



Biological controls on marine volatile organic compound emissions: A balancing act at the sea-air interface

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ABSTRACT

Volatile organic compounds (VOCs) comprise a vast pool of low molecular weight and rapidly diffusible chemicals that are emitted from all cells as well as by photolysis of dissolved organic matter and burning of fossil fuels. In the ocean, VOCs are an important component of the marine carbon cycle, serving as plankton growth products and substrates and also as info-chemicals that influence phytoplankton life cycles. When VOCs are emitted from the ocean into the atmosphere, they alter Earth's radiative budget through oxidation reactions and secondary aerosol formation. Marine phytoplankton are the primary biotic source of marine VOCs, many of which are exploited as nutrient resources by ubiquitous bacterioplankton that have evolved specific mechanisms to consume these compounds. Thus, the balance of VOC production and consumption exerts control on the concentrations of dissolved VOCs at the sea-air interface. Current simulations of atmospheric chemistry do not take into account biological controls of dissolved VOCs. Linkages between phytoplankton communities, VOC composition, and surface ocean properties are promising avenues for improving the next generation of chemical transport models that quantify and predict VOC emissions. We suggest that VOC accumulation may be predictable by identifying periods when plankton communities are disrupted by biological or physical processes. Layered models that use remote sensing and ocean physics to measure the states and trajectories of plankton assemblages have promise for predicting ocean sea-air VOC transfer.

1. Introduction

Volatile organic compounds (VOCs) are a diverse collection of low molecular weight chemicals with high vapor pressures. VOCs in marine systems are products of cell metabolism and photodegradation of organic matter (Kieber et al., 1990; Moore et al., 2020; Mungall et al., 2017). In the open ocean microalgae are the primary sources of VOCs. These low molecular weight chemicals with relatively low water solubilities are released from cells under all conditions – or perhaps more accurately, there are no reports of cells that do not release VOCs. The diffusivity of VOCs makes them prone to emission into the atmosphere where their reactivity has climate impacts. Oxidation of VOCs in the atmosphere can affect Earth's radiative balance by forming secondary organic aerosols (SOA) that condense onto particles enabling growth of cloud condensation nuclei (O'Dowd et al., 1999). VOCs can also impact the oxidative capability of the atmosphere and the lifetimes of greenhouse gases. Nitrogen oxides react with VOCs, inhibiting SOA formation (NO_x; Lelieveld et al., 2008). Low NO_x conditions prevail in the atmosphere above the vast open oceans and thus favor VOC oxidation

pathways leading to SOAs, but little is known about the biological contributions to SOAs or how microbiology in the surface ocean regulates the pool of VOCs subject to sea-air emissions.

In the surface layer of the ocean, biological and chemical interactions with VOCs compete with their emission from the sea-air interface. Many VOCs exhibit antioxidant properties and can undergo rapid chemical oxidation yielding new chemical species of varying stabilities (Warneck, 2003b). VOCs also represent an important component of the marine carbon cycle because they are derived from phytoplankton photosynthetic metabolism, and they are also substrates for heterotrophic oxidation. The balance of VOC production and consumption appears to be driven mainly by biology and exerts significant control on in-water VOC concentrations.

Research suggests that the pool of VOCs in the surface ocean is large and turns over rapidly, on the scale of hours to days, similar to labile dissolved organic matter (LDOC) pools. Understanding the biological processes impacting VOC pools is needed to constrain and quantify the VOC source terms used in chemical transport models. Technologies are now available to measure with high resolution the VOCs present in

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seawater (Fig. 1), temporal VOC dynamics, and the molecular mechanisms involved in VOC metabolism. Here we discuss microbial sources and sinks controlling the pool of VOCs in the surface ocean and their rates of accumulation. We also consider the magnitude of the VOC pool in the context of much more well-studied carbon cycle processes, including primary and bacterial production. Early evidence suggests a large and constitutive flux of VOCs is derived from photosynthesis and used by diverse marine bacteria as sources of carbon and energy for growth. Seasonal variation in the most abundant VOCs, and new analytical tools that are fueling a rapid pace of discovery of new VOCs in seawater, point to new opportunities for investigations that will explain seawater VOC dynamics in mechanistic terms that account for biology. Integrating this research with remote sensing capabilities and vast ocean genome databases has promise to yield improved predictions of VOC accumulation and sea-air flux.

This review describes the major biological processes that are known that control VOC concentrations in the surface ocean, identifies questions that limit our understanding of marine VOCs, and considers how knowledge about the biological controls on VOCs can be related to satellite remote sensing to advance carbon cycle and climate research. The diversity and amounts of VOCs released from cells change depending on the species and the growth conditions. To quantify seasonal and geographical variation in VOC standing stocks and their fluxes from the ocean into the atmosphere will require the exploration of new approaches, particularly if the goal is to predict fluxes globally from currently available data types. To achieve this goal, it may be necessary to infer aspects of plankton community structure and physiological status from more easily determined properties, such as productivity, water parcel history, and physical and biological forcing.

2. Why do phytoplankton produce VOCs? It's not all about stress

There are several explanations for why phytoplankton produce VOCs. Some VOCs are metabolic end-products, suggesting their production is a regulated response to environmental stressors, including high light (Sinha et al., 2007), nutrient deprivation (Bromke et al., 2013), grazing (Fink, 2007) and viral-induced mortality, temperature

(Yoch, 2002), and ocean acidification (Arnold et al., 2013). For example, the two most well-studied VOCs, isoprene and dimethyl sulfide (DMS), have antioxidant activities (Archer et al., 2010; Sunda et al., 2002; Vickers et al., 2009). Unstressed phytoplankton, growing under balanced conditions, constitutively produce isoprene or DMS. Release increases when phytoplankton cells are shifted from their growth irradiance to higher light intensities (Dani and Loreto, 2017), suggesting these compounds might be regulated by stress responses. VOC production by phytoplankton is commonly light-dependent (Gantt et al., 2009; Halsey et al., 2017; Meskhidze et al., 2015; Shaw et al., 2003), indicating these chemicals are fundamentally associated with photosynthetic metabolism. The relationships of VOC production to diel light cycles have only been described for a few VOCs (Exton et al., 2012; Royer et al., 2016; Sinha et al., 2007). For example,

DMS and methanethiol, both products of dimethylsulfoniopropionate (DMSP) metabolism, sometime exhibit maxima during the daytime (Davie-Martin et al., 2020; Gali et al., 2013; Royer et al., 2016). DMSP is present in high intracellular concentrations and has been attributed roles in osmoregulation, thermal, nitrogen, light, and piezometric stress (Stefels, 2000; Sunda et al., 2002; Zheng et al., 2020), and does not mirror DMS diel production patterns (Gali et al., 2013). Peak DMS concentrations that are coincident with maximum daily irradiance support the idea that DMS is produced by cells because of its antioxidant properties. However, at midday, light energy can easily exceed photosynthetic electron transport capacity, which is consistent with the alternative hypothesis that DMS production could be a strategy to dissipate excess light energy (Stefels, 2000). Indeed, the highly reduced and lipophilic nature of many VOCs make them potentially effective chemicals for protection against photoinhibition. VOC synthesis in principle could be a convenient energy sink from a metabolic perspective because VOCs can diffuse through membranes into the surrounding seawater, obviating the need for active transport.

