CHAPTER

12

The volatile organic carbon component of dissolved organic matter in the ocean

Kimberly H. Halsey, Vaishnavi G. Padaki, and Stephen Giovannoni

Department of Microbiology, Oregon State University, Corvallis, OR, United States

OUTLINE

Biogeochemistry of Marine Dissolved Organic Matter
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12.1 Introduction

Awareness of volatile organic compounds (VOCs) in the ocean has shifted from sparse information about a handful of chemicals to an appreciation that they are an important fraction of the rapidly cycled marine organic carbon pool and recognition that complex abiotic and biotic processes give rise to this diverse and pervasive collection of molecules. VOCs are low molecular weight chemicals with high vapor pressures and sufficiently large diffusion coefficients to escape from cells and be emitted from a dissolved state in the ocean into the atmosphere as gases. These chemical properties make them challenging to study individually or collectively as a bulk pool. New technologies have expanded the range of VOCs detected in the oceans from short-chained alkanes and alkenes (Swinnerton and Linnenbom, 1967) to an array of volatile organic sulfur, nonmethane hydrocarbon, halogenated and oxygenated VOCs. Identification of new VOC species in marine systems continues alongside research on their roles in primary production, trophic interactions, carbon cycle and climate science, and natural product and alternative energy discovery.

VOC emissions from the ocean into the atmosphere have important impacts on atmospheric chemistry and climate. In the atmosphere, VOCs can condense with each other and with existing particles to form secondary organic aerosols (SOA; Carpenter et al., 2012; Gantt et al., 2009; O'Dowd et al., 1999). SOA contribute to cloud formation and, thus, to precipitation and Earth's albedo (Charlson et al., 1987; Lana et al., 2011). The chemical reactivity of many VOCs can also deplete the hydroxyl radical, OH, a vital reactant in methane removal and maintenance of stratospheric ozone (Crutzen, 1988; Lelieveld et al., 2008).

The ocean serves as both a source and sink for VOCs (Dachs et al., 2005; Jurado et al., 2008; McKay et al., 1996; Ruiz-Halpern et al., 2010). Plankton are the primary source of most VOCs in the ocean, but photochemical production of VOCs in the surfactant-enriched sea-surface microlayer (Fig. 12.1) is also a significant source of atmospheric VOCs (Brüggemann et al., 2018). Atmospheric deposition into the ocean, especially of some oxygenated VOCs, including methanol and acetone, at times exceeds direct ocean emissions into the atmosphere. These deposition events provide substrates for plankton respiration and may explain why rates of plankton respiration sometimes outpace marine primary production (Duarte et al., 2013). Sea-air flux is controlled by the gradient differential between concentrations of atmospheric VOCs, originating from terrestrial plants or anthropogenic emissions that are transported offshore and VOCs dissolved in the ocean (Fuentes et al., 2000; Guenther et al., 1995; Heikes et al., 2002; Millet et al., 2008, 2010). Atmospheric deposition of VOCs occurs when the surface ocean is undersaturated in VOCs relative to the overlying atmosphere. Whether air-side processes or in-water processes control air-sea flux depends upon the VOC and its chemical reactivity (Warneck, 2003) as well as microbial activities that act upon a wide range of VOCs (Moore et al., 2020; Yang et al., 2014). Table 12.1 gives global estimates of marine VOC emissions and depositions. The importance of biology in driving the direction of VOC flux has gained recognition as the mechanisms involved have become known. The dynamic behaviors of ocean biology and physics acting on VOCs make predicting the magnitude of their emissions, and even their directionality (sea-to-air or air-to-sea), unreliable at this time (Beale et al., 2013; Exton et al., 2012; Li et al., 2021).

Microbial production and consumption drive active VOC cycling in the ocean (Fig. 12.1). Phytoplankton metabolism and micro- and mesozooplankton grazing are the primary sources of VOCs in the ocean. These compounds are biogenic VOCs (BVOCs). An important

