

Reactive VOC production from photochemical and heterogeneous reactions occurring at the air-ocean interface

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Conspectus

The ocean surface serves as a source and sink for a diverse set of reactive trace gases in the atmosphere, including volatile organic compounds (VOC), reactive halogens, and oxidized and reduced nitrogen compounds. The exchange of reactive trace gases between the atmosphere and ocean has been shown to alter atmospheric oxidant concentrations and drive particle nucleation and growth. Uncertainties in cloud radiative forcing and aerosol-cloud interactions are among the largest uncertainties in current global climate models. Climate models are particularly sensitive to cloud cover over the remote ocean due to large changes in albedo between the ocean surface and cloud tops. Oceanic emissions contribute to cloud condensation nuclei concentrations, either through the direct emission of particles during wave breaking, or through the formation of secondary aerosol particles following the emission of reactive gas-phase compounds. Despite generally small and diffuse oceanic emission rates for reactive trace gases, it has been shown that oxidant and particle number concentrations are acutely sensitive to air-sea trace gas exchange rates and the chemical composition of emitted species. To date, *field* measurements of air-sea reactive gas exchange have focused primarily on the emission of gases of biological origin, such as dimethyl sulfide (DMS). While DMS emissions are relatively well constrained, the gas-phase oxidation that connects DMS to sulfate aerosol is less well understood. Recent *laboratory* measurements suggest that heterogeneous and photochemical reactions occurring at the air-sea interface can also lead to the production and emission of a wide array of reactive VOC. When laboratory-based measurements are used to derive global scale emissions, the calculated sea-to-air fluxes of reactive VOC generated from heterogeneous and photochemical processes are comparable or larger in magnitude to the sea-to-air flux of DMS. It is not yet clear how the mechanisms proposed in these laboratory experiments translate to atmospheric conditions. The proposed abiotic emissions are also a potential source of VOC in regions of low biological activity which carries important implications for regional and global modeling.

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This account reviews recent laboratory and field experiments of biotic and abiotic ocean VOC emissions with a specific focus on exploring open questions related to proposed abiotic reactive VOC emissions and the impact of including a large, abiotic VOC emission source on atmospheric oxidants and aerosol particles. To date, abiotic emissions are not typically included in global chemical transport models. The proposed abiotic emissions mechanisms discussed here have the potential to drive significant changes to current understanding of chemistry in the marine atmosphere if present at the magnitudes suggested by laboratory studies. In order to validate their proposed significance, a coordinated set of laboratory, field, and modeling studies under ocean-relevant conditions are necessary.

1. Biological production and sea-to-air transfer of reactive VOC

Emissions of volatile organic compounds (VOC) from the ocean surface have been shown to impact oxidant loadings and secondary aerosol formation in the marine atmosphere.¹⁻⁵ To date, marine VOC research has primarily focused on the seawater production and emission of dimethyl sulfide (DMS) and its links to cloud formation, the foundation for the CLAW hypothesis⁶ which proposed a self-regulating climate feedback loop between DMS, cloud cover and surface temperatures. While supporting evidence for the complete feedback loop is mixed,^{7,8} there are many lines of evidence which demonstrate the impact of DMS emissions on aerosol, clouds, and oxidative capacity of the marine atmosphere. Comparatively less work has focused on other marine biogenic VOC (BVOC) sources including isoprene and monoterpenes. Monoterpene and isoprene emissions are known to be considerably smaller than DMS but may still have significant impacts on aerosol formation due to their high secondary organic aerosol (SOA) yields⁹ and ability to produce extremely low volatility oxidation products.¹⁰ In addition, isoprene and monoterpenes also have substantially faster biomolecular reaction rate constants for reaction with ozone and hydroxyl (OH) radicals compared to DMS.

DMS is produced in the surface ocean from the cleavage of dimethylsulfoniopropionate (DMSP), a metabolite found in a wide range of macro- and micro-algae. Extensive global data sets of dissolved DMS concentrations and DMS emission fluxes has been collected over much of the global oceans. This database of global surface seawater DMS measurements and detailed studies of DMS air-sea transfer rates have led to the development of well constrained DMS emissions inventories, where the global, annual average DMS emission rate is estimated to be between 14.7

to 21.1 Tg C yr⁻¹.¹¹⁻¹⁴ While there remain uncertainties in elements of the DMSP and DMS production and conversion pathways, the spatiotemporal distribution of DMS waterside concentrations and emissions flux observations are generally well described in global models. For a comprehensive review of DMS production, chemistry, and air-sea exchange see Carpenter et al. (2012).¹⁵

Once emitted into the atmosphere, DMS is oxidized by OH and halogen radicals (Cl and BrO) to form lower volatility products, which can contribute to new particle formation after further oxidation to sulfate (SO₄²⁻), or particle growth following oxidation to methyl sulfonic acid (MSA). The lifetime of DMS to oxidation by OH is roughly 1.2 days for an OH concentration of 2 × 10⁶ molecules cm⁻³. The OH-oxidation of DMS proceeds by either OH addition (primarily forming MSA) or hydrogen abstraction (primarily forming SO₂), where the branching fraction is a strong function of temperature.¹⁶ Reported yields of SO₂ from DMS oxidation vary significantly from ~30-100%.¹⁷ Much of this uncertainty in SO₂ yield can be linked to an incomplete understanding of the intermediate oxidation steps following reaction with OH and uncertainties in halogen and multiphase chemistry.¹⁶ Recent laboratory and field observations have shown the significance of a previously unknown DMS oxidation pathway leading to the formation of a stable intermediate (C₂H₄O₃S; hydroperoxy methylthioformate; HPMTF) which is not included in any current global chemistry models. HPMTF is formed in the OH initiated H-abstraction pathway, following two intramolecular H-shift reactions, which outpace bimolecular reactions at low NO_x.^{18,19} Ambient observations over wide regions of the global marine boundary layer on the NASA Atmospheric Tomography (ATom) campaign confirmed that HPMTF is ubiquitous in the remote marine atmosphere and suggest that *ca.* 40% of emitted DMS goes on to form HPMTF.²⁰ Determination of the atmospheric fate of HPMTF is an active area of research,¹⁹ as this chemistry may necessitate significant updates to our understanding of sulfur processing in the marine atmosphere. These observations highlight the important gaps in current understanding for even the most well studied marine VOC.