Recent work suggests that VOCs are not only stress-induced metabolic end-products, but are also intermediates in pathways that can diffuse out of cells (Moore et al., 2020). Many metabolic pathways in central carbon metabolism are associated with VOC production (Schmidt et al., 2015). The total VOC pool within phytoplankton cells

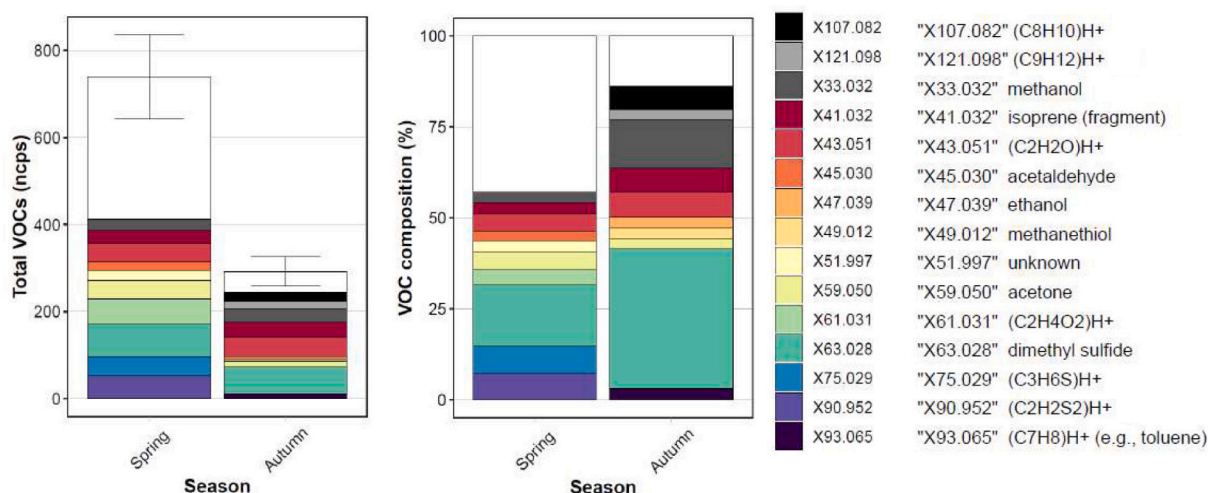


Fig. 1. The top ten most abundant VOCs in the western North Atlantic Ocean in Spring (March, $n = 82$) and Autumn (September, $n = 85$) during the NAAMES campaigns (Behrenfeld et al., 2019). VOCs are shown as normalized counts per second (left panel) and relative composition (right panel). VOCs were detected in surface seawater samples (0.1 l) transferred to dynamic stripping chambers (DSC; Halsey et al., 2017). VOC-free air was passed through the samples at 50 ml min^{-1} for 5 min to strip VOCs in the mass range 30–270 a.m.u., which were detected by a proton transfer reaction time-of-flight mass spectrometer (PTR-MS) using H_3O^+ as the ion source (see Davie-Martin et al., 2020 and Moore et al., 2020). VOCs are colored by their $m/z + 1$ values and either chemical formula or likely tentative compound identifications determined using the GLOVOCs database (Yanez-Serrano et al., 2021). The white sections in the stacked bar charts are all other $m/z + 1$ values in lesser abundances, which contributed about 45% of VOCs in spring and 12% of VOCs in autumn. Reported are $m/z + 1$ values that were at least two standard deviations above levels detected in seawater that was passed through a $0.2 \mu\text{m}$ Sterivex filter prior to being transferred to DSC for measurement by PTR-MS.

has been estimated to be 0.28–5.17% of cell carbon content (Ruiz-Halpern et al., 2014). Cells may have little control over the loss of these low molecular weight metabolic intermediates. For example, acetaldehyde is a central molecule in organic carbon transformations involving carbohydrates, protein, fatty acids, nucleic acids, and aromatic compounds (Lees and Jago, 1978). Although acetaldehyde metabolism has not been elucidated in phytoplankton, it is likely to function as an important hub of central carbon metabolism, similar to plants (Laothawornkitkul et al., 2009). Inherent loss of acetaldehyde from phytoplankton cells, by virtue of its diffusivity, may thus require continuous activity of acetaldehyde-producing pathways to support ongoing central carbon metabolism. Increased flow into a metabolite pool relative to its subsequent enzymatic or chemical transformation will augment the pool, at least temporarily, and facilitate its diffusion out of the cell. Thus, imbalanced phytoplankton growth caused by a suddenly changing environment could be a factor in VOC emissions. Diffusion of VOC intermediates from phytoplankton will also be driven by processes that consume VOCs outside of the cell, establishing concentration gradients. VOC loss terms include microbial consumption, sea-air flux, and other abiotic processes, particularly for reactive VOCs (Heikes et al., 2002; Singh et al., 2003). Microbial VOC uptake is discussed in detail later in this review.

A distinction is made here between VOCs that are metabolic end-products and those that are intermediates. End-products are molecules that are produced by metabolic pathways and either accumulate in cells or are released, whereas intermediates are reactants that are subsequently transformed into other compounds by the cell. End-products include compounds that contribute to maintaining phytoplankton homeostasis (i.e., protection against oxidative stress, release of excess energy, thermal tolerance), secondary metabolites that communicate with, enhance or inhibit other organisms, (i.e. grazer defense; Amavizca et al., 2017; Fink, 2007; Pohnert, 2005; Xu et al., 2017; Zuo et al., 2012), or metabolites that are waste products of metabolism (i.e. DMS, in some cases -Sun et al., 2016). Metabolic intermediates, on the other hand, are required for steps in metabolism, although they may be unintentionally lost by diffusion if they are membrane soluble. In principle, the loss of diffusible metabolic intermediates from a phytoplankton cell would require enhanced photosynthetic activity to refill metabolite pools (Bjornsen, 1988; Moore et al., 2020; Shaw et al., 2003). The distinction between end-products and intermediates is important to understanding the relationships between the biological states of cells, VOC release, and VOC sea-air flux, which we discuss further below.

3. Is the diversity of VOCs related to phytoplankton taxonomy and physiology?

Exploration of the diversity of VOCs produced by phytoplankton is at an early stage. Mass spectrometry technologies are revealing complex mixtures of VOCs present in the ocean and in phytoplankton cultures (Fig. 1; Analytical techniques and some applications being used for monitoring VOCs have been reviewed elsewhere (Mansurova et al., 2018).

