


## REVIEW

# Impacts of ocean biogeochemistry on atmospheric chemistry

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Ocean biogeochemistry involves the production and consumption of an array of organic compounds and halogenated trace gases that influence the composition and reactivity of the atmosphere, air quality, and the climate system. Some of these molecules affect tropospheric ozone and secondary aerosol formation and impact the atmospheric oxidation capacity on both regional and global scales. Other emissions undergo transport to the stratosphere, where they contribute to the halogen burden and influence ozone. The oceans also comprise a major sink for highly soluble or reactive atmospheric gases. These issues are an active area of research by the SOLAS (Surface Ocean Lower Atmosphere) community. This article provides a status report on progress over the past decade, unresolved issues, and future research directions to understand the influence of ocean biogeochemistry on gas-phase atmospheric chemistry. Common challenges across the subject area involve establishing the role that biology plays in controlling the emissions of gases to the atmosphere and the inclusion of such complex processes, for example involving the sea surface microlayer, in large-scale global models.

**Keywords:** Halogens, Surface microlayer (SML), Tropospheric ozone, Stratospheric ozone, Volatile organic compounds

## Introduction

Ocean biogeochemistry has long been recognized to impact the composition of the atmosphere. These impacts extend from influence on the abundance of both long- and short-lived gases that drive the atmospheric oxidation capacity to secondary aerosol abundance and composition. In turn, this can affect air quality and climate.

The focus of this perspective article is on 3 topics. Section 1 addresses our evolving understanding of biogeochemical controls on the chemistry of reactive halogen gases that impact tropospheric ozone and air quality. Section 2 treats oceanic emissions, largely halogen-containing, that make their way to the stratosphere and influence the

atmospheric chemistry there. The main processes concerning halogens treated in this article are schematized in **Figure 1**. Section 3 examines the release of volatile organic compounds (VOCs) to the troposphere, both via primary emissions and via reactive processes that occur at the ocean–atmosphere interface (see **Figure 2**). Each section reviews new findings that have occurred in the past decade, while also providing a perspective on atmospheric impacts and need for future studies. Several of the trace gases discussed in this article strongly influence particulate atmospheric chemistry, which is discussed in more detail by Sellegri et al. (2023) and are particularly relevant for polar regions, as discussed by Willis et al. (2023).

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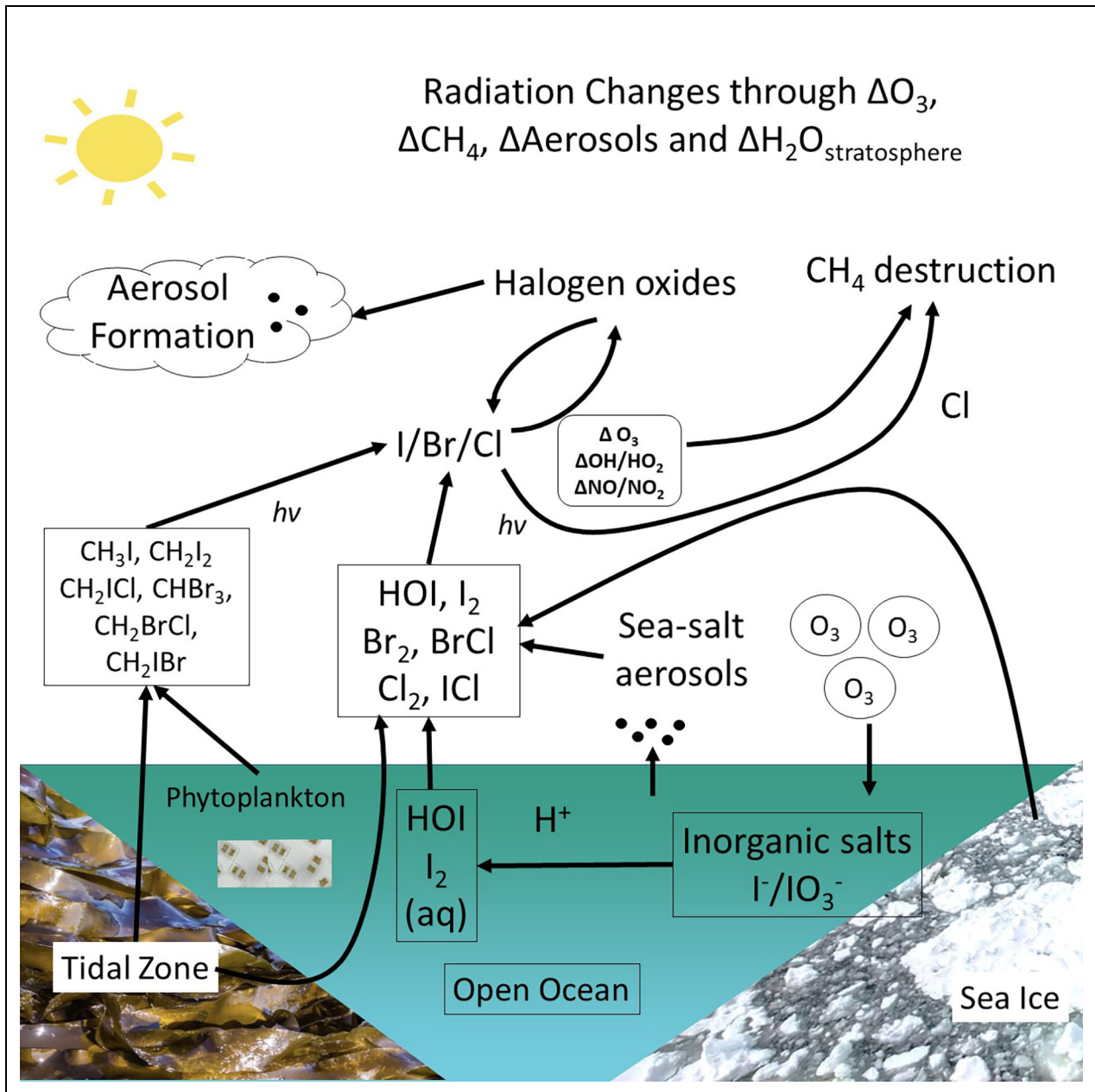
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**Figure 1. Overview of the role of marine halogens released in the atmosphere.**