In addition to DMS, laboratory monoculture studies have demonstrated that marine phytoplankton can efficiently produce isoprene and select monoterpenes, with production rates dependent on phytoplankton speciation, solar radiation, temperature, and nutrient loadings.²¹ Surface seawater isoprene concentrations have been reported in the range of 0.1-100 pM, with higher concentrations

often, but not always,²² correlated with chlorophyll *a*.²¹ Phytoplankton monoculture studies indicate that isoprene production rates are an order of magnitude larger than total monoterpene production rates.²³ Marine gas-phase isoprene mixing ratios have been observed as high as 375 ppt during a phytoplankton bloom.²⁴ Average MBL monoterpene mixing ratios from that study
95 were 125 ppt (phytoplankton bloom) and 5 ppt (non-bloom) in the southern Atlantic Ocean. A review of non-bloom measurements shows gas-phase isoprene mixing ratios are typically less than 20 ppt.²¹ Speciated monoterpenes measurements over several cruises in the Atlantic and Arctic showed average concentrations from 0.5 to 2.9 pM, with no clear correlation to biological productivity.²⁵

100 Estimates of isoprene emissions, parameterized from dissolved concentrations (bottom-up) and remote sensing products (top-down) result in emission estimates from 0.1 to 12 Tg C yr⁻¹ respectively.^{26,27} Marine monoterpene emissions are even more uncertain, with estimated global flux ranging between 0.01 and 29.5 Tg C yr⁻¹ from bottom-up and top-down methods respectively.²⁸ Modeled global monoterpene emissions of 0.16 Tg C yr⁻¹ were determined by
105 incorporating extensive observations of dissolved monoterpenes from a wide spatial area in the Atlantic and Arctic.²⁵

Our group reported the first simultaneous, eddy covariance measurements of DMS, isoprene, and monoterpene air-sea fluxes as part of the High Wind Gas Exchange Study (HiWinGS) over the Northern Atlantic Ocean during fall.²⁹ Average isoprene and monoterpene emission fluxes were
110 small, consistent with prior calculations, with campaign averages of 5.0×10^7 and 2.6×10^7 molecules cm⁻² s⁻¹, respectively. For the campaign mean, the sum of isoprene and monoterpene fluxes were significantly lower than the average DMS flux (1.04×10^9 molecules cm⁻² s⁻¹). However, in localized hotspots during an upwelling event, the maximum monoterpene flux (1.62×10^9 molecules cm⁻² s⁻¹) was larger than coincident DMS emissions, highlighting the importance
115 of local biological variability on BVOC emissions. The frequency of these high monoterpene emitting bloom events are not well constrained but appear to be linked to upwelling events that redistribute nutrients to the surface, stimulating phytoplankton blooms. Scaling the observed emission fluxes during this study to the global oceans results in annual emissions of 4.71, 0.57, and 0.60 Tg C yr⁻¹ for DMS, isoprene, and monoterpenes, respectively. Those emissions weighted
120 by OH reactivity and normalized to DMS are 1, 1.02, and 0.28 for DMS, isoprene, and

monoterpenes respectively, highlighting the significance of terpenes on atmospheric oxidative capacity despite smaller mass emissions. An overview of DMS, monoterpene, and isoprene emissions are presented in **Figure 1**. This brief review of select reactive biogenic emissions highlights the known importance of DMS, isoprene, and monoterpene emissions on the marine atmosphere and provides a calibration point for the scale of marine reactive carbon emissions and their potential impacts on SOA and oxidant loadings.