In addition to the most well-studied VOCs (i.e., isoprene, DMS, acetaldehyde, acetone, methanol), many other VOCs have been detected, and some are significant contributors to the VOC pool in the surface ocean (Fig. 1). For example, five $m/z + 1$ values corresponding to unique VOCs are produced by all three phytoplankton species shown in Fig. 2, but each of the three species produces compounds that are not produced by the other two. The collections of VOCs produced by algae and soil bacteria appear to be related to taxonomy (Choudoir et al., 2019; Kuntzel et al., 2018; Steinke et al., 2018). Of 32 VOCs measured in five *Symbiodinaceae* coral endosymbionts, six were produced by all species (Lawson et al., 2019). Dani and Loreto (2017) suggested that the shared antioxidant properties of isoprene and DMS obviate the need for individual phytoplankton species to produce both chemicals in high amounts. Haptophytes and dinoflagellates are strong DMS producers and green algae, diatoms, and cyanobacteria are strong isoprene

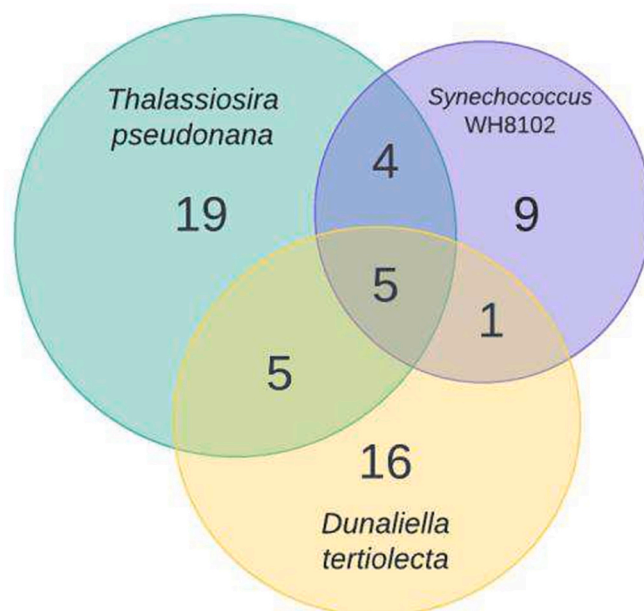


Fig. 2. Venn diagram of numbers of detected $m/z + 1$ values (corresponding to unique VOCs) produced by different phytoplankton species. Phytoplankton cultures were growing in nutrient replete $f/2 + Si$ medium in exponential phase under constant moderate light intensity ($\sim 50 \mu E$). Cultures (0.1 l) were transferred to dynamic stripping chambers and VOC-free air passed through the samples at 50 ml min^{-1} for 5 min to strip VOCs in the mass range 30–270 a.m.u. from cultures for detection by PTR-MS using H_3O^+ as the ion source (as in Moore et al., 2020). $m/z + 1$ values that were at least two standard deviations above levels detected in $f/2 + Si$ artificial seawater medium are reported.

producers (Meskhidze et al., 2015). Several halogenated VOCs and aromatic hydrocarbons are produced by distantly related phytoplankton, including the abundant cyanobacteria, *Synechococcus* and *Prochlorococcus* sp. (Colomb et al., 2008; Lovelock and Maggs, 1973; Rocco et al., 2021).

The types and amounts of VOCs produced by phytoplankton depend on the physiological states of cells. Methanol and halogenated VOCs appear to be produced during distinct phases of phytoplankton growth and senescence (Colomb et al., 2008; Lim et al., 2018; Mincer and Aicher, 2016). Short chained alkanes and alkenes that may be products of lipid oxidation were observed in phytoplankton cultures during their decay (McKay et al., 1996). Density-dependent production of some aldehydes points to a potential role in regulating diatom life cycles (Pohnert, 2005). Because they are easily diffusible, VOCs would seem to be good signal molecules (Saha and Fink, 2022), although such roles in phytoplankton have been challenging to prove conclusively.

The relevance of VOC production by non-growing plankton (i.e., cells in stationary phase) to sea-air emissions has not been established. Phytoplankton rarely enter senescence, especially in the open ocean. Throughout much of the yearly cycle phytoplankton growth is tightly coupled to loss by predator grazing activity. Phytoplankton growth rates accelerate during bloom events, but bloom demise can occur even before cells attain their maximal growth rates (Behrenfeld, 2010; Behrenfeld and Boss, 2018). Senescence typically occurs when cells become starved for needed resources. For example, phytoplankton can become trapped in darkness following physical transport below euphotic mixed layers, resulting in a loss of energy from photosynthesis and reliance on respiration, leading eventually to senescence and the release of decomposition products.

Most controlled studies on VOC production have been conducted using traditional batch culture approaches, where the onset of stationary phase indicates growth has ceased because one or more nutrients have become limiting. The abrupt shifts in physiology observed in laboratory

cultures are unusual in the surface ocean. Studies on VOC production that mimic nutrient limited growth through use of semi-continuous or continuous culture approaches more closely mimics realistic nutrient availability and phytoplankton growth rates. During the spring-summer transition, as nutrients become increasingly depleted, and light intensity increases in the surface mixed layer, phytoplankton continually acclimate by altering pigment content and Calvin cycle activity (Halsey and Jones, 2015). Even during periods of severe nutrient limitation phytoplankton are in balanced growth, which is also true of exponential phase cell cultures. In central gyres where nitrogen concentrations can be $<1 \mu\text{M}$ and growth is fueled by regenerated nutrients, phytoplankton growth rates are ca. one division per day (Christie-Oleza et al., 2017). On average, phytoplankton community growth rates vary about 10-fold (0.14 to 1.4 divisions per day) depending on season and geography (Fox et al., 2020). The changing distributions of photosynthetic energy through different metabolic pathways that occur as a function of phytoplankton growth rate (Halsey et al., 2012; Halsey et al., 2010; Halsey et al., 2013) suggest patterns of VOC production by phytoplankton might also be functions of growth rate.

Although phytoplankton are thought to be the primary source of most VOCs, there are other processes that release VOCs. Heterotrophic bacteria release VOCs during degradation of dissolved organic matter. DMSP metabolism by marine bacteria releases DMS or methanethiol depending on the catabolic pathway expressed (Moran and Durham, 2019; Sun et al., 2016). DMS and methanethiol can be further metabolized by bacteria or react with light and DOM, forming non-volatile sulfur compounds (Kiene and Linn, 2000). Acetone is released during amino acid degradation by bacteria (Nemecek-Marshall et al., 1995), and it is reasonable to expect that other VOCs are released during the breakdown of organic matter, as in the case of monoterpene production observed in soil and decomposing litter (Leff and Fierer, 2008; McGenity et al., 2018; Wagner et al., 1999).