## 1. Biogeochemical controls on the emission of reactive halogen gases impacting tropospheric ozone and air quality

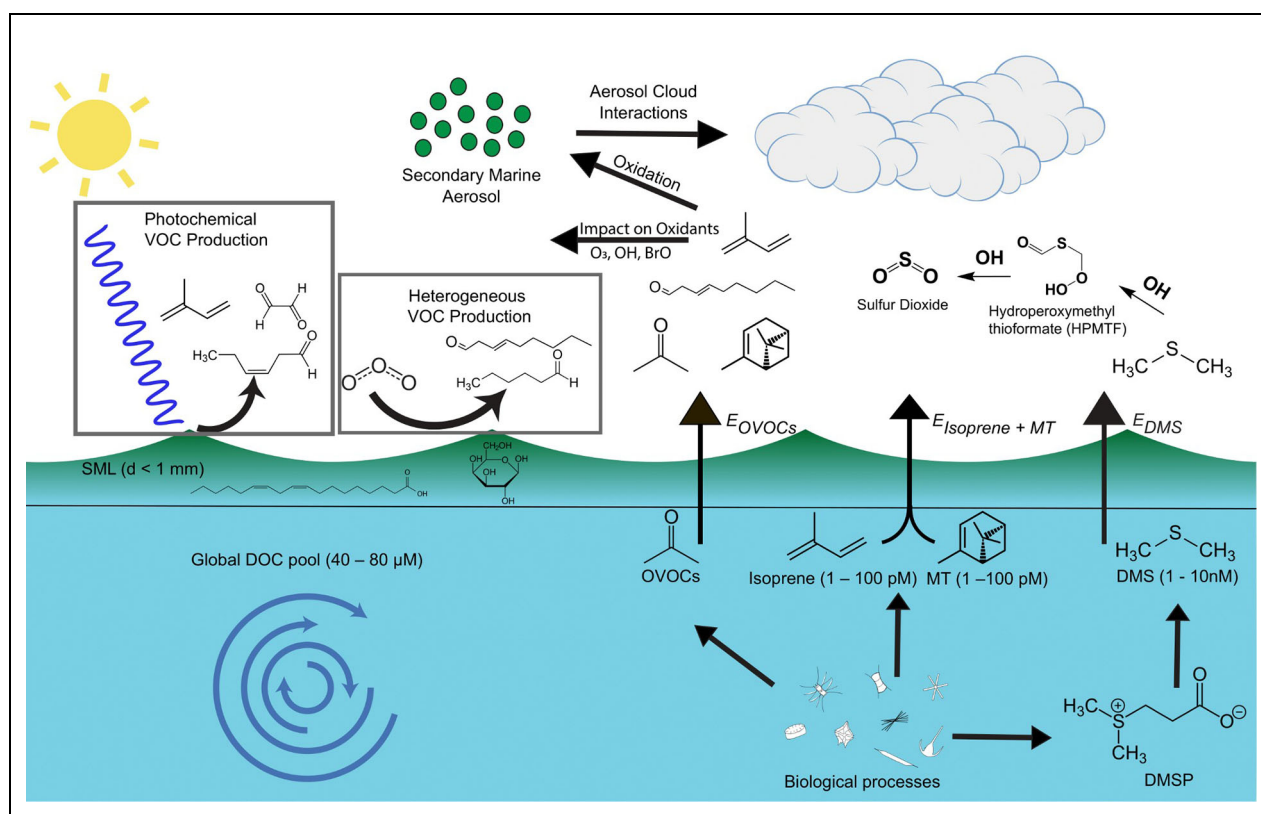
### 1a. Tropospheric iodine

Perspective:

- Recent studies show that iodine plays a substantial role in the depletion of tropospheric ozone, through dry deposition and the initiation of catalytic cycles, and can initiate particle formation.
- Iodine emitted from the oceans has largely increased compared to preindustrial times, leading to a more important role of iodine in tropospheric ozone destruction.
- Oceanic emissions of iodine are not entirely understood to date. In particular, emissions of one of the largest predicted fluxes of iodine, hypoiodous acid (HOI), remain elusive, mainly due to analytical limitations.

- The role of organics and particularly of the sea surface microlayer (SML) on ozone deposition and its reaction with iodide needs to be better understood as a control on iodine emissions. Changing oceanic temperatures and other conditions will affect these emissions, an issue that has little been addressed.
- Further development of iodine cycling in oceanic modeling and the coupling between ocean and atmospheric models will improve the estimates of atmospheric emissions in a changing earth system.

The influence of iodine in the marine troposphere has attracted attention, following observations of inorganic iodine species in the marine boundary layer that could not solely be explained by organic iodine release from the ocean (e.g., Jones et al., 2010; Mahajan et al., 2010). Since, it was demonstrated that inorganic iodine is an important



**Figure 2. The role of the surface microlayer (SML) and release of volatile organic compounds (VOCs) to the atmosphere.** Adapted with permission from Novak and Bertram (2020). Copyright 2020 American Chemical Society.

source of atmospheric iodine, estimated as high as 75% of total atmospheric iodine (Prados-Roman et al., 2015b), competitive or even higher than the release of marine organic iodine compounds, which are mainly driven by biological processes (Saiz-Lopez and Plane, 2004; Carpenter et al., 2013; MacDonald et al., 2014). Other sources of iodine in the troposphere are terrestrial emissions of gaseous iodine from salt marches, rice fields, peatland, and forest systems, and combustion of fossil fuel and biomass. Inorganic iodine is mainly emitted following the reaction of iodide with ozone at the ocean surface (dry deposition), leading to the release of HOI (approximately 70% of oceanic I emitted) and to a lesser extent molecular iodine ( $I_2$ ) (Garland et al., 1980; Magi et al., 1997; Sherwen et al., 2016). Ultimately, iodine is removed from the atmosphere through deposition mainly as HOI,  $INO_3$ , and aerosols, and mostly back to the ocean (Sherwen et al., 2016).

Iodide reacts very rapidly with ozone, much faster than the equivalent reactions of  $Cl^-$  and  $Br^-$  (Harvey, 1956). The fast reaction of iodide with ozone explains the major influence of iodide on the dry deposition of ozone over oceans, despite its low concentration in seawater, and is currently the only reaction for ozone removal through dry deposition in models (Hardacre et al., 2015; Luhar et al., 2018; Pound et al., 2020). However, organic iodine, and in particular iodomethane ( $CH_3I$ ), remains an important source for iodine above the marine boundary layer due to its longer lifetime (Koenig et al., 2020). Emissions of iodocarbons have been compiled in emission inventories (Bell et al., 2002; Ordóñez et al., 2012).

The renewed interest in iodide concentrations, which are poorly documented, led to several parametrizations for iodide concentrations in the sea surface waters. These used either a reported relationship with a biogeochemical parameter (e.g., chlorophyll [Oh et al., 2008] or nitrate [Ganzeveld et al., 2009]), a limited range of observed iodide concentrations (Coleman et al., 2010) or were based on multivariate linear regression (Chance et al., 2014) or Arrhenius behavior (MacDonald et al., 2014). Since, a new effort to compile global iodide observations was made, including digitized historical, unpublished, and new data for critically under-sampled areas such as the Indian and Southern Ocean (Chance et al., 2019). This compilation showed that surface iodide concentrations show a strong latitudinal trend, with maxima around the tropics and span a range from less than 10 to over 2,000 nM, with a mean of 94.8 nM globally. A machine learning algorithm was applied to this new, more complete data compilation providing an improved global iodide climatology (Sherwen et al., 2019).

Oceanic iodide is primarily produced in the mixed layer by biological activity of microalgae and bacteria (Ducklow et al., 2018; Hepach et al., 2019; Hughes et al., 2021) and seems coupled to carbon uptake, although evidence is rather limited (Hepach et al., 2019 and references therein). A recent study has used a variable I:C ratio and primary productivity climatology to model the oceanic iodine speciation, including iodide (Wadley et al., 2020). The comparison with hitherto described parametrizations for iodide concentrations shows that the largest differences

with the oceanic model occur in zones where little to no observations exist. This raises the question of whether all processes involved in determining surface iodide have been captured and underlines the need for more observations, in particular in the Arctic and coastal seas where the biogeochemical cycling of iodide is understudied.

Recent atmospheric modeling studies have used different parametrizations to predict iodine emissions and their impact on the troposphere. A comprehensive iodine-bromine gas-phase chemistry scheme was first incorporated into the global chemistry-climate model (Community Atmospheric Model coupled with Chemistry), where the oceanic source of iodine was estimated at 1.9 Tg(I)/year (Ordóñez et al., 2012; Prados-Roman et al., 2015b). Of this oceanic iodine source, abiotic iodine contributed about 75% to iodine oxide (IO) concentrations. Halogen chemistry, including iodine, was also added to the global model Goddard Earth Observing System Chemistry (GEOS-Chem). In a first study, a contribution of 3.83 Tg(I)/year from oceanic sources was estimated using the Chance et al. (2014) sea-surface iodide field (Sherwen et al., 2016), whereas the oceanic iodine source was estimated at only 2.7 Tg(I)/year using the MacDonald et al. (2014) iodide parametrization with the same model (Sherwen et al., 2016). In a model study using the SOCOL-AERv2-I model with the MacDonald et al. (2014) parametrization, the total oceanic iodine source was estimated at 2.9 Tg(I)/year (Karagodin-Doyennel et al., 2021). These differences in total oceanic iodine flux can thus partially be explained by the underestimation of sea surface iodide concentrations compared to all available observations when using the MacDonald et al. (2014) parametrization and an overestimation using the Chance et al. (2014) parametrization (Chance et al., 2019; Sherwen et al., 2019). As demonstrated for the Indian Ocean (Inamdar et al., 2020), a global iodide climatology might be less applicable in under-sampled regions, where regional parametrizations better capture regional specificities of, for example, sea surface temperature and salinity and seem more suitable if representative regional data sets are available.