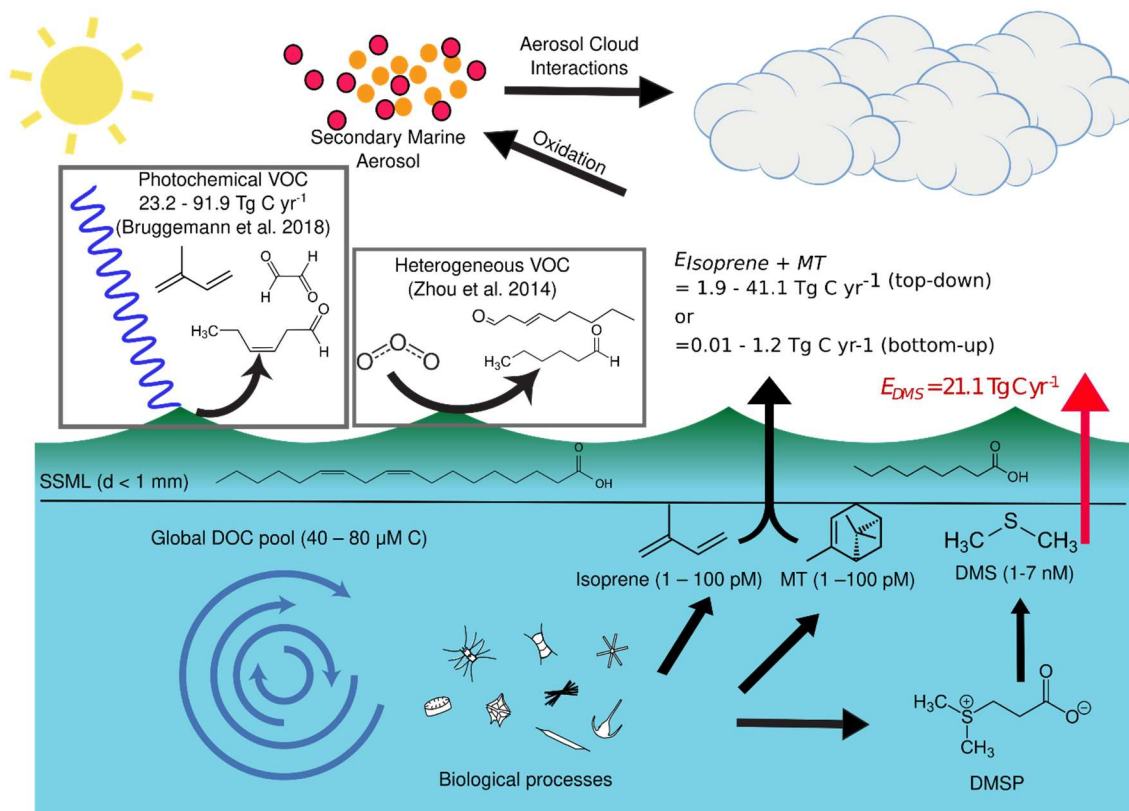


Figure 1. Overview of marine biotic (DMS, monoterpenes (MT), and isoprene) and abiotic (photochemical³⁰ and heterogeneous³¹) ocean VOC emission sources. Quoted DMS emissions are from the Lana et al. (2011) climatology.¹¹ MT and isoprene emission estimates are separated into top-down^{28,32} and bottom-up^{21,28,33} methodologies.

2. Known photochemical production of VOC at the ocean surface

To date, study of marine VOC production mechanisms and emission rates have focused primarily on biochemical processes with a specific focus on DMS. However, photochemical emissions of a small number of species including alkyl nitrates,³⁴ acetone,³⁵⁻³⁷ and acetaldehyde^{37,38} have previously been investigated. For example, alkyl nitrates have a well-established photochemical production pathway, where photochemically produced RO₂ and NO₂ react in the surface waters to

form RO₂NO₂ species.³⁹ Dark, bacterial-mediated RO₂NO₂ production has also been observed.³⁹ Alkyl nitrate emissions are significant as a source of NO_x to the remote marine atmosphere, where O₃ production is severely NO_x limited.⁴⁰ Field measurements have shown that acetone air-sea exchange is bidirectional with a net sink in the Northern Hemisphere oceans and a net source in the tropical oceans.³⁶ Globally, acetone in the ocean is in near equilibrium with the gaseous acetone in the atmosphere, acting as net atmospheric sink of 2-7.5 Tg yr⁻¹.^{35,36} Ocean acetone production has been shown from both photochemical and biological pathways³⁷, with *in situ* gross production rates reporting 48-100% of acetone production is from photochemical sources.³⁷ Acetone does not produce significant SOA through gas phase reactions and SOA yields are small from heterogeneous reactions (0.3 – 0.5%).⁴¹ Acetone reacts slowly with OH ($k = 2.2 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) but can be photolyzed to produce OH, influencing the HO_x budget, particularly in the upper troposphere.⁴² Acetaldehyde marine photoproduction is also well supported, with studies showing production from photolysis of colored dissolved organic matter (CDOM).^{38,43} Gross production measurements showed that photochemical production accounted for up to 68% of the total source.³⁷ Net global marine acetaldehyde emissions have been modeled to be from 19 to 31 Tg C yr⁻¹.^{44,45} Acetaldehyde does not contribute to SOA production but has a fast bimolecular rate constant with OH ($k = 1.62 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) and thus is an important term in the marine OH budget.⁴⁶ These photoproduction sources all have relatively well-studied global emission climatologies which allows for inclusion in chemistry models.

3. Laboratory measurements of interfacial marine abiotic VOC emission sources

3.1 Photochemical production of VOC at the ocean surface

Recently, a series of laboratory experiments have suggested that photochemical and heterogeneous reactions occurring at the ocean-atmosphere interface could be a significant source of reactive VOC. VOC formed through abiotic mechanisms encompass a wide range of oxygenated and unsaturated molecules distinct from those discussed previously, with potential impacts on the marine HO_x and SOA budget. A schematic diagram of biotic and abiotic emission sources and estimates of their magnitudes is presented in **Figure 1**. Measurements of the chemical composition of the sea-surface microlayer (SSML) have indicated that it is strongly enriched in dissolved organic matter with chromophoric functional groups,⁴⁷ which could react with OH and O₃ or undergo photochemical reactions, all of which can lead to VOC production. For example,

photolysis of both a proxy SSML (nonanoic acid, NA) as well as authentic SSML samples with added humic acid (HA) as a photosensitizer both showed photoenhanced isoprene production.⁴⁸

170 Scaling these laboratory results to ocean conditions suggested that photochemical isoprene fluxes could be as large as $0.8 - 1.7 \times 10^9$ molecules $\text{cm}^{-2} \text{s}^{-1}$, which is comparable in magnitude to DMS emission rates and higher than the expected isoprene emissions from bulk biogenically produced isoprene.^{29,48} Additional laboratory photochemical studies of proxy and authentic SSML samples have demonstrated prompt formation of a variety of reactive species including saturated and

