegradation may reduce the organic reactivity toward ozone. This is qualitatively consistent with the observations that for temperate waters, the mean OUE is significantly higher at night (0.432 with standard error of 0.005) than during the day (0.410 with standard error 0.005).

4. Ozone Chemical Deposition Velocity and Reactivities

In this section, following previous laboratory approaches (Brown et al., 2024; Martino et al., 2012) we convert the OUE data into a chemical deposition velocity (V_{dc}):

$$V_{dc} = -(\mathrm{Ln}(1-\mathrm{OUE_{corr}}) - \mathrm{Ln}(1-\mathrm{OUE_{blank}}))\,(V_a/S)/t_{\mathrm{SFCE}} \tag{2}$$

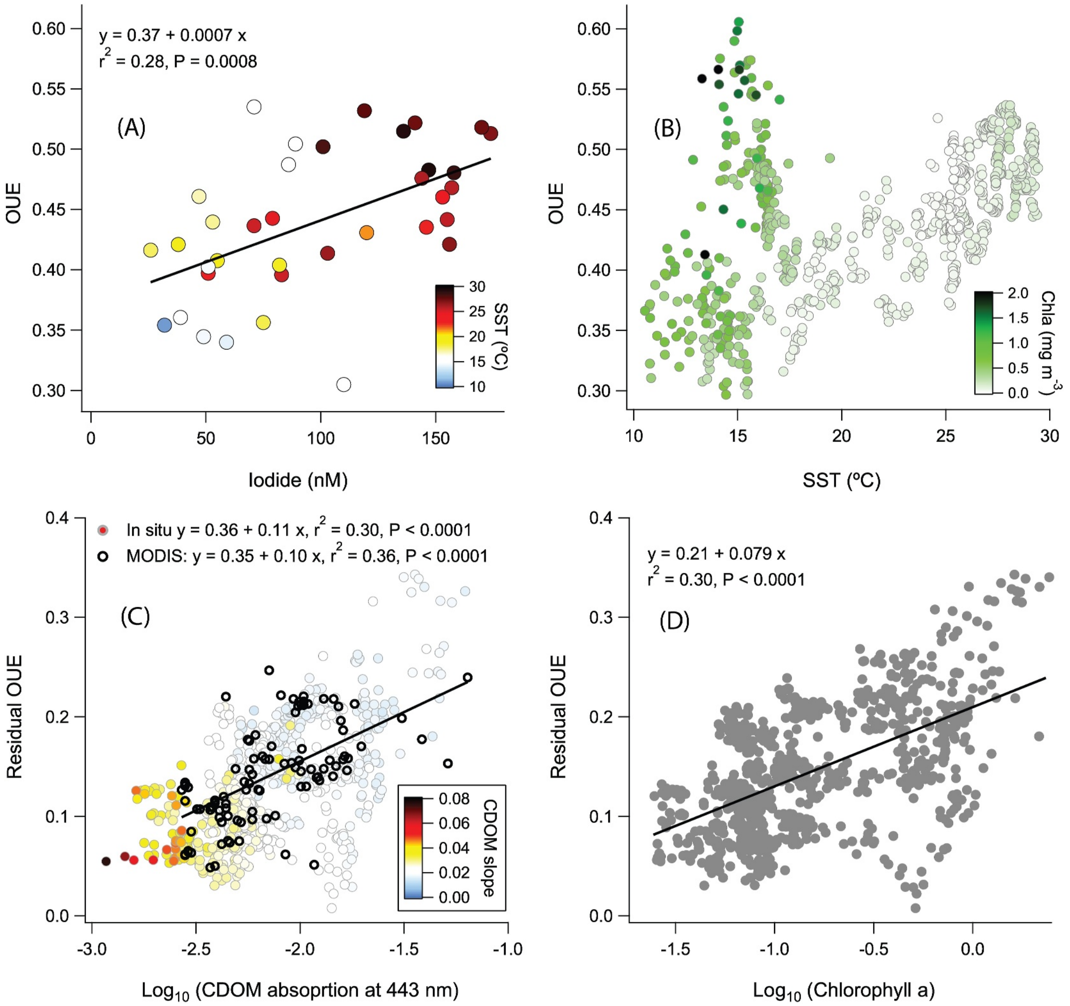

Figure 2. Correlations between (a) surface ozone uptake efficiency (OUE) and iodide, color-coded by sea surface temperature (SST); (b) OUE and SST, color-coded by Chlorophyll *a* concentration; (c) residual OUE versus colored dissolved organic material (CDOM), log-scaled and color-coded by the CDOM slope; and (d) residual OUE versus Chlorophyll *a*, log-scaled. Total OUE shows some relationship with iodide concentration and SST, while the residual OUE broadly correlates with biological proxies including CDOM and Chlorophyll (*a*).