In order to estimate fluxes of inorganic iodine, most models use the parametrization proposed by Carpenter et al. (2013). The calculated fluxes and their kinetic models are still subject to substantial uncertainties, not in the least due to the lack of observation of certain key species, such as HOI. Another source of uncertainty is the incomplete understanding of the influence of the organic compounds on the reaction of iodide and ozone. Multiple experimental studies show that organics have a suppressive (e.g., Reeser and Donaldson, 2011), enhancing (e.g., Hayase et al., 2011), or no effect (e.g., MacDonald et al., 2014) on  $I_2$  emissions from iodide solutions, implying that the underlying mechanisms are not well understood. Two recent studies concur on a strong suppression of the  $I_2$  flux over natural SML and natural organic material from phytoplankton cultures (Schneider et al., 2020; Tinel et al., 2020). Both conclude that the emission of volatile organic iodine does not offer a satisfactory explanation for the lower  $I_{2(g)}$  observed in presence of organics. Other hypotheses can explain the lower  $I_2$  emissions such as changes in

solubility of  $I_2$  in the organic-rich solution or the reactive loss of  $HOI_{(aq)}$  or  $I_{2(aq)}$ . Further, a suppressive effect of  $Cl^-$  on  $I_{2(g)}$  emissions was confirmed in both studies, although the reason for this suppression was not univocally elucidated. It seems clear that more investigation in these fundamental reactions is needed to fully understand the  $I_{2(g)}$  suppression in presence of chlorine. Schneider et al. (2020) also confirmed the influence of pH on the  $I_2$  flux, with lower pH leading to higher  $I_2$  fluxes. This can lead to higher emissions from seaspray aerosols which have lower pH than seawater (Rouvière et al., 2010; Angle et al., 2021). Recently, a modeling study in the Indian Ocean suggests that a significant reduction in the  $HOI/I_2$  flux from the sea surface is needed to replicate the observed gas-phased IO (Mahajan et al., 2021). Emissions, calculated using the flux parameterization from Carpenter et al. (2013) needed to be reduced by 40% to match the gas-phase IO observations.

Changes in tropospheric ozone concentrations have already affected the amount of iodine in the atmosphere, as demonstrated using iodine deposition in historic ice cores from Greenland (Cuevas et al., 2018) and the French Alps (Legrand et al., 2018). Both studies, of which the longest historic atmospheric iodine record is 260 years (1750–2011) show a sharp 3-fold increase in atmospheric iodine deposition since 1950. This increase coincides with a marked increase in observed tropospheric ozone concentrations (+30% since 1950), which led in turn to higher inorganic iodine emissions (+33%) (Cuevas et al., 2018). Consequent catalytic destruction of ozone by atmospheric iodine is estimated to have reduced tropospheric ozone concentrations by 10% over the North Atlantic between 1950 and 2010 (Cuevas et al., 2018) and to significantly affect the radiative ozone budget (Sherwen et al., 2017). Enhanced sub-ice phytoplankton production, associated with sea ice thinning, likely also played a role in the increase in iodine concentrations found in the Greenland ice-core. Isotope  $^{127}I$  concentrations in spruce tree rings from the Tibetan plateau partially confirmed the trend in iodine record observed in the Greenland ice core ( $R = 0.77$ ,  $P < 0.01$ ) (Zhao et al., 2019). A recent study in the high Arctic has shown the ubiquitous presence of iodine in the gas- and particle-phase, which was not observed regularly in the past (Benavent et al., 2022). A negative feedback loop between higher ozone concentrations, higher oceanic iodine emissions, and more ozone destruction following the increase of reactive atmospheric iodine was demonstrated by several studies (Prados-Roman et al., 2005a; Sherwen et al., 2017; Sekiya et al., 2020). This means that oceanic iodine emissions buffer the increase in tropospheric ozone pollution and its associated radiative forcing. Sherwen et al. (2017) model a reduction of the global ozone burden from 416 Tg to 339 Tg due to the feedback from halogens in present day. Iodine chemistry accounts for approximately 57% of this ozone reduction. Iodine also participates in particle formation, which would have an additional indirect influence on the radiative budget (Gómez Martín et al., 2020; Huang et al., 2022). Coastal seawater tends to have higher iodide concentrations, with a higher potential for feedback on ozone and

coastal air quality. Prados-Roman et al., 2015a) modeled that in regions of continental ozone-rich outflow, the iodine-mediated ozone loss rate has increased by about 6 times (up to  $2 \text{ nmol mol}^{-1} \text{ d}^{-1}$ ) compared to the global average of  $0.35 \text{ nmol mol}^{-1} \text{ d}^{-1}$ , a trend that was confirmed in a study in coastal Los Angeles (Muñiz-Unamunzaga et al., 2018). However, our understanding of iodine cycling in complex coastal systems is limited, notably the interplay of biological sources and inorganic iodine, and warrants more research to predict the influence of iodine on future coastal air quality with certainty.

### 1b. Tropospheric bromine

Perspective:

- Reactive bromine-containing species affect tropospheric chemistry through the budget of ozone,  $\text{HO}_x$ , and  $\text{NO}_x$  perturbations; formation of secondary organic aerosol (SOA); and the fate of pollutants such as VOCs, sulphur, and mercury (Schmidt et al., 2016; Chen et al., 2017; Abrahamsson et al., 2018; Peng et al., 2021).
- Field measurements and modeling studies suggest that reactive bromine arises mainly from the oxidation and photolysis of organobromine molecules and sea salt aerosol (SSA) debromination, however, reported values varied in a large range with a degree of uncertainties.
- The relative importance of anthropogenic sources is still uncertain, due to lack of research on anthropogenic short-lived bromine substances, unrefined anthropogenic emission inventories and uncertainties in the knowledge of tropospheric bromine chemistry.
- Further investigation in the sources and influences of reactive bromine species in the troposphere requires multiscale observations in time and space for bromine species. Including bromine chemistry in climate and chemistry models will improve our understanding of the above atmospheric effects, and associated impacts on the radiation budget.

The main sources of reactive bromine in the troposphere are oxidation and photolysis of organobromine molecules ( $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_3\text{Br}$ ) and SSA debromination (Schmidt et al., 2016; Wang et al., 2019b). Minor sources of  $\text{Br}_y$  are transport from the stratosphere where  $\text{Br}_y$  originates from photochemical decomposition of organobromine molecules and halons (Wales et al., 2018). For the sinks,  $\text{Br}_y$  ( $= \text{BrO} + \text{Br} + \text{Br}_2 + \text{HOBr} + \text{BrCl} + \text{HBr} + \text{BrNO}_3 + \text{BrNO}_2$ ) is primarily removed from the troposphere via wet and dry deposition (Schmidt et al., 2016). The biogeochemical cycle of bromine is dominated by major sources to the atmosphere, such as sea spray, saline lakes, volcanoes, and marshes, but also anthropogenic sources, such as power plants, industrial processes, industrial boilers, and residential burning (Li et al., 2021b; Peng et al., 2021; Al-Adilah et al., 2022). However, observations of bromine (especially short-lived) species in areas with moderate or high anthropogenic emissions are scarce, so that it is not easy to determine the corresponding

abundance and composition in anthropogenic emissions (Hossaini et al., 2012; Lee et al., 2018). Inventories of anthropogenic emissions from bromine sources and calculation of emission factors are not sufficiently well developed and refined (Li et al., 2021a). There are also some uncertainties in the tropospheric bromine chemical mechanisms (especially in heterogeneous reactions) (Simpson et al., 2015). Therefore, direct and multiscale measurements for bromine species are required to validate emission inventory and model simulation results. The combination of simulation and observation experiments is an effective tool for studying bromine chemistry.

$\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$ , short-lived bromocarbons, are ubiquitous in the oceans, where they are formed by macro- and microalgae (Fiehn et al., 2017; Lim et al., 2018). Additionally, together with other halocarbons, they are also produced through abiotic processes (Keppler et al., 2000). The results from a global 3-dimensional ocean biogeochemistry model found high bromoform levels in the extratropics ( $3\text{--}10 \text{ pmol L}^{-1}$ ), a decrease toward the subtropics (approximately  $1 \text{ pmol L}^{-1}$ ), and a peak at the equator (approximately  $2 \text{ pmol L}^{-1}$ ) (Stemmler et al., 2015), consistent with observations in the northwest Pacific.