175 unsaturated aldehydes.⁴⁸⁻⁵⁴ Emissions from these studies generally show a wide array of products with lower emission fluxes than those described above for isoprene. For example, Bruggemann et al.⁵³ reported photoenhanced emissions of 1.1×10^8 , 4.4×10^8 , and 71×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$ for octanal, isoprene, and acetone respectively, along with many other products, from irradiance of biofilms scaled to an ambient mean solar flux of 92 Wm^{-2} . These photochemical production studies

180 have generally included the addition of a photosensitizing agent to the SSML sample, typically 4-benzoylbenzoic acid (BBA) or commercial HA. A comparison of photochemical production from NA with BBA, HA, and authentic marine dissolved organic matter (m-DOM) as photosensitizing agents showed that authentic m-DOM did not result in enhanced photochemical VOC production, while the BBA and HA samples showed photochemical emissions consistent with prior studies.⁵⁵

185 This raises questions as to appropriate proxies of photosensitizers and SSML constituents to use in laboratory studies. However, Rossignol et al.⁵⁴ demonstrated photoenhanced VOC production from concentrated NA with no added photosensitizers. While aqueous NA at the solubility limit does not absorb in the UV-visible spectral range of actinic flux at Earth's surface ($>280 \text{ nm}$), the authors demonstrated that concentrated interfacial NA does show weak absorption in the actinic

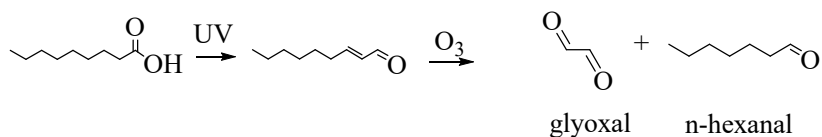
190 flux wavelengths. They propose this absorbance is driven by the presence of a weakly absorbing reactive state of NA which is enhanced at the interface, allowing photochemistry in the absence of traditional photosensitizing groups. While these studies have provided new molecular insight into photochemical VOC production mechanisms, it is not yet clear how representative these studies are of the significantly more dilute and chemically complex SSML. Future laboratory studies

195 should focus on measuring VOC production and emission from multicomponent systems representative of the authentic SSML.

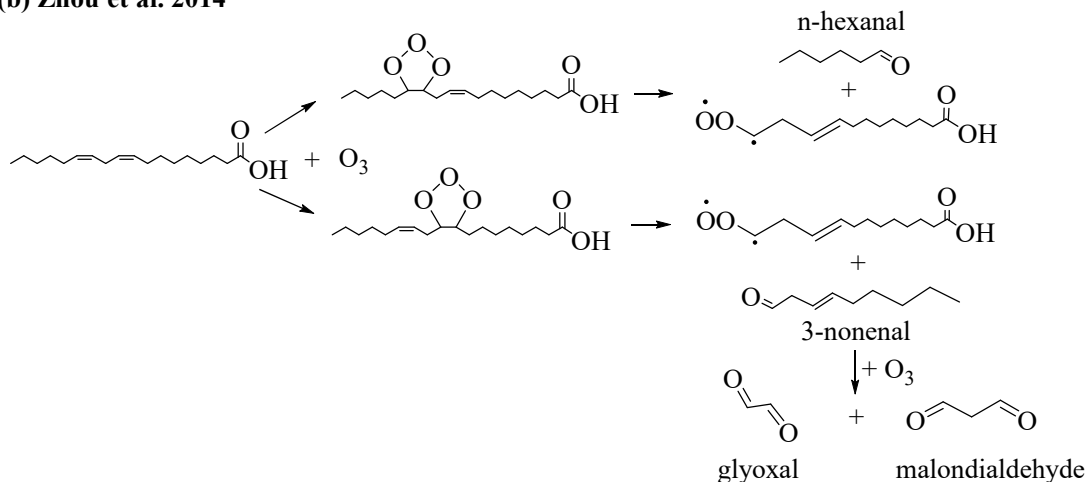
3.2 Production of VOC from heterogeneous reactions occurring at the ocean surface

Heterogeneous reactions of ozone (O_3) with model and authentic SSML samples also efficiently produce reactive VOC including alkanals and alkenals in laboratory studies.^{31,56} Ozone is known to react efficiently with both iodide and a variety of DOC compounds at the ocean interface, representing an important global loss term for O_3 .⁵⁷ Interfacial marine reactions of O_3 are a central driver of reactive halogen emissions to the atmosphere, contributing up to 75% of the observed iodine oxide levels over the tropical Atlantic.⁵⁸ Laboratory exposure of a proxy SSML containing linoleic acid to O_3 resulted in emission of carbonyls at near 100% total molecular yield.³¹ Exposure of authentic SSML samples also showed prompt production of a wider set of gas phase carbonyl products.³¹ Heterogeneous reactions of O_3 with the SSML generated by a laboratory grown phytoplankton culture produced C7-C10 carbonyls and also drove new aerosol particle formation and growth.⁵⁶ These studies provide intriguing evidence that heterogeneous reactions of O_3 at the ocean surface may be an important abiotic heterogeneous source of reactive VOCs in the marine atmosphere. An overview of proposed photochemical and heterogeneous reaction mechanisms discussed here are presented in **Figure 2**.