Ultraviolet (wavelengths $<365 \text{ nm}$) photochemical degradation of colored DOM (cDOM) is an important source of carbonyl VOCs (e.g., formaldehyde, acetaldehyde, and acetone) (de Bruyn et al., 2011; Kieber et al., 1990; Mopper and Kieber, 1991). Photochemical production of acetaldehyde and acetone can sometimes account for up to 68% and even 100% of total production of those compounds, respectively (Dixon et al., 2013). Photochemical degradation of the complex organic matter in the sea surface microlayer produces volatile alkanes, alkenes, alcohols, ketones, and aldehydes (Ciuraru et al., 2015). The character of the sea surface microlayer is discussed in more detail later in this article. The relative contributions to VOC production by direct phytoplankton production, bacterial production, and cDOM photodegradation are poorly characterized. Experiments that are specifically designed to account for one or more of these processes are important to understanding VOC cycling and the conditions leading to VOC accumulation in the surface ocean.

4. The balance of the VOC pool

Concentrations of VOCs in the surface ocean are controlled by the balance between biological and abiotic process. VOC production, mainly by phytoplankton, and subsequent VOC consumption by bacteria, are the most important biological processes. Many VOCs are known carbon nutrients for bacterial oxidation. For example, acetaldehyde, methanol, acetone, and isoprene are consumed by the ubiquitous marine heterotrophic bacteria, SAR11, with some VOCs supporting biomass accumulation and others supporting energy (ATP) generation through oxidation of VOCs to CO_2 (Moore et al., 2020; Moore et al., 2022; Sun et al., 2011). Bacteria capable of oxidizing isoprene (Dawson et al., 2021; Simo et al., 2022) are responsive to hydrocarbon production in marine environments, and some marine bacteria appear to have the capacity to degrade less volatile long-chained n -alkanes (Love et al., 2021). These microbial VOC transformations can create VOC cycles (Giovannoni et al., 2019; Halsey et al., 2017), that are recognized as having an important role in

mediating sea-air fluxes (Beale et al., 2015; Dixon et al., 2011a; Dixon et al., 2013; Sargeant et al., 2016). VOCs are a special component of the total pool of dissolved organic compounds (DOC) in the surface ocean, but VOCs cannot be captured in DOC measurements because the acidification and combustion techniques used to quantify DOC remove the volatile molecules. Recognition that VOC cycling is active, and potentially rapid, is raising new questions about the magnitude of the VOC pool in the surface, and the relative influences of bacterial consumption, chemical transformations and physical loss through sea-air transfer. Biological controls on in-water VOC concentrations are poorly constrained, with few measurements of VOC production ($\text{VOC}_{\text{production}}$) and biological consumption of VOCs ($\text{VOC}_{\text{biol_consumption}}$) in seawater.

At steady state, the balance of the VOC pool is described by Eq. 1.

$$\text{VOC}_{\text{production}} = \text{VOC}_{\text{biol_consumption}} + \text{VOC}_{\text{chemical_oxidation}} + \text{VOC}_{\text{sea_air_exchange}} + \text{VOC}_{\text{mixing}} \quad (1)$$

where $\text{VOC}_{\text{chemical_oxidation}}$ are abiotic reactions with oxidants (Warneck, 2003a), $\text{VOC}_{\text{sea_air_exchange}}$ is the VOC flux from the ocean into the atmosphere and $\text{VOC}_{\text{mixing}}$ is turbulent-driven diffusion into the deeper ocean. Similar to the VOC production side of the equation, there is much to learn about the rates, physiologies, and taxonomic relationships associated with biological VOC consumption. Simo et al. (2022) showed that biological consumption of isoprene increases exponentially with isoprene concentration. They next calculated isoprene production using the isoprene biological consumption rate and rate constants for the abiotic terms in Eq. 1. The resulting positive relationship between isoprene production and surface chlorophyll concentrations agreed with other work in the North Atlantic Ocean (Davie-Martin et al., 2020). However, the values reported in those studies highlight the considerable discrepancies in the measured rates of isoprene production, as well as more generally $\text{VOC}_{\text{production}}$, reported to date in the literature.

5. Possible explanations for the large range in reported VOC production rates

$\text{VOC}_{\text{production}}$ values for acetaldehyde, acetone, DMS and isoprene are commonly in the range of -0.23 to 2 nmol L h^{-1} and -19 to 8 nmol L h^{-1} for methanol (Dixon et al., 2013; Meskhidze et al., 2015; Milne et al., 1995; Royer et al., 2016). Negative $\text{VOC}_{\text{production}}$ is caused by VOC losses that outpace production and can only occur when the VOC pool has sufficiently accumulated prior to the measurement. Thus, temporary imbalances in the VOC cycle, caused by decoupling of $\text{VOC}_{\text{production}}$ and $\text{VOC}_{\text{biol_consumption}}$ and/or abiotic loss terms will augment or deplete the VOC pool. Most of the $\text{VOC}_{\text{production}}$ values summarized above were determined by measuring in water VOC concentrations before and after bottle incubations of varying duration (2–48 h) (Dixon et al., 2013; Meskhidze et al., 2015; Simo et al., 2022). Incubations in the light should yield a $\text{VOC}_{\text{production}}$ value that accounts for the biological activities, which for the most well-studied VOCs are the largest terms (Dixon et al., 2013; Simo et al., 2022). Incubations in the dark yield the fraction of the VOC pool lost to $\text{VOC}_{\text{biol_consumption}}$.

A very different approach to measuring $\text{VOC}_{\text{production}}$ yielded values for acetaldehyde, acetone, DMS and isoprene that were -3.5 to 43 nmol L h^{-1} and -153 to $859 \text{ nmol L h}^{-1}$ for methanol (Davie-Martin et al., 2020). These values encompassed those given in the above paragraph and previously reported, but the 10–100-fold range of these values is much greater. In contrast to static bottle incubations, Davie-Martin and colleagues contained seawater samples collected in the North Atlantic Ocean in ‘dynamic stripping chambers’ (DSCs) with VOC-free air continuously flowing through the chambers at a high rate as fine bubbles. This apparatus design is intended to ‘strip’ VOCs from the water sample continuously. In the DSC approach the steady state VOC concentration in the stripping gas exiting the chambers, multiplied by the rate of gas flow and integrated over time, provides a measure of net VOC production. This approach measures instantaneous VOC production in a

quasi-steady state wherein the stripping gas is competing with biological VOC consumption, whereas bottle incubation methods measure the steady state balance between production and consumption over a protracted incubation period. DSC approaches typically have higher temporal resolution than headspace approaches (up to five – 1 h incubations per day compared to incubation times up to 2 d). The shorter incubations that are typical of DSC measurements in principle make it possible to capture variation in VOC production driven by short term changes in metabolism (Sun et al., 2016). A potential drawback of the DSC approach is the high rate of air-flow needed to achieve the steady-state conditions for the measurement, which could impose stress on plankton.