Here OUE_{corr} has been adjusted to a typical marine atmospheric ozone mixing ratio of 30 ppbv (Monks et al., 2015) following the empirical relationship (Figure S2 in Supporting Information S1), but not yet blank subtracted. V_a is the volume of an individual air segment (0.38 cm^3). The surface area for exchange/reaction (S) is taken to be the total surface area of a cylindrical air segment (4.0 cm^2). We note that the ratio between V_a and S is fairly insensitive to the length of the air segments. The transit time within the SFCE system (t_{SFCE}) is estimated as the interior volume divided by the combined water and air flow rates (4.8 s). Equation 2 assumes that within the timescale of t_{SFCE}, the change in log-transformed ozone mixing ratio within the SFCE is linear. Note that the total ozone deposition velocity (V_d), including the effect of turbulence, will be higher than V_{dc} (see e.g., Equation 6 from Helmig et al., 2012).

The estimated V_{dc} from OUE ranges from 0.012 to 0.034 cm s^{-1} (mean of 0.020 cm s^{-1}; Figure 3a). These values, representing the chemical contribution to uptake only, are understandably on the lower end of most field observations of V_d (e.g., Helmig et al., 2012; Loades et al., 2020). Analogously, from Equation 2 and laboratory iodide uptake experiments (Figure S3 in Supporting Information S1) we can estimate V_{dc} due to iodide based on its contribution toward OUE. V_{dc} due to iodide averages 0.012 cm s^{-1}, which amounts to 62% of total V_{dc} in the mean.