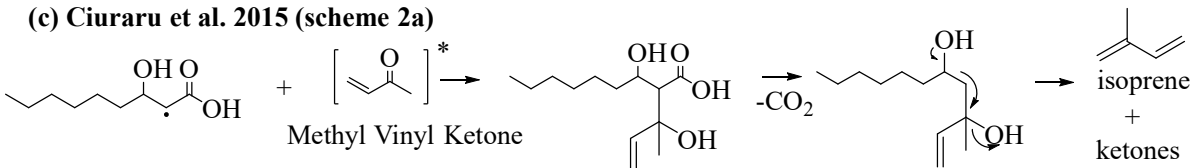
(a) Chiu et al. 2017



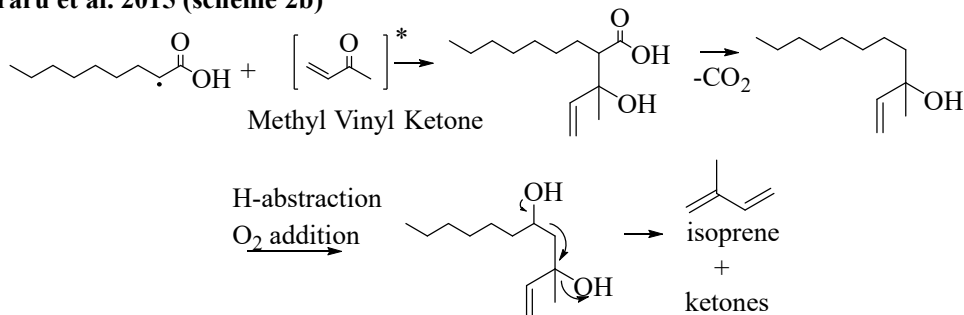
(b) Zhou et al. 2014



(c) Ciuraru et al. 2015 (scheme 2a)



(d) Ciuraru et al. 2015 (scheme 2b)



215 **Figure 2.** Overview of proposed abiotic VOC formation pathways from photochemical and heterogeneous mechanisms. Panels (a), (c), and (d) are photochemical mechanisms.^{48,49} Panel (b) is a heterogeneous reaction of O₃ at the marine interface.³¹

3.3 Models of interfacial abiotic VOC emission magnitudes

220 Enrichment of organic molecules in the SSML has been suggested to be ubiquitous across the global ocean when wind speeds are moderate (<13 m s⁻¹), suggesting abiotic emission sources may be viable over a broad spatiotemporal distribution.⁵⁹ The SSML is enhanced in organic material by factors of 2-4 over bulk surface water (bulk DOC = 40-80 μM C), which is still significantly

less than compact monolayer coverage used in laboratory studies.^{59,60} SSML enrichment factors are similar across regions of high and low biological productivity, suggesting abiotic emissions, if present, could be viable even in regions removed from local biological productivity.⁵⁹ A global modeling study applying laboratory derived photochemical emission factors and SSML coverage parameterized to windspeed proposed a total photochemical emission source of 23.2–91.9 Tg C yr⁻¹.³⁰ This emission term is competitive with global DMS emissions (21.1 Tg C yr⁻¹) even at the lower range of the estimate.¹¹

To the best of our knowledge, there are no global modeling studies of O₃ driven VOC emissions. To estimate the magnitude of the VOC source stemming from O₃ deposition, we conducted a simple model calculation constrained by measured O₃ deposition velocities and laboratory-derived VOC yields. Reported ozone deposition velocities to the ocean surface are typically from 0.01 to 0.05 cm s⁻¹.^{57,61} Taking a representative deposition velocity of 0.02 cm s⁻¹ and an O₃ concentration of 30 ppbv results in an O₃ deposition flux of 1.5×10^{10} molecules cm⁻² s⁻¹. Assigning effective VOC yields of 10 or 50% from O₃ deposition corresponds to emissions of 1.5×10^9 and 7.2×10^9 molecules cm⁻² s⁻¹ respectively. Crudely scaling this emission across the global ocean and assigning an average VOC structure containing 5 carbons results in an emission source of 17.5 to 87.3 Tg C yr⁻¹, comparable to DMS emissions of 21.1 Tg C yr⁻¹.¹¹ Clearly there are several large uncertainties in this exercise, with the effective VOC yield and molecular structures being almost entirely unconstrained. Further, ozone deposition is known to be dominated by reactions with iodide at the ocean surface, meaning a 50% VOC yield is likely an upper limit.⁵⁷ The lower bound of 10% used in the calculation is arbitrary and only used for illustration, the yield from the actual ocean interface may be orders of magnitude lower. This exercise is intended to emphasize that significant further constraints on VOC emissions from O₃ deposition are necessary and is not intended to be a rigorous prediction of the emissions from heterogeneous production of O₃ at the ocean interface. Still, within the currently available laboratory and field study constraints, this heterogenous VOC production mechanism could be significant,^{31,56} but relies heavily on the ratio of the reaction rates between O₃ and iodide compared with O₃ and DOM.

These laboratory measurements and modeling studies provide strong motivation for the field measurement community to determine the extent to which heterogeneous and photochemical reactions at the air-ocean interface impact gas and aerosol concentrations in the marine boundary

layer. At present, it is not clear how laboratory measurements, conducted on quiescent surface films with model surfactant systems represent the heterogeneous, chemically complex, and significantly more dilute SSML interface.