Variability in $VOC_{production}$ values reported in the literature could also point to VOC sinks that are not included on the right side of Eq. 1 and are yet to be identified. One such potential sink is the rich and biologically active sea surface microlayer defining the ocean-atmosphere interface. The sea surface microlayer, the surface-most millimeter of the ocean, consists of a specialized microbial community that shapes the layer's chemical composition. Both the microbial and chemical composition of the microlayer are fundamentally distinct from the bulk seawater immediately below (Kurata et al., 2016; Michaud et al., 2018). Surface tension stabilizes the sea surface microlayer and are hypothesized to limit gas (including VOCs) sea-air flux (Wurl et al., 2016). The sea surface microlayer was depleted of VOCs in the North Atlantic Ocean (Davie-Martin, pers. commun.), but whether depletion was caused by microbial VOC uptake, chemical or photo-oxidation, or enhanced emission is not known. A bacterial community in the sea surface microlayer that is adapted to VOC uptake is reasonable to expect, considering the constitutive production and diffusive delivery of VOCs from the sunlit zone below and photochemically induced VOC production from surfactants within the sea surface microlayer (Ciuraru et al., 2015; Mungall et al., 2017).

6. Are VOCs an important component of the marine carbon cycle?

Marine cycling of VOCs, and indeed all labile organic compounds, is inherently challenging to quantify because of their rapid turnover times (Table 1), the diversity of chemicals making up the metabolite pool, and the sparse information available about rates of microbial metabolism. In this section we aim to place into context the magnitude of the VOC pool relative to the carbon cycle. Table 2 gives estimates of the contribution of VOCs to key carbon stocks in the surface ocean: phytoplankton cell carbon, photosynthetically fixed carbon, and labile dissolved organic

Table 1

Turnover rates of commonly studied VOCs in comparison to labile dissolved organic matter (LDOC).

Compound	Turnover rate (d ⁻¹)	Season/region	Reference
LDOC	>1	Global average	(Carlson and Hansell, 2015) (Beale et al., 2015; de Bruyn et al., 2017; Dixon et al., 2013; Mopper and Stahovec, 1986) de Bruyn et al., 2021 (Jian et al., 2017)
Acetaldehyde	0.028–2.1	Open ocean, coastal, estuarine	(Simo et al., 2022)
DMS	0.54–1.2	China Sea Tropical Pacific, Mediterranean, Atlantic, Southern Ocean	(Dixon et al., 2011b)
Isoprene	1.4–15.5	Coastal shelf, open ocean	(Beale et al., 2015; Dixon et al., 2013)
Methanol	7–33	North Atlantic	
Acetone	16 / 165	Winter / Summer	

Table 2

Contribution of VOCs to key marine carbon cycle stocks.

Carbon pool	Pool description	VOC pool (% of carbon pool)	Culture studied or approach	Reference
Phytoplankton cell carbon	Phytoplankton cell biomass	0.25–5.18	<i>Prochlorococcus marina</i> <i>Synechococcus</i> sp. <i>Micromonas pusilla</i> <i>Phaeodactylum tricornutum</i> <i>Dunaliella</i> sp. <i>Phaeocystis</i> sp. <i>Amphidinium carterae</i> <i>Melosira nummuloides</i> <i>Thalassiosira</i> sp. <i>Thalassiosira pseudonana</i>	(Ruiz-Halpern et al., 2014)
Photosynthetic carbon fixation	Total carbon produced through photosynthesis (gross carbon fixation)	18–20		(Moore et al., 2020)
LDOC	Labile dissolved organic carbon in the surface ocean	30–40	Determined as the exchangeable organic carbon component of DOC	(Dachs et al., 2005; Ruiz-Halpern et al., 2010)

carbon (LDOC). Much more is known about LDOC accumulation and depletion in the surface ocean (Carlson and Hansell, 2015) than the dynamics of the VOC pool (e.g., turnover and composition).

Because phytoplankton are believed to be the main producers of VOCs, an important question in marine ecology is, “How much of the carbon fixed by photosynthesis is lost as VOCs?” Recent measurements suggest the fraction of photosynthesis lost as VOCs is an important and variable component of carbon fixation, and may compose up to 20% of gross photosynthetic carbon production. Moore et al. (2020) observed that CO₂ fixation rates in the model diatom, *Thalassiosira pseudonana*, were 20% faster when cultured with SAR11 bacteria. They speculated that intracellular VOCs that diffused out of the diatom were consumed by SAR11, creating a flux sufficiently strong to require the diatom to increase CO₂ fixation rates to replenish intracellular pools. This idea was confirmed when a nearly identical result was obtained by putting a hydrocarbon trap in a gas loop circulating through a culture of pure *T. pseudonana*.

That 20% of photosynthetically fixed carbon could be transferred to bacteria in the form of VOCs suggests that the answer to the question posed in the heading of this section is emphatically, “Yes, VOCs are a major component of the marine carbon cycle.” Net VOC production measured in the North Atlantic Ocean was used to estimate the fraction of gross carbon production that was lost from phytoplankton cells through VOC production. We summed the net VOC production rates for the seven VOCs measured during the North Atlantic Aerosols and Marine Ecosystem Study (NAAMES; (Behrenfeld et al., 2019; Davie-Martin et al., 2020) to determine the net production rate of the VOC pool (VOC_{pool}) and compared it to other well-studied carbon cycling processes (Fig. 3). The absolute values of VOC_{pool} were generally larger than net particulate carbon production and lower than gross carbon production. Negative VOC_{pool} in March and November show VOC_{biol} consumption outpacing $VOC_{production}$, at least during the short time-scales of the incubations used (1 h). Recall that negative VOC_{pool} necessitates VOC accumulation prior to the measurement, which could result from enhanced production or interrupted consumption. The seasonality