The cycling of  $\text{Br}_y$  occurs between  $\text{BrO}_x$  radicals ( $\text{BrO}_x = \text{Br} + \text{BrO}$ ) and reservoirs (Zhu et al., 2018; Bougoudis et al., 2020). Autocatalytic reactions of SSA are the most important source of  $\text{Br}_2$  and  $\text{BrCl}$ . For instance, gaseous  $\text{HOBr}$  is degassed from SSA and then reacts with  $\text{Cl}^-$  and  $\text{Br}^-$  to converted  $\text{BrCl}$  and  $\text{Br}_2$ , respectively (Hara et al., 2018). The efficiency of the sea-salt recycling process, referred to as sea-salt aerosol dehalogenation (Engel et al., 2019), depends on the halogen enrichment within the aerosol and the rate of gas-phase halogen reactive uptake. Sea-salt recycling requires the initial presence of inorganic halogen reservoirs (such as  $\text{HBr}$ ,  $\text{HOBr}$ ,  $\text{BrNO}_2$ ,  $\text{BrNO}_3$ , and  $\text{Br}_x\text{O}_y$ ) in the gas-phase. These are usually formed by photochemical decomposition of brominated and chlorinated very short-lived halogenated substances (VSLS), although iodine can also represent the initial step on the sea-salt dehalogenation process (Fernandez et al., 2014). SSA-dehalogenation is estimated to provide a bromine source of 1.4 to 3.5  $\text{Tg Br yr}^{-1}$  (Fernandez et al., 2014; Hossaini et al., 2016; Schmidt et al., 2016; Chen et al., 2017). For bromine, this source was estimated to be between 2 and 4 times larger than the global tropospheric emissions from brominated VSLS (Yang et al., 2005; Schmidt et al., 2016).

The effective washout of hydrophilic reservoir species (eg.,  $\text{HBr}$ ,  $\text{HOBr}$ ,  $\text{BrNO}_2$ ,  $\text{BrNO}_3$ ,  $\text{BrCl}$ ) depends on the solubility of individual halogen species (Sander, 2015). Heterogeneous recycling or the presence of sulfate or nitrate can reduce the washout efficiency, by transforming the soluble reservoir species into more volatile and photolabile compounds. Inclusion of these recycling processes in the upper troposphere is necessary to reconcile satellite tropospheric columns with global modeling studies (Parrella et al., 2012; Schmidt et al., 2016), as well as to reproduce the inorganic bromine vertical profiles throughout the tropical free and upper troposphere (Fernandez et al., 2014).

Reactive bromine containing species have significant effects on atmospheric chemistry in the troposphere, the most prominent being depletion of ozone and impacts on OH/HO<sub>2</sub> (Monks et al., 2015; Wang et al., 2015; Fernandez et al., 2017; Wang et al., 2019b). Bromine chemistry is widespread in the Antarctic and Arctic near-surface troposphere (Abrahamsson et al., 2018; Prados-Roman et al., 2018; Wang et al., 2019b), tropical and subtropical free troposphere (Wang et al., 2015), volcanic plumes (Gutmann et al., 2018; Roberts et al., 2018), and above saline lakes (Liu et al., 2018b; Mitroo et al., 2019). Direct atmospheric bromine atom measurements have verified that ozone depletion is linked to elevated bromine concentrations, caused by photochemically driven release of molecular bromine and nitrogen oxides from snow (Wang et al., 2019b).

Evidence from aircraft and satellite observations indicates that the dominant mechanism for the Br-Cl-driven tropospheric ozone decrease is oxidation of NO<sub>x</sub> by formation and hydrolysis of BrNO<sub>3</sub> and ClNO<sub>3</sub> (Schmidt et al., 2016). Measurements in the Weddell Sea, Antarctica, found 10 times more bromocarbons emitted to the atmosphere than from Southern Ocean waters, and substantially more than over summer sea ice (Abrahamsson et al., 2018). The sea ice-emitted bromocarbons dispersing throughout the troposphere can pose significant impacts on the global tropospheric ozone budget. In addition to observations by various means that can illustrate the effect of bromine chemistry on ozone, model simulation results further illustrate this phenomenon. By conducting Community Multi-scale Air Quality (CMAQ) modeling with and without bromine and iodine chemistry for the Asia-Pacific region indicated that the bromine- and iodine-mediated O<sub>3</sub> loss reaches a maximum of 15.9 ppbv (44.3%) over the ocean and 13.4 ppbv (38.9%) over continental Asia (Huang et al., 2021). Based on the simulations by the GEOS-Chem model, Oman et al. (2016) suggested that bromine from VSLs is responsible for the significantly later recovery of Antarctic ozone. By implementing a bromine release mechanism from sea-ice- and snow-covered land surfaces in the global chemistry-climate model (ECHAM/MESy Atmospheric Chemistry), ozone depletion events are very well reproduced in the Arctic and in the Antarctic coastal regions (Falk and Sinnhuber, 2018).

In addition to its effect on ozone, bromine chemistry has significant effects on atmospheric oxidation and on secondary aerosols. By utilizing the regional Weather Research and Forecasting Chemistry coupled (WRF-Chem) model involving oceanic halogen emissions, Li et al. (2020) found halogens substantially enhance the total atmospheric oxidation capacity in polluted areas of China, typically 10% to 20% (up to 87% in winter) by significantly increasing OH. Upon incorporation of updated halogen chemistry and anthropogenic chlorine and bromine emissions in WRF-Chem, halogens enhance the loading of fine aerosol in northern China (on average by 21%) and especially its secondary aerosols (Li et al., 2021a). Besides, including bromine and dimethyl sulfide (DMS) in the CMAQ model, a 10% increase in SOA was found over the urban area of Los Angeles, USA (Muñiz-Unamunzaga et al., 2018).

### 1c. Tropospheric chlorine

Perspective:

- Chlorine, emitted by both anthropogenic and natural sources perturbs the composition and oxidation capacity of the troposphere. With imbalanced regional development, anthropogenic sources of chlorine have been experiencing noticeable changes in different areas according to bottom-up emission inventories.
- The global integrated tropospheric chlorine burden and its atmospheric impacts are expected to undergo further changes throughout the century. Long-term field measurements are needed to monitor such variations.
- Multiscale modeling and laboratory experiments can improve our understanding in the multiphase mechanisms of reactive chlorine species, particularly in the presence of anthropogenic pollutants.

Chlorine species are emitted through anthropogenic activities (coal-, biomass-, and waste-burning), acid displacement (e.g., HNO<sub>3</sub>), halogen-mediated heterogeneous reactions on chloride-containing aerosols (e.g., sea-alt aerosol), and ocean-surface biogenic activities. Chlorine-containing species undergo photochemical reactions and generate chlorine atoms (Cl). Cl oxidizes methane (CH<sub>4</sub>, a significant greenhouse gas) and other VOCs, increasing the level of tropospheric oxidants (OH and HO<sub>2</sub>) and air pollutants (O<sub>3</sub> and secondary aerosols) when nitrogen oxides are present. In remote areas and the free troposphere, ClO<sub>x</sub> (Cl + ClO) is involved in self-reactions and reactions with BrO and IO radicals leading to net loss of odd oxygen (O<sub>3</sub> and those species it recycles with, mainly O(<sup>1</sup>D), O(<sup>3</sup>P), and NO<sub>2</sub>), hence decreasing tropospheric O<sub>3</sub> and OH.

Studies of tropospheric chlorine species have increased in recent years. An example is research on nitryl chloride (ClNO<sub>2</sub>), which is a product of heterogeneous reaction between chloride-containing aerosol and N<sub>2</sub>O<sub>5</sub>, involving anthropogenic air pollutant NO<sub>2</sub> and O<sub>3</sub> (Finlayson-Pitts et al., 1989). Following the first field detection of ClNO<sub>2</sub> (Osthoff et al., 2008), novel measurement methods have been used to detect ClNO<sub>2</sub> and other relevant chlorine species in various (coastal and inland) locations across the Northern Hemisphere. For instance, ClNO<sub>2</sub> has been detected at levels ranging from a few pptv to thousands of pptv on the west coast of North America (Mielke et al., 2013), the south coast of China (Wang et al., 2016), the United Kingdom (Bannan et al., 2017), the east coast of North America (McDuffie et al., 2018), South Korea (Jeong et al., 2019), Mediterranean Sea (Eger et al., 2019), and in global remote region (Veres et al., 2020). Other chlorine-containing reactive species have also been observed at levels of a few pptv to hundreds of pptv, along the coasts in North America (Cl<sub>2</sub>, BrCl) (Lee et al., 2018; Haskins et al., 2019), Europe (ICl) (Tham et al., 2021), and China (Cl<sub>2</sub>, BrCl) (Peng et al., 2022; Xia et al., 2022), South Africa (very short-lived chlorine, VSL-Cl) (Kuyper et al., 2019; Say et al., 2020), Australia (Advanced Global Atmospheric Gases Experiment, AGAGE network; VSL-Cl) (Prinn et al., 2018), and the global remote troposphere (VSL-Cl) (Apel et al.,

2019). These observations reveal the widespread existence but fluctuating levels of chlorine species along the coast and in the remote oceanic regions, implying active interaction between the lower atmosphere and the surface ocean with probably large perturbation by human activities. With the proposed global scale environmental policy in regulating air pollutants and greenhouse gases, as well as the ongoing rapid changes in global climate, the atmospheric abundance of tropospheric chlorine, in connection to climate, oceanic biogeochemistry and human activities, is expected to undergo significant changes in the future. Future long-term measurements are advised to monitor such changes to further comprehend the changing role of chlorine in the troposphere.