255 **4. Field measurements of interfacial marine abiotic VOC emission sources**

There are several lines of evidence from field observations that provide insight on the extent to which emissions from SSML interfacial chemistry may or may not be important for reactive VOC budgets: 1) Observations of strong (>20x) enrichment in low molecular weight carbonyls in the SSML, relative to the subsurface waters, with a diel cycle peaking in the afternoon suggesting
260 carbonyl production in the SSML may be driven by photochemistry.³⁸ 2) *In situ* and remote sensing instruments have shown elevated concentrations of glyoxal in the MBL, and nighttime emission flux of glyoxal from the ocean surface,⁶² which cannot be accounted for by gas-phase oxidation of biogenic VOC alone, suggesting a role for SSML chemistry⁶²⁻⁶⁴ 3) Direct measurements of isoprene ocean emission fluxes *via* eddy covariance were shown to be independent of shortwave
265 radiation intensity.²⁹ 4) Observations of elevated formic acid concentrations over the Arctic Ocean during periods of low wind speed and high solar irradiance have been attributed to a photochemical SSML ocean source.⁶⁵ The combined effect of these results and others make clear that our understanding of emissions to the marine atmosphere is incomplete and that abiotic sources need to be constrained.

270 Recent results from the NASA Atmospheric Tomography study (ATom) have provided an extensive chemically detailed dataset over large regions of the global remote oceans. ATom was a series of flights from 2016-2018 sampling the remote marine atmosphere with the goal of improving understanding of trace gases and short lived greenhouse gases throughout the global remote atmosphere.⁶⁶ A key finding from the ATom campaign was the observation of a persistent
275 missing source of acetaldehyde in the boundary layer and free troposphere.⁶⁷ Inclusion of an interfacial ocean acetaldehyde source of 34 Tg yr⁻¹ improved model to measurement agreement in the boundary layer, but given the short atmospheric lifetime of acetaldehyde (<4 hr) it was not sufficient to explain the enhanced acetaldehyde observed at higher altitudes. This enhanced acetaldehyde acts as a missing sink of hydroxyl (OH) radicals in the marine atmosphere which is
280 not accounted for in current chemistry models. Despite the missing acetaldehyde source, analyses conducted using the GEOS-Chem chemical transport model were able to successfully simulate

OH radical magnitudes and vertical profiles within the combined uncertainties of the measurement and model.⁴⁶ Notably, the global modeling analysis of Travis et al. (2020)⁴⁶ incorporated photochemical abiotic emissions following Bruggemann et al. (2018),³⁰ which together with an enhanced biogenic emission scheme increased modeled OH reactivity (OHR) over the ocean by 10%. Additionally, a chemical box model simulation using Master Chemical Mechanism v3.3.1 (MCM) chemistry was consistent with observations for OH and hydroperoxyl (HO₂) radicals within the measurement uncertainty.⁶⁸ These results suggest that oxidant loadings in the remote marine atmosphere are generally consistent with currently understood emissions and chemistry. In slight contrast, direct measurements of OHR during ATom were larger than the cumulative OHR of the trace gases measured and of OHR in the GEOS-Chem modeling study which suggests a missing OHR on the order of 0.5 s⁻¹ in the marine boundary layer.^{46,69} The authors suggest a missing sea surface VOC emission source of unknown composition may be responsible for the missing OHR term. Any missing species added to account for the missing OHR would also have to efficiently recycle OH in order to remain consistent with the measured OH and HO₂ concentrations and could not contribute to PAN formation to remain consistent with observed PAN.⁴⁶ Given those requirements and the wide suite of VOCs measured during ATom, it is challenging to invoke a large missing VOC that is consistent with all of measured constraints.⁴⁶ Together these results suggest that oxidative capacity during ATom was generally well captured in the remote marine troposphere, but that a persistent missing source of acetaldehyde and possibly OHR is present.

5. Impact of marine reactive VOC emissions on SOA production

The extent to which marine trace gases impact particle number and mass concentrations following oxidation to low vapor pressure compounds is a complex function of trace gas emission rates, oxidation kinetics and mechanisms, and meteorology. Model determinations of the global ocean contribution to the organic fraction of marine aerosol (OC) vary significantly, ranging from a cumulative primary and SOA source of 8 Tg C yr⁻¹ to 25-40 Tg C yr⁻¹ considering only SOA.^{70,71} Additional modeling work suggests that the global aerosol burden from marine isoprene emissions is less than 0.05 Tg C yr⁻¹.^{32,72} Our group measured VOC fluxes during HiWinGS to estimate the range in secondary organic aerosol production rates (P_{SOA}) from measured isoprene and monoterpene emissions. Using an organic aerosol yield of 0.05, P_{SOA} was calculated to be 0.2 ng m⁻³ d⁻¹ and 25 ng m⁻³ d⁻¹ for mean and maximum monoterpene fluxes observed during HiWinGS,

which roughly scales to 0.016 and 1.97 Tg yr^{-1} .²⁹ A general version of this calculation is presented in **Figure 3** for global P_{SOA} from VOC emissions of generic composition as a function of SOA yield. Taking E_{VOC} of 1×10^{10} and 1×10^{11} molecules $\text{cm}^{-2} \text{ s}^{-1}$ and SOA yields of 1% drives total annual SOA production of 6.1 and 40.8 Tg yr^{-1} respectively, which cover the range of model determinations of total marine SOA. Bruggemann et al.³⁰ calculated that their proposed interfacial photochemistry source would contribute SOA mass of $0.48 - 0.60 \text{ Tg yr}^{-1}$, which corresponds to 1.5-7.5% of the estimated total SOA source described above. Given the paucity of field observations, direct measurements of air-sea flux magnitudes and speciation will be critical to quantitative assessments of the impact of air-sea gas exchange on aerosol particle composition, where the modeling approach of Kim et al. (2017)²⁹ provides a framework for assessing the impact of observed air-sea emissions of other VOCs on aerosol particle number and mass concentrations.