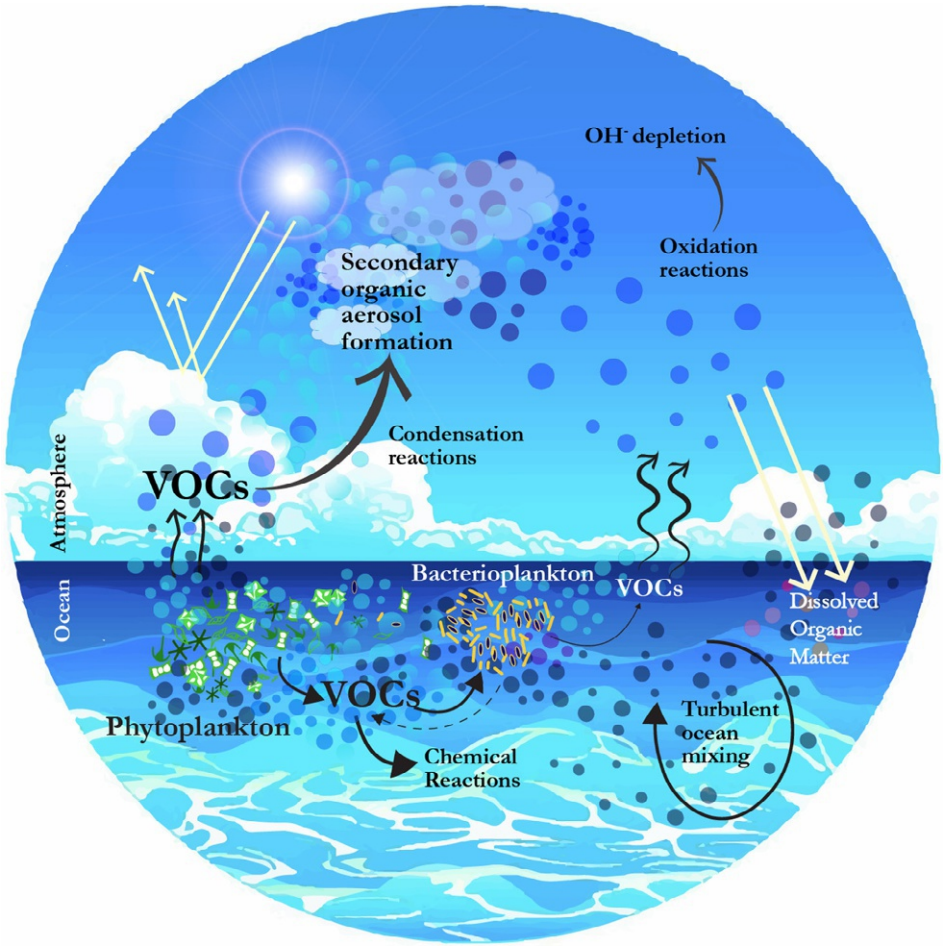

FIG. 12.1 Ocean sources and sinks of volatile organic compounds (VOCs). Phytoplankton (green microbes) are a major source of marine VOCs. Bacterioplankton (brown microbes) can also release VOCs (dotted arrow), and VOCs are also released from photochemical interactions with dissolved organic matter. The air-sea interface is defined by the sea-surface microlayer and is indicated by the boundary between the ocean and the atmosphere. In the atmosphere, VOCs are involved in oxidation reactions and condensation reactions leading to secondary aerosols that can seed clouds.

secondary source of VOCs is abiotic chemical and photochemical reactions with dissolved organic matter (DOM). VOC production via photodegradation of DOM can sometimes outpace BVOC production (de Bruyn et al., 2011; Dixon et al., 2013). VOC concentrations in the surface ocean are low (pmol L^{-1} to nmol L^{-1}) and appear to be largely maintained by VOC assimilation and oxidation by bacterioplankton (Dawson et al., 2021; Halsey et al., 2017; Rocco et al., 2021; Sun et al., 2011). A key challenge to understanding ocean VOCs is quantifying VOC flux between phytoplankton producers and bacterioplankton consumers. Genomic evidence is accumulating for widespread VOC oxidation by bacteria (Dixon et al., 2011b; Halsey et al., 2012, 2017; Moore et al., 2022; Neufeld et al., 2007; Schäfer et al., 2007; Sun et al., 2011).

TABLE 12.1 Contributions of VOCs to ocean and ocean–atmosphere processes and photosynthetic carbon cycle pools.