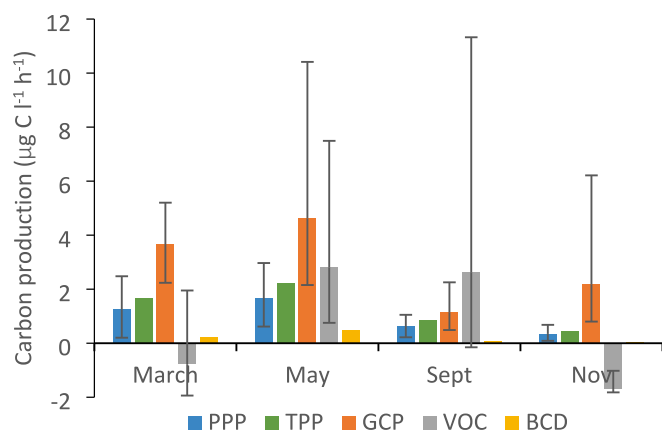


Fig. 3. VOC production rates (grey bars) compared to key carbon cycle properties in the North Atlantic Ocean from four one-month cruises during the North Atlantic Aerosols and Marine Ecosystem Study (NAAMES; Behrenfeld et al., 2019). Net particulate production (PPP, blue bars); Particulate and dissolved organic matter production (TPP, green, calculated by considering dissolved organic matter production is 25% of TPP; Moran et al., 2022); Gross carbon production (GCP, orange); Bacterial carbon demand (BCD, yellow, values are 0.06 in Sept and 0.04 in Nov) (Baetge et al., 2021). Bars give the mean values and error bars give the range of data (data ranges not available for BCD). Detailed methods for PPP are in Fox et al., 2020 and for VOC production rates are in Davie-Martin et al., 2020. VOC production rates were summed for acetaldehyde, acetone, acetonitrile, DMS, isoprene, methanethiol, and methanol. GCP was determined using 2 h ^{14}C uptake incubations in a temperature controlled photosynthetron (Halsey et al., 2010; Lewis and Smith, 1983). Samples were filtered, acidified and degassed prior to measurement using a scintillation counter. Photosynthesis-irradiance (PE) parameters were derived using a hyperbolic tangent model (Jassby and Platt, 1976) and used with average daily photosynthetically available radiation (PAR) for the mixed layer to calculate GCP. Total numbers of PPP and GCP measurements: (month/n), Mar/6; May/7; Sept/9; Nov/9. Total number of VOC production measurements: (month/n), Mar/56; May/50; Sept/74; Nov/14. Total number of BCD measurements: (month/n), Mar/5; May/11; Sept/11; Nov/6. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

exhibited by VOC_{pool} suggests an active source of VOCs supporting $\text{VOC}_{\text{biol.consumption}}$ during the winter and early spring. These VOCs may be supplied directly from phytoplankton growth, transported to the surface ocean from deeper water where bacterial degradation of DOM released VOCs, or from atmospheric deposition; for example methanol is the most abundant VOC in the troposphere (Singh et al., 2003). The upper ranges of VOC_{pool} highlight the potential for periodic VOC bursts supporting bacterial production and atmospheric emissions, which could induce large particle formation events in the marine boundary layer (Wen et al., 2006). Low but positive values of VOC_{pool} are either indicative of very low rates of VOC production by their primary producers (phytoplankton) or tight coupling of production and consumption rates.

7. The magnitude of the VOC pool

A recent report gave a careful accounting of the components of LDOC relative to classical ecosystem descriptors of carbon production in the ocean (Moran et al., 2022). That analysis agreed with previous estimates that LDOC supports heterotrophic oxidation of at least half of the net primary production in the ocean (Ducklow, 1999; Williams et al., 2000). The authors came to that conclusion using existing literature and constraining the sources of LDOC and the bacterial demand for LDOC. Their analysis highlighted the variability in reported LDOC sources and sinks caused by seasonal and geographic influences, methodological differences, and limited data. Notably, VOC cycling has not been considered by analyses such as these, that addressed the magnitude of rapidly-

cycled biological carbon turnover, because, as pointed out above, LDOC measurements underrepresent these compounds. Similar to the LDOC pool, the VOC pool in the surface ocean is subject to seasonality and latitudinal gradients (Yang et al., 2014).

The VOC pool appears to be an important but largely unrecognized source of the labile organic compounds fueling bacterial production (BP, in units per time) in the surface ocean. VOCs are known carbon nutrients for marine bacteria, but the biochemistry of their metabolism has been determined for only a small subset of VOCs. The most well-studied bacterial VOC oxidizers in the oceans are methylotrophs and methyl-ovores, which are discernable by genetic signatures. Methylotrophs require one-carbon compounds for assimilation into biomass and cannot grow without them, whereas methyl-ovores use one-carbon compounds to produce energy, but do not assimilate these compounds into biomass. Methylotrophs and methyl-ovores are an important sink for methanol produced by phytoplankton (Dinasquet et al., 2018; Halsey et al., 2012; Sun et al., 2011) and sourced from the atmosphere (Singh et al., 2003). In addition to methanol, these organisms metabolize an array of other one-carbon compounds, including formaldehyde, formate, and methylamines. Other low molecular weight VOCs, including acetaldehyde, acetone, cyclohexanone, and isoprene, are known carbon nutrients for abundant taxa of marine bacteria (Alvarez et al., 2009; Halsey et al., 2017; Moore et al., 2020; Moore et al., 2022). The gene initiating acetone and cyclohexanone oxidation is widely distributed across taxonomically diverse groups of marine bacteria (Moore et al., 2022). Similarly, the genetic capacities for bacterial degradation of the important sulfur containing compounds, DMS and methanethiol, have been elucidated (Carrión et al., 2015; Carrión et al., 2019; Eyice et al., 2018) and facilitate connections between genomic signatures and spatial and temporal variations.

8. Harnessing the power of satellite remote sensing to resolve VOC emissions

The current catalogue of remotely sensed data provides rich information about plankton communities that is germane to understanding VOC sea-air emission (Booge et al., 2016; Neukermans et al., 2018). Table 3 provides examples of satellite tools that can characterize phytoplankton abundances, distributions, and physiologies, and patterns in light and nutrient conditions in the surface ocean that can be used to predict shifts in the taxonomic composition and cell size distributions of planktonic communities (Behrenfeld et al., 2021), which may ultimately give rise to VOC accumulation or depletion. Current studies attempting to use satellite data to predict VOC concentrations and their potential for sea-air emission rely on chlorophyll and DOC concentrations, which are proxies for phytoplankton and CDOM, respectively. These stocks, combined with surface ocean properties such as irradiance, sea surface temperature, and/or derived properties such as net primary production, have yielded correlations with VOC production (Broadgate et al., 1997; Dani et al., 2017; Davie-Martin et al., 2020; Gantt et al., 2009; Halsey et al., 2017; Iyadomi et al., 2016; Royer et al., 2016; Simo et al., 2022; Sinha et al., 2007) and DMS concentration (Anderson et al., 2001), but predicting $\text{VOC}_{\text{sea-air flux}}$ and even the direction of the flux using selected ocean properties is challenged by wide spatial and temporal variability in standing stocks of VOCs (Exton et al., 2012; Li et al., 2021).

Knowledge of phytoplankton community composition became more important to the prediction of VOC pools when it was discovered that some components of VOC emissions are taxon-specific (Dani and Loreto, 2017; Fig. 2). A variety of approaches have emerged to describe phytoplankton community composition from satellite remote sensing. Community descriptions can be based on cell size distributions, taxonomies, or phytoplankton functional groups. A “users guide” was developed to assist oceanographers and ecologists in selecting satellite-based algorithms best suited for their purposes (Mouw et al., 2017). The hyperspectral ability of NASA’s upcoming Plankton Aerosol Cloud and

Table 3

Surface ocean biological and geophysical properties retrievable by remote sensing, or using models that assimilate in situ observations, that can provide information about the equilibrium-disequilibrium state of the plankton community and likelihood for VOC sea-air emissions.