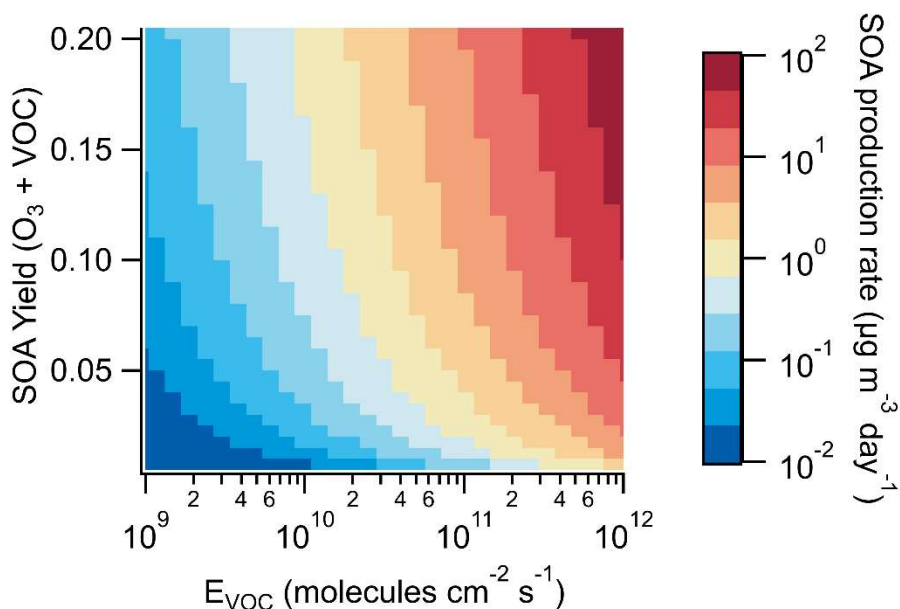


Figure 3. Modeled secondary organic aerosol production rate (P_{SOA}) as a function of ocean VOC emission flux (E_{VOC}) and condensable SOA product yield. Figure generated following all details of the modeling approach of Kim et al. (2017)²⁹ extended out to larger E_{VOC} rates.

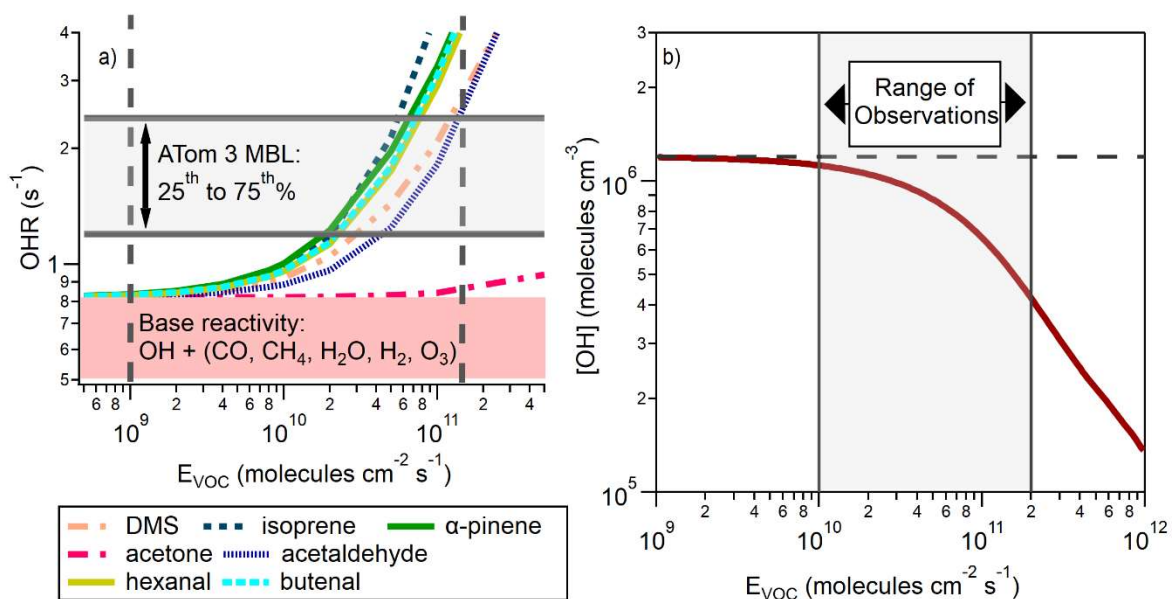
6. Impact of marine reactive VOC emissions on atmospheric oxidative capacity

Air-sea gas exchange can also impact oxidant concentrations by altering OHR and/or oxidant production rates following photolysis (e.g., acetone). Results from the ATom campaign provide constraints on the contribution of non-methane hydrocarbons (NMHC) to OHR in the remote marine boundary layer. Modeled OHR is highly sensitive to VOC emission and speciation. To

make this point, we constructed a 0-D VOC emissions box model with the Framework for 0-Dimensional Atmospheric Modeling (F0AM)⁷³ using MCM chemistry to assess impacts of VOC emissions (E_{VOC}) on OHR (**Figure 4a**). Emissions are mixed into an 800 m boundary layer height with a 1-day lifetime to dilution. The model is constrained by mean ATom 3 marine boundary layer meteorology and the mixing ratios of all major inorganic species and methane. A baseline OHR of 0.8 s^{-1} is set by reactions with inorganic species and methane. Model runs of different VOC speciation and E_{VOC} rates were run for three days to allow all secondary products that may also contribute to OHR to stabilize, with the day three noontime OHR values reported. The ATom 3 reported 25th-75th percentile range of measured boundary layer OHR were $1.2\text{-}2.4 \text{ s}^{-1}$. The largest E_{VOC} consistent with observed OHR is *ca.* $1.1 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1}$ for acetaldehyde. The minimum VOC emission rates consistent with the ATom observations are less clear but are likely to be at least $1 \times 10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$, which is a typical baseline emission rate of DMS.²⁹ This model framework provides a method to assess sensitivity of OHR to changes in prescribed VOC air-sea fluxes as new E_{VOC} source terms are developed.