VOC pool	Magnitude	Location	Approach/Notes	References
Sea-air VOC emission	$5\,Tg\,C\,y^{-1}$	Global	Large uncertainties due to sparse data and unknown VOCs.	Guenther et al. (1995)
Air-sea deposition	$130–270\,Tg\,C\,y^{-1}$	Global		Goldstein and Galbally (2007)
VOC emission from sea-surface microlayer	$32.5–129\,Tg\,C\,y^{-1}$	Global		Brüggemann et al. (2018)
VOC fraction of dissolved organic carbon in the upper 80 m of the water column	6.7%–67%	Subtropical NE Atlantic Subarctic fjord Antarctic Peninsula	Underestimate because only SOCs quantified.[a] Determined as EDOC: VOCs were purged from samples and trapped in C-free water with $pH < 2$.	Dachs et al. (2005), Ruiz-Halpern et al. (2014), and Ruiz-Halpern et al. (2010)
VOC fraction of photosynthetic carbon fixation	18%–20%		Change in carbon fixation rate between a cultured diatom growing with and without VOC removal by a VOC trap or VOC-using bacteria.	Moore et al. (2020)
VOC fraction of phytoplankton biomass	0.25%–5.18%		Survey of cyanobacteria and eukaryotic phytoplankton.	Ruiz-Halpern et al. (2014)

[a] *SOC, semivolatile organic carbon defined as carbon with low Henry's constants and trapped in acidified water.*

Other VOC sinks, namely sea-air flux and chemical oxidation, are important in atmospheric regulation for the reasons mentioned before, but are insufficient on their own to balance in-water VOC production rates (Beale et al., 2013; Carpenter et al., 2004; Dixon et al., 2013; Heikes et al., 2002; Marandino et al., 2005; Taddei et al., 2009; Williams et al., 2004). Knowledge of VOC turnover in the ocean is not yet able to provide mechanism-based constraints in VOC flux models (Booge et al., 2016; Palmer and Shaw, 2005), and aside from a few chemicals such as the dimethylsulfide, methanethiol, and isoprene, little is known about the metabolism and regulation of VOCs in plankton cells. Concentrations of VOCs in the surface ocean are very low ($pmol\,L^{-1}$ to $nmol\,L^{-1}$) and do not exhibit reliable correlations with any single biological or geophysical property (i.e., chlorophyll, Exton et al., 2012; Li et al., 2021), suggesting more complex interactions at play (Halsey and Giovannoni, 2023). These knowledge gaps are exciting opportunities to explore VOC-mediated biological and environmental interactions and their widely ranging impacts on ocean carbon cycling and climate.

12.2 The chemical nature of VOCs

VOCs are low molecular weight compounds typically having two to 20 carbon atoms, low boiling points, high vapor pressures, and moderate to high hydrophobicity. VOCs are

dissolved gasses in seawater. Dissolved organic carbon (DOC) is the overarching term for organic matter in seawater that passes through glass fiber filters with a nominal pore size of 0.7 μm (e.g., Whatman type GF/F). VOCs are clearly a component of DOC, but VOCs are not accounted for in bulk DOC measurements because volatile chemicals are lost during DOC collection, sample sparging, and analysis. For example, following bulk water collection, VOCs are subject to diffusive loss during each successive water transfer into containers. Vacuum filtration, typically used to remove particles in a bulk water sample, will also remove VOCs, as will acidification, sparging, and combustion steps used to quantify DOC (Spyres et al., 2000; Halewood et al., 2022).

From a carbon mass perspective, the sparse measurements that are available indicate that VOCs might be substantial component of the total pool of organic molecules in the surface mixed layer of the ocean, where most VOC measurements have been made. The few bulk VOC measurements suggest the VOC pool can make up 6.7%–67% of DOC pool but is not accounted for in bulk DOC measurements. VOCs contribute a greater fraction of organic compounds in the Antarctic where DOC is low (Table 12.1; Dachs et al., 2005; Ruiz-Halpern et al., 2010; Ruiz-Halpern et al., 2014). Unlike DOC, there is no consensus on standard methods for measuring the bulk dissolved VOC pool. The VOC pool data before were determined as exchangeable dissolved organic carbon (EDOC) by sparging seawater to equilibrium with N_2 and redissolving the evolved gaseous molecules in acidified water for later organic carbon analysis. Hauser et al. (2013) added sorbent traps to a similar apparatus to capture VOCs with high Henry's law constants that passed through acidified water. This approach increased the total VOC pool by 7.2%–33.6% and emphasized that the air-water partitioning properties of individual VOCs range widely. Operational definitions of the VOC pool based on air-water partitioning properties may be especially important to interpreting the directionality and magnitude of VOC sea-air flux.