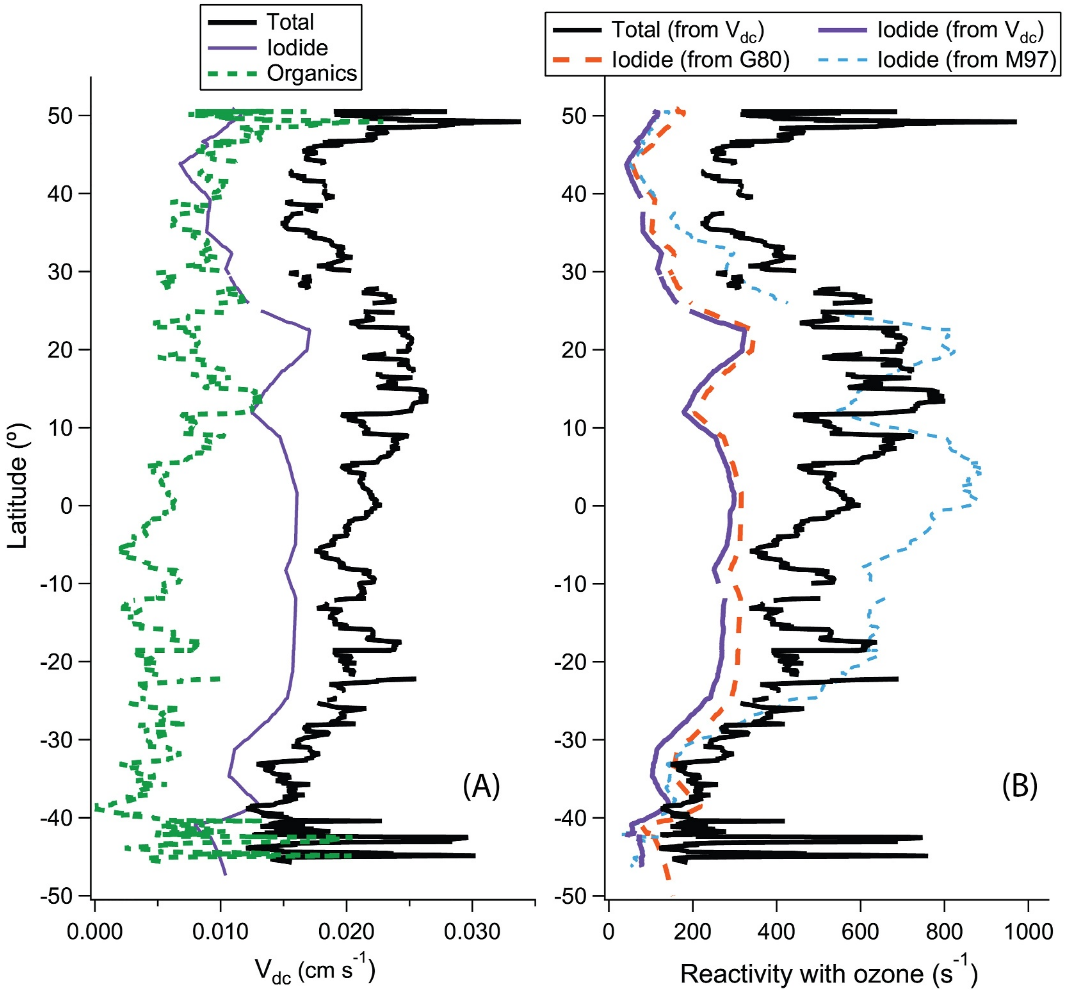

Figure 3. Latitudinal distributions of (a) chemical deposition velocity of ozone: total as well as contributions from iodide and organics (latter by difference); (b) reactivities toward ozone: total as well as iodide. Two approaches were used to estimate the iodide reactivities: (1) from measured chemical deposition velocity and (2) from iodide concentration and published reaction rate constants (Garland et al., 1980, abbreviated as G80, and Magi et al., 1997, abbreviated as M97).

The reactivity of iodide toward ozone ($\lambda_{\mathrm{iodide}}$, in s^{-1}) can be estimated with two separate approaches. First, knowing the iodide concentration $[\mathrm{I}^-]$ and assuming a reaction rate constant between ozone and iodide (k_{iodide}), we can calculate $\lambda_{\mathrm{iodide}}$ as $[\mathrm{I}^-]\ k_{\mathrm{iodide}}$. Two sources of k_{iodide} are tested here: the temperature-independent form from (Garland et al., 1980) (G80), as well as the temperature-dependent form (Magi et al., 1997) (M97). The two rate constants yield similar iodide reactivity at room temperature. However, in tropical waters the iodide reactivity computed using M97 is nearly three times higher than using G80.

Second, Garland et al. (1980) formulated the chemical uptake of ozone in bulk seawater as:

$$V_{dc} = \alpha(\lambda D)^{0.5} \tag{3}$$

Here α and D are the dimensionless solubility and diffusivity of ozone in seawater (here computed following Johnson, 2010). We then rearrange Equation 3 to solve for $\lambda_{\mathrm{iodide}}$ from V_{dc} that is due to iodide. As shown in Figure 3b, $\lambda_{\mathrm{iodide}}$ derived from V_{dc} is in good agreement with the computed $\lambda_{\mathrm{iodide}}$ using the G80 k_{I^-}, whereas the computed $\lambda_{\mathrm{iodide}}$ using the M97 k_{iodide} seems unreasonably high in warm waters. This is consistent with our observed lack of temperature dependence in the ozone-iodide reaction as well as findings from Brown et al. (2024). We can further estimate V_{dc} due to organics (mean of 0.008 cm s^{-1}) from the difference between total and iodide-driven V_{dc}. This leads to the highest organic-driven V_{dc} in temperate waters and lower contributions in the tropics, qualitatively similar to residual OUE. As with residual OUE (Figures 2c and 2d), organic-driven V_{dc} broadly correlates positively with Chlorophyll *a* concentration and CDOM (Figure S5 in Supporting Information S1).