Total OH concentration ($[\text{OH}]$) also serves as a constraint on the potential E_{VOC} term.¹ Donahue and Prinn (1990)¹ used a box-modeling approach to calculate $[\text{OH}]$ as a function of E_{VOC} and to determine the range of E_{VOC} consistent with observations in the marine boundary layer, constrained by observed speciated NMHC as well as CO and CH₄. They found that E_{VOC} from 1×10^{10} to $2 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1}$ were consistent with observations, with the range driven either by uncertainty in measurements or true atmospheric variability. An adapted version of these results are shown in **Figure 4b**. A model run for E_{VOC} of $5.4 \times 10^{10} \text{ molecules cm}^{-2} \text{ s}^{-1}$ yielded diel average $[\text{OH}] = 8.4 \times 10^5 \text{ molecules cm}^{-3}$ which is in line with $[\text{OH}]$ derived from inversions of methyl chloroform mixing ratios. Other box modelling work showed that isoprene emissions of $0.1 - 6 \times 10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$ suppressed OH and HO₂ radical concentrations by as much as 26 and 13% respectively. The measurements and modelling of OHR and $[\text{OH}]$ made during ATom suggest that $[\text{OH}]$ is well captured with currently known chemistry in the marine boundary layer but that OHR is underpredicted. It is unclear what speciation and magnitude of interfacial abiotic VOC emissions would be consistent with those observations. The net impact of an interfacial abiotic E_{VOC} of $1 \times 10^{10} \text{ molecules cm}^{-2} \text{ s}^{-1}$ with SOA yield of 1% and a reactivity with OH equivalent to acetaldehyde would result in a P_{SOA} of 6.1 Tg yr^{-1} and an increase in ROH of nearly 0.1 s^{-1} . Both of those terms

would have important impacts on chemistry of the remote marine atmosphere which need to be further constrained.



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Figure 4. a) Modeled OH reactivity (OHR) as a function of VOC emission rates (E_{VOC}) for various VOC speciation. Horizontal solid lines are the 25th to 75th percentile range of R_{OH} observations made during ATom 3. Dashed vertical lines are the corresponding minimum and maximum E_{VOC} consistent with the observed ATom OHR. b) Modeled dependence of diel average [OH] on E_{VOC} . The shaded region represents the range in calculated E_{VOC} flux constrained by NMHC gas observations in the marine boundary layer (adapted from Donahue and Prinn (1990)¹).

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7. Outlook: Linking field and laboratory observations

Recent laboratory and field observations have challenged the long-standing assumption that ocean biochemical processes are the primary driver of marine trace gas emissions and SOA chemistry.

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Laboratory studies have highlighted the potential for heterogeneous and photochemical reactions at the ocean interface as new sources of VOC in the marine atmosphere, which may have very different spatial and temporal distributions compared to biogenic emissions. Large scale field campaigns suggest a large missing source of acetaldehyde and possibly OH reactivity in the remote marine atmosphere. However, there remains significant uncertainty in scaling laboratory observations of interfacial VOC production to the ambient atmosphere which provides a clear motivation for targeted research to close the gap between laboratory model system studies and large-scale atmospheric concentration measurements. This effort will necessitate a coordinated set of studies, including laboratory measurements under atmospherically relevant conditions, direct

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field observations of ocean-atmosphere VOC eddy covariance flux, and global climate modeling
385 constrained by those observations

In the laboratory it will be essential to understand how to develop a mechanistic understanding of
the link between SSML concentrations and composition with their photochemical and
heterogeneous VOC yields and speciation under ocean relevant conditions. In the field it will be
necessary to perform targeted studies probing air-sea exchange of reactive trace gases as a function
390 of photolysis rates and oxidant concentrations.

Recent efforts in our group have focused on the goals of constrained laboratory studies and field
observations. An eddy covariance flux experiment from Scripps Pier, La Jolla CA was carried out
in September 2019 with a latest generation PTR-ToFMS⁷⁴ with the aim of directly testing
suggested abiotic emission sources. Also during 2019, we conducted large-scale laboratory
395 measurements as part of a wave flume phytoplankton bloom mesocosm study with the goal of
investigating biotic and photochemical abiotic VOC emission sources in a controlled
atmospherically relevant system throughout a phytoplankton bloom and death cycle.

While it remains clear that ocean emissions of reactive VOCs are a central driver of aerosol
production and oxidative capacity over large regions of the surface atmosphere, recent field and
400 laboratory observations have raised intriguing questions about abiotic VOC emissions and their
relative significance compared to DMS and other biogenic species. This emerging topic has
multiple open questions but may contribute new insights on marine VOC cycling as further direct
observations are made.

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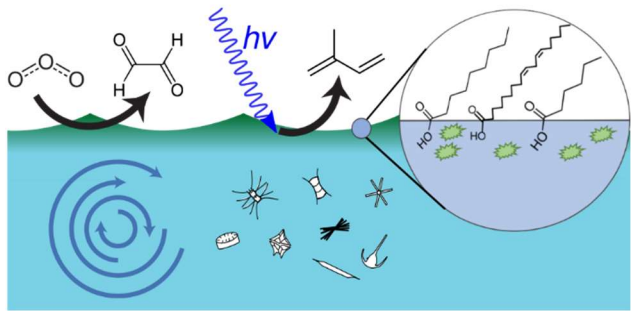
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