A few studies conducted laboratory experiments to explore the controlling factors of the production and loss of some key chlorine species. Ryder et al. (2015) quantified the role of organic species in controlling the production of  $\text{ClNO}_2$  at the air-sea interface. Peng et al. (2022) revealed the critical impact of anthropogenic nitrate aerosol on the activation of  $\text{Cl}_2$  from chloride-containing natural SSA while Xia et al. (2022) suggested that the same process could also activate  $\text{Br}_2$  from bromide-containing natural SSA. The rates of reactive chlorine production and loss, particularly those involving multiphase reactions with complex aerosol compositions, remain understudied, and future laboratory works are recommended to strengthen our understanding on this aspect.

Studies of direct chlorine emissions have also continued. Hossaini et al. (2016) compiled a comprehensive list of the lower-boundary conditions for key very short-lived (VSL)-Cl species. Claxton et al. (2020) further developed an emission inventory for 2 VSL-Cl ( $\text{CH}_2\text{Cl}_2$  and  $\text{C}_2\text{Cl}_4$ ), while An et al. (2021) used atmospheric observations and inferred a rapid increase in  $\text{CH}_2\text{Cl}_2$  from China calling for an update of sources. Other authors also showed the large and possibly dominant source strength of chlorine from acid displacement reactions, that is, formation of HCl via reaction of  $\text{HNO}_3$  on SSA (Hossaini et al., 2016; Wang et al., 2019d; Li et al., 2022). Regional and global emission inventories of inorganic chlorine document significant changes in anthropogenic emissions in recent years (e.g., Fu et al., 2018; Liu et al., 2018a; Zhang et al., 2022). These inorganic chlorine emissions can influence the release of reactive halogens from both pollutant aerosols and natural SSA. Modeling of chlorine species and their impacts has traditionally been embedded in reactive halogen modeling studies (Ordóñez et al., 2012; Sherwen et al., 2016). Several authors simulated the abundance and potential impacts of  $\text{ClNO}_2$  in the Northern Hemisphere, China, and Europe (Sarwar et al., 2014; Li et al., 2016; Zhang et al., 2017; Sommariva et al., 2018). Shipping emissions are also simulated to influence the activation of chlorine from SSA and affect lower tropospheric composition (Dai and Wang, 2021; Li et al., 2021b). Other authors adopted TOMCAT, GEOS-Chem, and Community Earth System Models, respectively, and quantified the impacts of tropospheric chlorine on atmospheric composition (Hossaini et al., 2016; Wang et al., 2019d; Li et al., 2022). Future modeling studies incorporating the latest laboratory- and field-based

results are warranted to quantify the impacts of chlorine species on tropospheric composition and chemistry.

## 2. Biogeochemical controls on the emission of reactive gases impacting stratospheric ozone

### 2a. Very short-lived substances

Perspective:

- The atmospheric degradation of ocean-emitted VLSLs leads to ozone destruction both in the troposphere and stratosphere.
- VLSLs are mostly produced in the surface ocean by biological and photochemical processes and emitted via air/sea gas transfer.
- Quantifying the influence of VLSLs on tropospheric and lower stratospheric ozone requires knowledge of their atmospheric transport and conversion into reactive halogen species.
- Assessing future atmospheric impacts of oceanic VLSLs in a warmer world will require incorporating their chemistry and biology into coupled chemistry-climate models.

VLSLs have tropospheric chemical lifetimes similar to their transport times to the stratosphere (i.e.,  $\tau < 0.5$  years [Engel et al., 2019]). VLSLs can be injected into the stratosphere chemically unaltered (source gas injection, dominated by organic halogens) or first processed in the troposphere (product gas injection, dominated by inorganic halogens) (Aschmann and Sinnhuber, 2013). As a result, VLSL impacts depend on the spatial/temporal variability in sources, atmospheric transport pathways, and tropospheric chemical processing (Fernandez et al., 2021).

VLSLs represent more than 25% of the total stratospheric bromine loading, with bromoform ( $\text{CHBr}_3$ ) and dibromomethane ( $\text{CH}_2\text{Br}_2$ ) as the major species (Liang et al., 2010; Engel et al., 2019). The largest air-sea fluxes of brominated VLSLs are observed in coastal and tropical upwelling regions (e.g., Ziska et al., 2013), although the contribution from open ocean regions has been suggested to drive the observed variability in the free troposphere within deep convection regions such as the Western Pacific (Butler et al., 2018). Aircraft  $\text{CH}_2\text{Br}_2$  observations in the free and upper troposphere indicate a pronounced seasonality which is not well captured by global models, presumably due to erroneous seasonality of emissions (Jesswein et al., 2022). Explicit treatment of oceanic  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$  sources captures the expected bromine source gas stratospheric injection, but underestimates tropospheric and stratospheric impacts compared with a full bromine chemical treatment (including sea-salt aerosol dehalogenation and heterogeneous recycling on ice-crystals (Section 1b) (Fernandez et al., 2021). Regional enhancements of inorganic bromine injection occur in regions such as the Western Pacific due to the coincidence of rapid vertical uplift and significant sea-salt production rate (Liang et al., 2014; Koenig et al., 2017).

Global emissions inventories have been developed to assess VLSL impacts on stratospheric ozone depletion using bottom-up or top-down approaches (Warwick et

al., 2006; Liang et al., 2010; Ziska et al., 2013; Hossaini et al., 2016). These involve satellite-derived ocean color or parameterizations based on seawater halocarbon concentrations (Ordóñez et al., 2012; Lennartz et al., 2015). Recent updates based on new observations show larger emissions of  $\text{CHBr}_3$  in the Indian Ocean and reduced global  $\text{CH}_2\text{Br}_2$  emissions (Fiehn et al., 2018; Wang et al., 2019c). There are minor but growing anthropogenic emissions of  $\text{CHBr}_3$  from aquafarming and oxidative water treatment (Quack and Wallace, 2003; Leedham et al., 2013; Maas et al., 2021; Jia et al., 2022), although neither oceanic nor terrestrial cultivation systems have been shown likely to produce a significant contribution to stratospheric bromine loading.

For chlorinated VSLs, anthropogenic sources are significantly larger than natural oceanic fluxes. Such sources are rapidly increasing over east Asia (Hossaini et al., 2019), with the largest contributions arising from China and India (Fang et al., 2019; Say et al., 2019). Emissions of  $\text{CH}_2\text{Cl}_2$  have been reported from the tropical North Atlantic ocean (Kolusu et al., 2017). Global inversion estimates suggest a net ocean source of 10%–20% of the total  $\text{CH}_2\text{Cl}_2$  sources, and a negligible (and often negative) oceanic source of  $\text{C}_2\text{Cl}_4$ . Slowing down of the rate of increase of  $\text{CH}_2\text{Cl}_2$  emissions from China has been observed after 2015 (An et al., 2021).