Surface ocean property	Relationship to surface ocean equilibrium/disequilibrium	Remote sensing tool
Chlorophyll	Proxy for phytoplankton biomass, sensitive to phytoplankton physiology	Ocean color
Irradiance	Light stress or large and rapid changes in light intensity	Satellite derived photosynthetically active radiation, “daily PAR product” (Frouin et al., 2018)
Ultraviolet radiation	Light stress and photodegradation of dissolved organic matter and CDOM	Derived from above surface irradiance at 324 nm (Frouin et al., 2018)
Surface mixed layer depth	Change in geophysical surface ocean	Derived from ocean circulation models (Yan et al., 1991; Zhang and Yan, 2014)
Ocean surface turbulence	Changes in geophysical ocean surface state	Derived from small eddy model (Esters et al., 2017)
Buoyancy-driven convection	Stability of surface ocean layer	Buoyancy flux (Cronin and Sprintall, 2001)
Wind speed	Changes in geophysical surface ocean state	Microwave radiometers, radar, and lidar
Particle size distribution	Decreasing slope signals bloom termination by zooplankton grazing	Particle size distribution slope (Behrenfeld et al., 2021; Kostadinov et al., 2009)
Phytoplankton biomass	High biomass associated with bloom peaks	Particulate backscattering coefficient, Lidar (Behrenfeld et al., 2005; Fox et al., 2022; Graff et al., 2015)
Phytoplankton physiology	Light or nutrient stress	Derived from the ratio of chlorophyll to phytoplankton carbon (Behrenfeld et al., 2005; Behrenfeld et al., 2016)
Primary production	Growth efficiency of phytoplankton assessed by gross-to-net primary production	Derived remote sensing products (Behrenfeld et al., 2005; Fox et al., 2020; Silsbe et al., 2016; Westberry et al., 2008)
Phytoplankton growth rate	Growth rate dependence of VOC composition	Derived remote sensing product (Behrenfeld and Boss, 2018; Fox et al., 2020)
Phytoplankton loss rate	Increasing loss rate signals bloom termination by viral or grazing activities	Derived remote sensing product (Behrenfeld, 2010; Behrenfeld and Boss, 2018)
Phytoplankton accumulation	Periods of rapid growth cause VOC production to outpace consumption	Particulate backscattering coefficient, Lidar (Behrenfeld and Boss, 2018)
Iron stress	Micronutrient stress	Chlorophyll fluorescence (Behrenfeld et al., 2009)
Phytoplankton community composition	Presence of key VOC producers; Changing composition can indicate shifts in ecosystem state; Presence of pigment degradation products	Absorption spectrum, multispectral ocean color, hyperspectral ocean color; derived from absorption and backscatter (Cael and Boss, 2017; Carpenter et al., 1986; Cotti and Bricaud, 2006; Fox et al., 2022; Lubac et al., 2008; Spooner et al., 1994)
CDOM, non-algal particles	Accumulation of detritus, dissolved organic matter and other particles subject to photodegradation	Non-algal component of spectral absorption spectrum; light scattering and backscattering, lidar (Lee et al., 2002; Neukermans et al., 2018; Siegel et al., 2002; Zhou et al., 2022)

ocean Ecosystem (PACE) mission promises higher resolution characterization of the phytoplankton community (Werdell et al., 2019). In anticipation of PACE, progress has been made to leverage pigments and their absorption features to estimate community composition (Catlett and Siegel, 2018; Chase et al., 2017). However, the factors driving VOC accumulation and sea-air emission are attributable not only to the diversity of phytoplankton cells in the system, but also phytoplankton time-dependent responses to geophysical and biological drivers, and the status of co-occurring bacterial populations that consume VOCs very actively. Combining satellite tools (Table 3) with our developing understanding of the complex factors controlling the VOC pool is a goal that will require interdisciplinary efforts.

Evidence suggests that conditions leading to positive $VOC_{sea,air}$ occur when the balance of biological VOC production and consumption is disrupted, such that $VOC_{production} > > VOC_{biol,consumption}$. Such conditions could occur over timescales ranging from hourly to daily to seasonal (Fig. 4). Below, examples are described of ecosystem shifts that could lead to states of surface ocean disequilibrium and VOC accumulation. On hourly timescales phytoplankton experience rapid shifts from low to high light as a consequence of deep mixed layer mixing, changing cloud cover (e.g., Omand et al., 2021) or mixed layer shoaling following a seasonal storm event (e.g., Behrenfeld et al., 2019). These conditions can induce transient stress responses (Diaz et al., 2021), in principle causing upshifts in phytoplankton VOC production that temporarily outpace consumption by the bacterioplankton community. Changes in daily integrated light or nutrients induce phytoplankton to alter their physiologies through a series of enzymatic and redox-regulated shifts (Geider et al., 1997). These shifts are collectively referred to as photoacclimation and typically require 1–2 days to register as changes in phytoplankton growth rate (MacIntyre et al., 2002; Penta et al., 2021; Ross and Geider, 2009). Ongoing photoacclimation in the absence of

division is expected to decrease phytoplankton growth efficiencies and is commonly associated with carbon excretion in the form of DOC, but VOCs are also likely to be released. Phytoplankton growth rates can accelerate if top-down pressure (i.e., zooplankton grazing) is relieved (Behrenfeld, 2010). Depending on the rate of positive change in phytoplankton growth rates, VOC production could again outpace consumption by a bacterioplankton community that is increasing in response to phytoplankton community succession and increases in growth substrates, including VOCs. Other events causing surface ocean disequilibrium can last from hours to days and include wind-driven surface ocean mixing during summer months when the surface mixed layer is well-stratified (Penta et al., 2021) and the degradation of phytoplankton blooms by zooplankton grazing and/or viral lysis.

Remote sensing technologies can be leveraged to describe equilibrium and disequilibrium states of the surface ocean that can drive VOC accumulation and emission. The VOC pool in the surface ocean is in equilibrium when $VOC_{production}$ is balanced with the biotic and abiotic loss terms on the right side of Eq. 1. The two terms, VOC_{mixing} and $VOC_{chem,oxidation}$ appear to be relatively constant and small, leaving the critical $VOC_{sea,air}$ term subject to the interplay of the two biological processes. Sea surface temperature and salinity are directly diagnosed by remote sensing, which together with irradiance fluxes modeled from satellite data products (Table 3), are crucial first-order indicators of the physical properties of the surface ocean. Relating surface ocean physics to information on phytoplankton stocks, growth and geochemical activities (Table 3) and in situ VOCs in principle would resolve the influence of these factors on VOC concentrations and emission. Accessing $VOC_{sea,air}$ is a primary goal in understanding ocean-atmosphere interactions that may be best extracted by harnessing remote sensing (Neukermans et al., 2018) to obtain a synoptic view of the factors impacting the balance of VOCs in the ocean.