It is tempting to estimate total λ from total V_{dc} via Equation 3, but this approach comes with a significant caveat. While ozone primarily reacts with iodide in bulk water within a reacto-diffusive depth scale of a few micron (Garland et al., 1980), reactions between ozone and organics may largely occur at the air–water interface (e.g., following Langmuir–Hinshelwood kinetics, Clifford et al., 2008), rendering the application of Equation 3 questionable. Bearing this caveat in mind, the estimated total λ using Equation 3 ranges between 121 and 972 s^{-1} (mean of 411 s^{-1}) for water from 5.5 m depth, with the highest reactivity in the tropics. In contrast to V_{dc} that varies by a factor of ~3 across the AMT29 track, total λ estimated this way varies by a factor ~8. Since organics account for about one third of observed V_{dc}, we can simplistically approximate that the mean organic reactivity on the AMT29 is on the order of 137 s^{-1} (411 s^{-1}/3). The surface ocean DOC in the Atlantic was previously determined to be 67 μM (Hansell et al., 2021; Ogawa & Tanoue, 2003; Romera-Castillo et al., 2016). This implies a bulk rate constant between ozone and DOC (k_{DOC}) of 2.0 s^{-1} μM^{-1}, which is of the same order of magnitude but lower than previous k_{DOC} estimates of 3.4–4.0 s^{-1} μM^{-1} from Coleman et al. (2012) and Sarwar et al. (2016) based on the Martino et al. (2012) measurements. Note that our derivation of total reactivity and partitioning between iodide and organic contributions above are rather crude. The combined uptake coefficient approach proposed by Moreno et al. (2018) may be more suitable, but its application to the AMT29 data set is beyond the scope of this paper. Our calculation also assumes that the ozone-organics reaction is temperature-independent and neglects any potential competition between the different reactants for ozone (see Martino et al., 2012).

Over the real ocean, ozone is deposited and absorbed at/near the sea surface. Previous measurements indicate that organics are enriched within the SML relative to the underlying water by ~50% (e.g., Mustaffa et al., 2018; Wurl et al., 2011). Neglecting details about the enrichment of specific reactants, our OUE measurements using underway seawater at ~5.5 m depth could be underestimating the importance of organics toward oceanic ozone uptake by ~50%. Since organics account for about one third of total chemical uptake of ozone in 5.5 m water, the underestimation in total OUE compared to the SML can be approximated to be ~14% ($=100\% \times (1 - 1/(2/3 + 1.5 \times 1/3))$). Indeed, measurements of concurrently taken samples from the SML and underlying water from the CONNECT cruise in the Equatorial Atlantic ($N = 6$) as well as from near the Plymouth coast ($N = 2$) suggest that the enhancement in ozone uptake in the SML relative to the underlying water is ~17% (Brown, 2024).

5. Ozone Reactivity of Deep Ocean DOC

The sources of organics that react with ozone in surface waters are not well understood but generally presumed to be related to recent biological activity. Blank-corrected OUE in discrete, 1,000 m water samples ($N = 12$) had a mean (standard deviation) of 0.21 (0.05), with lower values further south where the Antarctic Intermediate Water dominates. This surprising and substantial reactivity is qualitatively similar to the trend in DOC concentration at 1,000 m (Hansell et al., 2021). The deep OUEs convert to a mean equivalent V_{dc} of 0.0086 cm s^{-1} ("equivalent" because these deep waters are not in direct contact with the atmosphere). This amounts to about 44% of the total V_{dc} at the surface and is largely comparable in magnitude to organic-driven V_{dc} there (Figure 4a). The concentration of iodide at 1,000 m was not measured during AMT29 but is expected to be ≤5 nM (Chance et al., 2014), implying that the ability for deep water to take up ozone is essentially due to biologically refractory organics only. The substantial reactivity toward ozone in deep waters may be due to the abundance of highly unsaturated compounds that favor ozonolysis reactions, including aromatic compounds, in biologically refractory organics (Jiao et al., 2018).