Oceanic VSLs emissions are the dominant contributor to stratospheric iodine. Methyl iodide ( $\text{CH}_3\text{I}$ ) is the major organic iodine-containing source contributing to stratospheric ozone depletion (Engel et al., 2019), although its direct contribution is small because  $\text{CH}_3\text{I}$  photodecomposes before reaching the tropical tropopause (Tegtmeier et al., 2013; Saiz-Lopez et al., 2015). Inorganic iodine derived from  $\text{CH}_3\text{I}$  photodecomposition is estimated to comprise 30%–40% of the inorganic iodine injected into the stratosphere (Saiz-Lopez et al., 2015; Koenig et al., 2020), which in turn can influence the size and depth of the Antarctic ozone hole (Cuevas et al., 2022). The dominant form of iodine reaching the stratosphere is particulate iodine condensed into aerosols, derived primarily from sea surface emissions of  $\text{HOI}$  and  $\text{I}_2$  (see Section 1a). Although iodine levels are significantly smaller than those for VSLs bromine and chlorine, the faster recycling efficiency of iodine induces ozone depletion in the lowermost stratosphere that is equivalent or larger than that from natural VSLs bromine (Koenig et al., 2020).

Oceanic VSLs production and emissions are expected to increase during the 21st century due to climate-driven increasing sea surface temperature, wind-speeds, and net primary production (Ziska et al., 2017; Iglesias-Suarez et al., 2020; Keng et al., 2021). Future changes in iodine stratospheric injection are expected to follow the predicted changes of the ozone-driven iodide oxidation process described in Section 1a (Carpenter et al., 2013; Prados-Roman et al., 2015a). Similarly, the complex processes involved in heterogeneous processing of halogen species during their transport from the marine boundary layer to the free troposphere (see Sections 1b and 1c) will depend on the future evolution of sea-salt production, sulfate/nitrate aerosols, and tropospheric ice-crystals.

Given the large uncertainty in the physicochemical processes controlling the heterogeneous recycling of halogen reservoirs, the evaluation of the overall effect of heterogeneous chemistry on VSLs halogen input to the stratosphere is currently difficult to quantify.

## 2b. Methyl bromide

- Methyl bromide is a stratospheric ozone-depleting substance with a complex global biogeochemical cycle and an atmospheric lifetime of 0.8 years.
- Atmospheric methyl bromide levels have declined over the past 2 decades, consistent with the phase-out of industrial production under the Montreal Protocol. Models suggest that the oceans responded to the reduction in atmospheric methyl bromide by shifting from a net sink to a net source to the atmosphere.
- The global budget of atmospheric methyl bromide is not fully balanced. Better quantification of tropical terrestrial biogenic sources is needed.
- Climate- and land-use-driven changes in emissions from terrestrial and oceanic ecosystems will likely dominate future variability in atmospheric methyl bromide on decadal and longer time scales. Such changes could potentially offset reductions due to phase-out and are not accounted for in projections of future stratospheric ozone. Continued atmospheric monitoring and decadal ocean surveys of methyl bromide saturation state are needed to quantify such changes.

During the latter half of the 20th century, anthropogenic emissions of methyl bromide increased steadily, eventually exceeding natural emissions. As a result, atmospheric methyl bromide levels were elevated over preindustrial levels by roughly a factor of 2 (Butler et al., 1999; Saltzman et al., 2008). During the 1990s and early 2000s, the oceans were found to be predominantly undersaturated relative to the atmosphere, driving a large air/sea flux of methyl bromide into the ocean (King et al., 2002). This flux was estimated at about  $56 \text{ Gg y}^{-1}$  accounting for nearly one-third of the total atmospheric losses.

Industrial production of methyl bromide was phased out over several years starting in 1999 under the Copenhagen Amendments and subsequent Adjustments to the Montreal Protocol. Phase-out resulted in a decline in global industrial production from roughly  $70 \text{ Gg y}^{-1}$  to  $10 \text{ Gg y}^{-1}$  in 2018 (United Nations Environment Programme [UNEP], 2019). The decline in production constitutes a large-scale multidecadal “experiment” that can be used to test our understanding of the global budget. Atmospheric monitoring shows that atmospheric methyl bromide declined from a 1995–2000 global mean of  $9.4 \pm 0.2 \text{ ppt}$  to  $6.8 \pm 0.1 \text{ ppt}$  for 2015–2019 (Nicewonger et al., 2022). Global models indicate that this decline is consistent with national reporting for industrial production (Yvon-Lewis et al., 2009; UNEP, 2015; UNEP, 2019; Saltzman et al., 2022). There has been a long-standing imbalance in the global methyl bromide budget, with known



sinks exceeding known sources by as much as 30%. Recent inverse modeling suggests that an unknown tropical source of roughly  $15 \text{ Gg y}^{-1}$  (likely terrestrial) is required to balance the budget (Saltzman et al., 2022).

The decline in land-based emissions due to phase-out has also induced a significant change in the saturation state of the oceans. As noted earlier, the oceans were significantly under-saturated at the peak of industrial production. Subsequent ocean cruise surveys demonstrated that by 2010, the oceans were in near equilibrium with the atmosphere, a consequence of the declining atmospheric methyl bromide levels (Hu et al., 2012). Recent progress in understanding air/sea gas exchange has improved estimation of air/sea flux from observations of ocean surface saturation state (see also further discussion on the air-sea interface exchanges elsewhere in this special feature). Model hindcasts indicate that the oceanic methyl bromide saturation state should have continued to change over the past decade (Saltzman et al., 2022). The oceans should now be 5%–10% supersaturated and account for a net sea to air flux on the order of  $5 \text{ Gg y}^{-1}$  (or 6% of the total emissions). No oceanic surveys have been conducted over the past decade, so this finding is not validated (Saltzman et al., 2022). Conducting such a survey should be considered a priority for future research.

Oceanic biological production is one of the major uncertainties regarding the future trajectory of atmospheric methyl bromide. While methyl bromide production can be observed in microbial cultures, there is currently no way to directly observe oceanic production of methyl bromide at the scale needed for global models. As an alternative approach, oceanic production has been estimated by assuming steady state between production, air/sea gas exchange and water column chemical/biological loss. Using this approach, Hu et al. (2012) concluded that oceanic production remained relatively constant from the late 1990s to 2010s. This steady state approach is useful for budgetary purposes but does not provide mechanistic insight into the microbial processes or environmental factors controlling oceanic methyl bromide production.

The phase-out of methyl bromide industrial production has proven successful in reducing the atmospheric burden and contribution of methyl bromide to stratospheric ozone depletion. Global atmospheric methyl bromide levels appear to be steady at present, and are projected to comprise roughly 16% of the total equivalent effective stratospheric chlorine in 2050 (Laube and Tegtmeier, 2022; Lickley et al., 2022). Atmospheric monitoring provides evidence that agricultural utilization of methyl bromide may exceed reported levels in some regions (Choi et al., 2022). If such non-reported emissions are widespread and can be identified, then the potential exists for further reductions in the atmospheric burden of methyl bromide. On the longer term, changes in climate, ocean circulation, and ocean ecosystems introduce uncertainties into the future trajectory of atmospheric methyl bromide levels and their impact on stratospheric ozone. Future research on methyl bromide should include monitoring atmospheric levels on a global basis, conducting new

surveys of ocean surface saturation state, improving knowledge about biological production/loss, and validating parameterizations for air/sea transfer of soluble gases via direct flux measurements and laboratory studies.

## 2c. Methyl chloride

Perspective:

- Methyl chloride is a stratospheric ozone-depleting substance with a complex global biogeochemical cycle with the majority of emissions derived from natural sources.
- Unlike methyl bromide, methyl chloride is not a controlled substance under the Montreal Protocol. The atmospheric abundance of methyl chloride exhibits inter-annual variability, likely caused by fluctuations in the balance of the natural sources and sinks, but no obvious long-term trend is apparent.
- Future changes in atmospheric methyl chloride are likely to be driven primarily by changes in climate and terrestrial ecosystems. As with methyl bromide, such variability is not accounted for in projections of future stratospheric ozone. Continued monitoring of atmospheric methyl chloride is needed in order to detect such changes.

The global mean atmospheric abundance of methyl chloride is around 550–560 ppt and the global atmospheric lifetime is 0.9 years (Carpenter et al., 2014; Engel et al., 2019). The major sources of methyl chloride to the atmosphere are biomass burning, subtropical and tropical plants, the ocean, salt marshes, and fungi. Coal combustion is thought to be the only major anthropogenic source, but this contribution has not been reevaluated in over 2 decades (McCulloch et al., 1999). Previously unreported industrial emissions from China suggest the chemical industry may contribute more to atmospheric methyl chloride than formerly thought (Li et al., 2017). Several studies have proposed new sources of emissions from various sources such as bread baking and various coastal marshes but extrapolating the global impact of these unique sources is challenging (Rhew et al., 2014; Thornton et al., 2016). The major sinks of methyl chloride are oxidation with the hydroxyl radical, photolysis in the stratosphere, uptake by soils, and degradation in the ocean. The global budget of methyl chloride is unbalanced, with estimated sources about 20% lower than the estimated sinks.