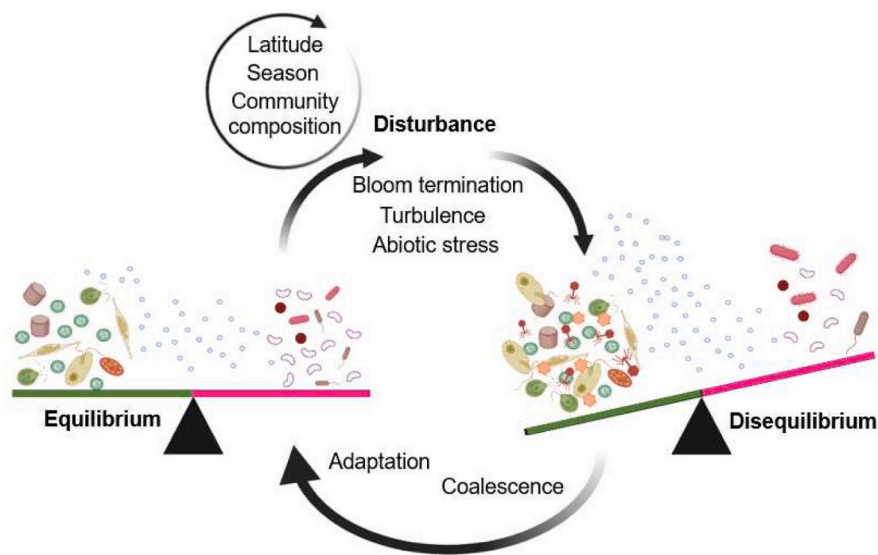


Fig. 4. Surface ocean VOC accumulation is hypothesized to be controlled by the balance of VOC production and consumption. The normal state of the surface ocean is equilibrium (left) and a variety of physical and biological processes can disturb the planktonic community such that VOC production outpaces VOC consumption, leading to VOC accumulation and sea-air emission (arrows leading to the right). Latitudinal, seasonal, and plankton composition influence the temporal and spatial outcomes of disturbance. The balance of VOC stocks is additionally determined by plankton coalescence and adaptive strategies (arrows leading to the left). In both states, VOCs are shown as small bubbles diffusing from phytoplankton above the green side of each see-saw. Heterotrophic bacteria shown above the pink side of each see-saw consume the VOCs. Disturbance leads to VOC accumulation as the plankton communities reassemble to achieve a new equilibrium state. In this figure, disturbance is caused by termination of a phytoplankton bloom by viral and grazer attack. The state of disequilibrium heightens the likelihood for accumulated VOCs to be emitted from the surface ocean into the atmosphere. Figure constructed using bioRender. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

We suggest that the key to assessing surface ocean shifts that will lead to VOC accumulation and emission is to use sequential time series to determine changes in biological and geophysical properties over time. For example, Behrenfeld (2010, 2014) evaluated differences in eight-day resolved satellite backscatter retrievals to disentangle phytoplankton growth and loss terms and identify periods where positive changes in growth rates lead to peaks in biomass (bloom climax). Evaluating time-series data will require careful attention to water mass histories (Brewin et al., 2021; Jonsson et al., 2009; Nencioli and Quartly, 2018) to avoid artefactual shifts in geophysical or biological properties that are associated with advection rather than true shifts that move the plankton community out of equilibrium. The anticipated geostationary satellite mission, GLIMR, will have the potential to resolve variability in surface ocean processes on sub-daily time scales in the Gulf of Mexico (Ocean Process Analysis Lab, n.d.). GLIMR's ability to capture high temporal resolution (up to six times during daylight hours) may be needed to capture transient disequilibrium states. The fleet of Biogeochemical-Argo (Bio-Argo) floats provide an important technology to help bridge a range of time and space scales, including vertical axis (depth), that may be crucial to discovery of the combination of interacting factors that result in VOC accumulation (Claustre et al., 2020; Claustre, 2010). Depending on the sensors carried on the Bio-Argo floats, increased resolution of key properties, including oxygen, nitrate, pH, and chlorophyll, may prove valuable to detect shifts in ecosystem equilibrium.

9. Conclusion

The discovery that many marine bacteria oxidize VOCs changed our perspective on ocean VOC biology and air/sea transfer. Active biological uptake pathways in heterotrophic bacteria indicate that VOC production, most of which is probably due to phytoplankton, represents a significant carbon and energy resource that consumer cells (heterotrophic microbes) have evolved to use, causing rapid VOC turnover (Table 1). It appears that VOCs are like many other common labile organic carbon compounds in the ocean: highly produced and rapidly consumed, with competition among consumers for VOC resources holding standing VOC stocks at low concentrations. Recent findings also indicate that phytoplankton may increase VOC production in response to consumer activity, which could increase the dynamic range of the flux through VOC

cycles without causing a major change in standing stocks of VOCs.

If VOC standing stocks are determined by a balance between production and consumption, then plankton community equilibrium becomes an important factor determining standing VOC stocks and rates of sea-air transfer. Our understanding of plankton community diversity has advanced greatly in recent decades - we now know that community assembly is very finely tuned to ocean conditions but also is susceptible to perturbations caused by ocean mixing, currents, weather and biological factors, such as predation. Thus, plankton community disequilibrium could exert as much or more control over standing stocks than gross rates of VOC production. Supporting this perspective, Davie-Martin et al. (2020) observed that that net VOC production in the North Atlantic varied between negative and positive values, as would be expected if community disequilibrium sometimes caused consumer capacity to exceed rates of VOC production.

Direct measures of plankton (phytoplankton and bacterioplankton) community structure are not practical for predicting sea-air VOC fluxes on a global scale, but it may be possible to predict plankton community disequilibrium from other data products, for example the first derivative of productivity and community coalescence estimated from physical mixing. It is likely that there is a relaxation coefficient that describes how fast consumers respond to excess supply, and that coefficient is likely to be more rapid than a community's relaxation to equilibrium composition, because physiology is plastic. These ideas need to be tested by creating community disturbances and measuring VOC production rates. Then appropriate data products need to be designed and tested for their potential to predict actual measurements of surface water VOC concentrations. Rather than trying to predict VOC surface water concentrations as a continuous variable, it might be more tractable to first attempt to predict the state of the systems as net positive or negative VOC production, and perhaps assign high or low states for each. The physics of air-sea transfer is another complex problem that can be treated separately.

10. Summary of major points

- VOCs once were thought of as products of photochemistry but many now are known to be produced actively by phytoplankton metabolism.

- The introduction of new mass spectrometry techniques led to the discovery that many known and unknown VOCs contribute to the VOC pool in the surface ocean
- Many pathways for VOC catabolism by marine heterotrophic bacteria were recently discovered.
- A new view emerged of VOC geochemical cycles in which standing stocks in the ocean surface are determined by equilibrium between production and consumption, suggesting the hypothesis that plankton community disturbances caused by physical and biological events can result in net changes in VOC flux across the sea-air interface.
- VOC sea-air flux prediction from satellite data likely will require a layered approach that uses a variety of complex data products, including water parcel history, and deep transfer learning approaches to predict the composition and state of equilibrium of surface plankton communities and assign VOC flux likelihoods.
- The hypothesis that disequilibrium caused by perturbation drives VOC sea-air flux should be tested experimentally by simulating plankton community disturbances in a framework of synoptic measurements that mirror products that can be remotely sensed or retrieved from ocean metadata.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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