For the 1,000 m samples, there is a clear positive correlation between V_{dc} and DOC concentration measured by Hansell et al. (2021) (Figure 4b). In contrast, no correlation is observed between organic-driven V_{dc} and DOC at the surface (Figure 4c), despite the much larger range in surface DOC. We speculate that a significant fraction of organic reactivity toward ozone in surface waters is due to aged, biologically refractory DOC. Recently produced organic matter from biological activity (as approximated by Chlorophyll *a* and CDOM, but not DOC) accounts for the rest of the surface organic reactivity. That biologically refractory DOC can also react with ozone rather efficiently is an important consideration for parametrizing surface organic reactivity toward ozone on a large scale.

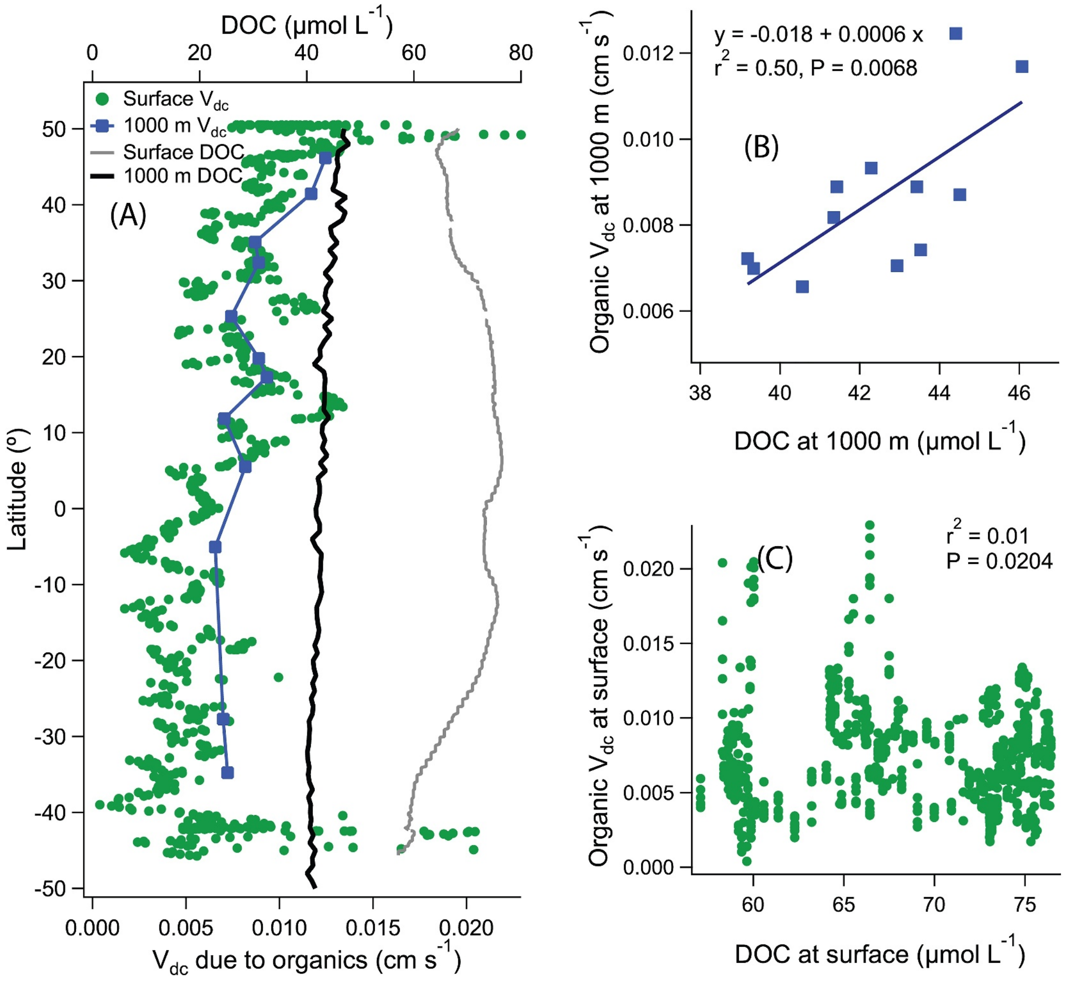

Figure 4. (a) Latitudinal distributions of organic-driven chemical deposition velocity at 1,000 m and at the surface, as well as dissolved organic carbon (DOC) concentration (b) Organic-driven chemical deposition velocity versus DOC concentration at 1,000 m, which shows a high degree of correlation; (c) Organic-driven chemical deposition velocity versus DOC concentration at the surface, which shows no correlation.

6. Implications and Conclusions

Our OUE measurements spanning 95 degrees of latitude across the Atlantic Ocean suggest that much of the variability in previous field observations of ozone deposition velocity at a given wind speed (e.g., Helmig et al., 2012; Loades et al., 2020) may well be due to the distributions of biogeochemically derived reactants in surface seawater. Iodide dominates ozone uptake in the tropics, while iodide and organics are of comparable importance in temperate waters. This partitioning is roughly consistent with earlier laboratory results from Martino et al. (2012). Among estimates of global ozone deposition to the ocean, the two lowest estimates (on the order of 100 Tg yr^{-1} from Luhar et al., 2018; Pound et al., 2020) only considered iodide as the reactant. By neglecting organics, their estimates of ozone deposition may be underestimated. The higher deposition