Multidecadal measurements of atmospheric methyl chloride now exist, and analysis of interannual variability may lead to additional insight into the global budget. The global budgets of methyl chloride and methyl bromide are linked, with many common sources and sinks. For example, interannual variability in biomass burning associated with the El Niño Southern Oscillation has been shown to strongly impact the atmospheric abundance of methyl bromide and has likely also influenced methyl chloride (Nicewonger et al., 2022). Future research should focus on the sensitivity of the natural sources and sinks of methyl chloride to changes in climate and on projecting how climate change and human activities will alter the

atmospheric abundance of this ozone depleting substance.

### 3. Biogeochemical controls on emissions of VOCs: New chemistry, biology, and the role of sea SML

#### 3a. Marine sources of VOCs

Perspectives:

- There remain considerable uncertainties in the atmosphere-ocean fluxes of many oxygenated VOCs and terpenoids, with impacts on the atmospheric oxidizing capacity and the formation of SOA.
- New approaches including satellite observations and inverse modeling, in-situ flux measurements via online mass spectrometry, and connecting SOA precursors to aerosol particle volumes should be pursued more extensively.
- Variable biology and the state of the SML likely drive spatial and temporal variability of ocean-atmosphere VOC fluxes.

To better understand the tropospheric oxidizing capacity, recent attention has been on refining uncertain global budgets. For example, there is a net oceanic source of acetaldehyde to the atmosphere but fluxes range widely between 3 and 57 Tg/year (Millet et al., 2010; Yang et al., 2014a; Wang et al., 2019a). There is evidence for a missing acetaldehyde source in the remote marine troposphere (Wang et al., 2019a), so better establishing this budget is important. The impacts of new measurements on the marine oxidizing capacity are not clear (Novak and Bertram, 2020). As well, there is no consensus for methanol but recent estimates point to a net sink (Stavrakou et al., 2011; Yang et al., 2014b), and measurements also imply a sink for acetone, especially at high latitudes with a source in equatorial regions (Yang et al., 2014a; Yang et al., 2014b; Brewer et al., 2017). The ongoing uncertainties in oxygenated VOC (OVOC) fluxes are due to variability in the marine emissions, which can be strongly dependent on location, biological activity, and time of day. Continuing developments in inverse modeling techniques coupled to more measurements, including from satellites (Stavrakou et al., 2011; Franco et al., 2018; Franco et al., 2019), will reduce these uncertainties.

Motivated by marine SOA formation, attention has been on the biologically driven marine emissions of isoprene and monoterpenes (Yu and Li, 2021). Given their low water solubility, the net flux of these compounds is to the atmosphere but their short lifetimes make their atmospheric measurements variable and localized to biologically productive regions. Despite having lower emission rates than isoprene, monoterpenes have much higher SOA yields than isoprene (Meskhidze et al., 2015). Nevertheless, compared to terrestrial sources, marine sources of isoprene are generally small (Conte et al., 2020). There is need for more studies of monoterpene oceanic and atmospheric abundance, such as by Hackenberg et al. (2017) who correlated oceanic concentrations to biological activity. The advent of online mass spectrometry systems now permits ocean-based eddy covariance field studies (Kim et

al., 2017). As well, there is merit to revisiting the fluxes of small alkanes and other small alkenes from the ocean (Bonsang et al., 1988).

In addition to isoprene and monoterpenes, work in the past decade has illustrated that glyoxal is another SOA precursor with potential marine origins. Measurements of this gas have been made both in and above the marine boundary layer, showing wide variability in atmospheric mixing ratios implying a source larger than from gas-phase oxidation pathways alone (Sinreich et al., 2010; Mahajan et al., 2014; Volkamer et al., 2015; Walker et al., 2022). For this reason, it has been hypothesized that glyoxal is an oxidation product from abiotic chemistry at the interface of the ocean or marine aerosol (see Section 3c-ii).

An alternate approach to estimate VOC fluxes hinges on aerosol size distribution field measurements. In the Arctic, a chemical transport model was used to predict the size of the SOA VOC precursor source required to reconcile with particle size distribution measurements (Croft et al., 2019). This research avenue will be useful when attempting to close the source budget of SOA VOC precursors.

Lastly, work on the marine source of atmospheric alkyl nitrates has continued, with a focus on bacterial sources, distributions, and aerosol nitrate impacts (Kim et al., 2015; Zeng et al., 2018; Burger et al., 2022). The atmospheric flux of these species is important as a photolytic source of NO<sub>x</sub>; as well, these species may hydrolyze to form aerosol nitrate (Rindelaub et al., 2015). In remote regions where anthropogenic and terrestrial input may be low, the NO<sub>x</sub> released can play a role in ozone formation (Neu et al., 2008; Andersen et al., 2023). This NO<sub>x</sub> source may grow in relative importance as we move away from combustion as an energy source, with its associated NO<sub>x</sub> emissions.

#### 3b. New insights in DMS oxidation

Perspective:

- The atmospheric fate of DMS impacts cloud formation and therefore earth's radiative balance and climate.
- Recently, an abundant, stable intermediate product of DMS oxidation, identified as hydroperoxymethyl thioformate (HPMTF, HOOCH<sub>2</sub> SCHO), was discovered. This discovery has revised our understanding of the oxidative fate of DMS in the atmosphere, with connections to clouds and climate.

The standard understanding was that DMS is oxidized by radicals to form either sulfur dioxide (SO<sub>2</sub>) or methane sulfonic acid (MSA, CH<sub>3</sub>SO<sub>3</sub> H) as the primary stable products, with a minor pathway forming carbonyl sulfide (OCS) (Barnes et al., 1994). The yield of SO<sub>2</sub> from DMS oxidation has varied widely between studies, indicative of an incomplete understanding (Faloona, 2009). Aqueous-phase reactions of DMS and its oxidation products are significant and can drive different yields of SO<sub>2</sub> and MSA compared to gas-phase chemistry alone (Hoffmann et al., 2016). Recently, the discovery of HPMTF has necessitated revisiting prior understanding of DMS oxidation mechanisms and product yields.

HPMTF is formed through a series of isomerization reactions of  $\text{CH}_3\text{SCH}_2\text{OO}$  (methylthiomethylperoxy radical, MSP) which is the first major product of hydrogen abstraction of DMS by OH. Previously, it was thought that MSP goes on to react with NO,  $\text{HO}_2$ , or  $\text{RO}_2$  radicals on a trajectory toward  $\text{SO}_2$  production. Calculations by Wu et al. (2015) showed that under the low NO, and  $\text{RO}_2$  conditions typical of the marine atmosphere MSP can instead undergo reactions to form HPMTF at a rate competitive with bimolecular chemistry. This mechanism of HPMTF formation was confirmed in a laboratory study as a stable product of DMS + OH reaction under low NO,  $\text{HO}_2$ , and  $\text{RO}_2$  conditions (Berndt et al., 2019). The first reported in situ measurements of HPMTF were airborne observations with near global coverage (Veres et al., 2020). It was shown that HPMTF is a major reservoir of marine sulfur, with over 30% of globally emitted DMS oxidized to HPMTF.

The fate of HPMTF via reaction with OH or heterogeneous chemistry may yield novel products. Laboratory studies have shown the OH lifetime of HPMTF is on the order of 1 day and that the primary product is  $\text{SO}_2$  (Ye et al., 2021; Jernigan et al., 2022a; Ye et al., 2022). However, Jernigan et al. (2022b) also showed that there is a 13% yield of OCS, representing the primary OCS production route from DMS oxidation and requiring an important revision to understanding secondary OCS production from DMS (Barnes et al., 1994). Field observations have demonstrated that HPMTF has important heterogeneous loss terms, being depleted in clouds and exhibiting fast dry deposition to the ocean (Veres et al., 2020; Vermeuel et al., 2020). A laboratory study has also measured the heterogeneous uptake coefficient to aerosol (Jernigan et al., 2022a). The importance of HPMTF uptake to cloud droplets was confirmed by Novak et al. (2021) who used eddy covariance flux measurements below a stratocumulus cloud to quantify the flux into clouds. This prompt irreversible uptake to clouds is significant as it terminates gas-phase oxidation toward  $\text{SO}_2$  and accelerates the formation of sulfate. Global chemical transport modeling calculated that 36% of DMS derived sulfur was lost to clouds as HPMTF, reducing  $\text{SO}_2$  production from DMS and increasing sulfate concentrations in the lower marine atmosphere.

### 3c. Sea SML and the atmosphere

Perspective:

- Strongly impacted by biology, the properties of the sea SML affect air/sea gas exchange and multiphase chemistry, both of which control the emission of volatile species.
- Many studies exploring the chemistry leading to the formation of volatile species use proxies to represent the SML and the underlying ocean water. Recent studies have emphasized the importance of capturing the full chemical complexity of the SML.
- A more detailed connection must be made between the biological processes, the chemical composition

of the SML, and the chemistry that forms volatile compounds.

#### 3c-i. Formation, composition, and role of biology of the SML

The SML is the uppermost layer of the ocean (Engel et al., 2017). Due to its interfacial properties, the SML influences the exchange of gases between the ocean and the atmosphere but has also been proposed as a direct source of VOCs (Liss and Duce, 1997; Mungall et al., 2017). In addition to photochemical and heterogeneous processes, various VOCs can be directly produced by marine, primarily autotrophic plankton and subsequently taken up by heterotrophic organisms. Most research on biogenic VOC cycling focused on DMS due to its role in cloud nucleation. DMS is produced from dissolved dimethylsulfoniopropionate (DMSP) through bacterial, mainly enzymatic, conversion, or released directly from phytoplankton during cell-lysis (Stefels, 2000; Yoch, 2002). In the SML, DMSP and DMS are frequently enriched, especially so during blooms dominated by phytoplankton producing DMSP (Yang et al., 2001; Matrai et al., 2008; Yang et al., 2009; Walker et al., 2016). Neuston also affects VOCs emission by turn-over of organic compounds that abiotically release VOCs (Kuzma et al., 1995; Nemecek-Marshall et al., 1995; Moran and Zepp, 1997; Obernosterer et al., 1999; Sinha et al., 2007). SML organic compounds include dissolved hydrocarbons, amino acids, and polysaccharides (Barthelmeß and Engel, 2022; van Pinxteren et al., 2022). High abundances of monocyclic aromatic hydrocarbons and aliphatic VOCs have been associated with the presence of polysaccharides (Astrahan et al., 2016). Recent studies further indicate floating microplastic particles as a source of VOCs (Royer et al., 2018; Lomonaco et al., 2020). Low-density microplastics can accumulate in the SML. Chemical, biological, and physical conditions, in particular increased exposure to ultraviolet radiation and oxygen, promote the thermal and microbial decomposition of plastic and contribute to VOC release (Wu et al., 2022). In the air, atmospheric bacteria may continue utilizing and oxidizing VOCs such as methane (Šantl-Temkiv et al., 2022).

#### 3c-ii. Oxidation and photochemistry of the SML

The production of VOCs can occur via heterogeneous ozonolysis and photosensitized chemistry of the SML (Novak and Bertram, 2020). Early photochemical studies observed the production of small carbonyls from SML samples, which corresponded to increasing chromophoric dissolved organic matter (DOM) (Kieber et al., 1990). This suggested that the VOC production mechanism occurs through indirect photochemistry, by forming a reactive intermediate such as an absorbing molecule in its triplet state, singlet oxygen, or OH. Rossignol et al. (2016) found that photosensitizers were not essential to instigate photochemistry for nonanoic acid surfactants, because they absorb weakly in the lower actinic region and can act as their own sensitizer. It is unclear if this would occur in the real SML. Stirchak et al. (2021) studied seawater and freshwater with

nonanoic acid and photosensitizers and found differing yields of VOCs, which suggests that the VOC formation mechanisms may be different in these 2 conditions. Trueblood et al. (2019) used marine-derived DOM as a photosensitizer to show it was less efficient than commercial humic acid and 4-benzoylbenzoic acid. This result raises questions about the validity of using terrestrial DOM (e.g., humic acid) and single component photosensitizers to represent DOM. Brüggemann et al. (2017) studied the VOCs produced from illuminated biofilms to show the highest VOC yield corresponded to microbial decay, which suggests that the biological processes that control DOM composition are important for photosensitized VOC production.

Heterogeneous ozonolysis is also a VOC source. Zhou et al. (2014) showed that the ozonolysis of genuine SML forms VOCs, suggesting that unsaturated fatty acids were the primary reactants toward ozone. The few studies using unsaturated fatty acid proxies found that film compression played a role in the yield, and potentially the kinetics, by orienting the double bond toward the gaseous phase (Wadia et al., 2000; Schneider et al., 2019). Since it is unclear how this would translate to the real SML samples, caution should be used in interpreting the yield of VOCs from pure fatty acid SML proxies. Schneider et al. (2019) used a fatty-acid rich diatom to show that the VOC yield was sensitive to the growth cycle of phytoplankton, due to the availability of reactive fatty acids. The highest yields were observed after cell lysis, however they did not take into account the bacterial processes which could deplete the fatty acids. Most recently, riverine SML samples were exposed to gaseous ozone to form volatile nitrogen-containing compounds (Wang et al., 2022).

Compared to the lab, there are comparatively few field measurements of VOCs with abiotic sources. In the Canadian Arctic, OVOC abundance correlated with DOM-enriched seawater, suggesting an abiotic source (Mungall et al., 2017). Observations of glyoxal fluxes in the remote marine environment have been associated with oxidation of the SML (Coburn et al., 2014). Observations of glyoxal, acetaldehyde and methylglyoxal have been linked to ozonolysis or photochemistry in the SML (Zhu and Kieber, 2019). While it is shown that isoprene can be photochemically generated, one field study indicated that the isoprene flux was biologically driven, since it did not correlate with the radiation flux (Kim et al., 2017).

#### 4. Conclusions and outlook

This paper has summarized recent advances in our understanding of the marine influence on atmospheric chemistry, highlighting the essential role that biology plays in driving these ocean–atmosphere interactions. The impacts on the atmosphere are widespread, from DMS leading to climatically active cloud condensation nuclei, to inorganic and organic halogen-containing species with direct impacts on odd oxygen in both the troposphere and stratosphere, to VOCs that affect the atmospheric oxidation capacity and participate in the formation of SOA. The field is highly vibrant, as illustrated by the new perspectives presented above on how DMS is oxidized in the

atmosphere and the variety of mechanisms by which VOCs can be released to the atmosphere.

Some of the topics described in the paper are tightly connected. For example, the sea SML plays a strong role in modulating VOC fluxes to the atmosphere, as described in Section 3. However, the SML also impacts the chemical interactions between ozone and seawater described in Section 1, which ultimately lead to the formation of the volatile inorganic iodine compounds  $I_2$  and HOI. Overall, understanding the detailed SML chemistry at the molecular level is essential for both VOC and inorganic halogens. Similarly, there is uncertainty in the degree to which organohalogens, described in both Sections 1 and 2, are also affected by biology and perhaps SML processes. A second theme running through the topic is the challenge in incorporating many of the detailed processes controlling ocean–atmosphere fluxes within large-scale global models. These processes may involve intricate multiphase chemistry or biology, the details of which are still being explored. At present, we rely on relatively crude parameterizations of these processes when making predictions of large-scale atmospheric behavior.

New directions for study interface closely with potential societal implications. One example, briefly mentioned above, is the role for microplastics as a source of contaminants such as VOCs. While many of these contaminants are likely to remain in the ocean, the degree to which some may be expelled to the atmosphere is largely unknown at present. Another field rich for future studies is the impact of ocean–atmosphere interactions in coastal regions. While much of the discussion above has addressed processes in relatively pristine conditions, the chemistry that proceeds in polluted marine settings is worthy of future studies given that a large fraction of the world's population lives close to an ocean. Interactions of interest include reactions between nitrogen oxides, especially the nitrate radical, with marine emissions, and coupled halogen-organic chemistry that can occur when emissions of both precursors are elevated and can lead to the formation of organo-halogen species.

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