estimate (300 Tg yr^{-1}) of Ganzeveld et al. (2009) considered iodide, DMS, alkene and Chlorophyll *a* as a proxy for organic reactants. The correlations we observe between residual OUE and organic proxies (CDOM and Chlorophyll *a*) suggest that their approach has some merit. Parametrization of surface iodide concentration based on commonly observed ocean variables already exist (e.g., Chance et al., 2014; Sherwen et al., 2019). Observed relationships versus Chlorophyll *a* and CDOM (Figures 2c and 2d; Figures S5 in Supporting Information S1) suggest that the organic contribution to ozone uptake could also be approximated based on those satellite-observable parameters. Given the large seasonal variations in biological activity in temperate oceans, we expect to see large variations in ozone deposition in those waters.

Reactions between ozone and organics at the sea surface have recently been suggested to be a source of volatile organic compounds (VOCs) to the marine atmosphere (e.g., Chiu et al., 2017; Zhou et al., 2014). The magnitude of this chemically-mediated source globally is unknown, but our measurements provide a rough constraint. We assume the global ozone deposition to the ocean is 2–6 Tmol yr^{-1} (100–300 Tg yr^{-1}) and one third of the ozone reacts with organics in seawater. If VOCs are outgassed with a unity yield, this would imply a likely upper limit ozone-mediated VOC emission of 0.7–2.1 Tmol yr^{-1}. This converts to 42–126 Tg C yr^{-1} if the VOCs average five carbons (Novak & Bertram, 2020). Our simplified estimate is of the same order of magnitude compared to other recent estimates of this source of 18–87 Tg C yr^{-1} from Novak and Bertram (2020), 11–167 Tg C yr^{-1} from Kilgour et al. (2024), and 13–136 Tg C yr^{-1} from Schneider et al. (2024). It is also comparable in magnitude to the estimate of photochemical VOC production of 23–92 Tg C yr^{-1} from Brüggemann et al. (2018).

Data Availability Statement

Observations from this paper are archived and freely accessible at the British Oceanographic Data Centre (Yang & Phillips, 2024).

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