Much of the information available for constraining the magnitude of the VOC pool comes from the study of a handful of VOC compounds that appear to dominate the VOC pool (e.g., Wohl et al., 2019). As discussed later, many of these have been subjects of detailed studies aimed at understanding their origins, biological sinks, and flux rates. The measurements provided do not fully represent the entire bulk pool due to its complex nature. Small molecules that make up the VOC pool can be incredibly complex because the number of isomers for a given molecular formula increases exponentially with the number of carbon atoms.

Atomic substitutions for carbon, like halogens, amines, S, Se, N, P, and As, inflate the number of chemical structures compatible with m/z data to >1,000,000 for C10 compounds (Goldstein and Galbally, 2007). Accordingly, the molecular diversity of marine VOCs is uncertain. To put this in perspective, Halsey and Giovannoni (2023) reported that the top 10 most abundant VOCs ($m/z+1$ values) accounted for <60% of the integrated signals from the detector of a PTR-MS recording VOCs from spring phytoplankton blooms in the North Atlantic. In summary, because VOCs are diverse, measurements of the bulk VOC pool are needed to appreciate its role in ocean and atmosphere biogeochemistry, and assembling an estimate of the size of the bulk pool from measurements of individual VOC compounds is not yet possible because of the unresolved complexity of the VOC pool.

A more common approach to investigating marine VOCs is to focus on individual compounds to study biotic and abiotic processes controlling in-water concentrations and sea-air fluxes. Dimethylsulfide (DMS), methanethiol, isoprene, certain oxygenated VOCs

TABLE 12.2 Review articles on some of the volatile organic compounds discussed in this section.

VOC	Review references
Dimethylsulfide and methanethiol	Moran and Durham (2019) Dani and Loreto (2017)
Isoprene	McGenity et al. (2018) Dani et al. (2017) Dawson et al. (2021) Dawson et al. (2023)
Organohalides	Gribble (1992) Paul and Pohnert (2011) Urhahn and Ballschmiter (1998) Cabrita et al. (2010)

(methanol, acetone, acetaldehyde), and volatile organic halogens (methyl chloride) have received the greatest attention because of their abundance in the atmosphere, known roles in SOA formation, and impacts on tropospheric and stratospheric ozone (Bonsang et al., 1992; Kim et al., 2017a,b; Yassaa et al., 2013). The partitioning properties (Henry's constants) of even this small collection of VOCs vary dramatically, as do their production by abiotic and biotic processes (see later). For example, the ocean is commonly undersaturated in methanol, but pulses of sea-air fluxes are observed, presumably due to the relatively high methanol concentrations in surface seawater. In contrast, acetone saturation in the ocean ranges from 50% to 200%, causing sea-air acetone flux to vary with season and geography (Table 12.1).

Narrowing the focus of research to selected VOCs has value. This approach provides a more thorough understanding of their geochemical roles, functions in plankton metabolism, and the complex factors impacting their in-water concentrations and potential sea-air flux. Indeed, genetic mechanisms involved in the production and consumption of some VOCs can now be mapped using global ocean genomic databases (Moore et al., 2022; Shemi et al., 2023). Following, we introduce the most well-studied marine VOCs from each major VOC class (Table 12.3, Fig. 12.2), focusing on their relevance to climate and their abiotic and biotic sources and sinks. Note that comprehensive reviews on some of these VOCs are provided to the reader in Table 12.2. Detailed discussion and description of experimental design and methods used to study marine VOCs are available elsewhere (Mansurova et al., 2018; Pozzer et al., 2022; Ruiz-Hernández et al., 2018; Yu and Li, 2021).

12.2.1 Organic sulfur volatiles: Dimethylsulfide and methanethiol

Abiotic sources and sinks: DMS is estimated to be 70% of oceanic sulfur emissions (Carpenter et al., 2012; Schlesinger and Bernhardt, 2013; Simó et al., 2011) and is thought to be a major source of cloud condensation nuclei over the oceans (Quinn and Bates, 2011). Indeed, that observation led to the CLAW hypothesis, which proposed climate feedbacks associated with temperature-induced DMS production by phytoplankton (Charlson et al., 1987). Despite lacking evidence for a DMS-driven feedback loop, DMS and other organic sulfur volatiles

TABLE 12.3 Major classes of VOCs in the marine ecosystem and contributions of the most well-studied VOCs to ocean carbon cycle and emissions.

VOC Class	Examples	Chemical formula	Concentrations in seawater (nmol L^{-1})	Turnover rate (in water)	Global ocean sea-air flux[a]	References
Nonmethane hydrocarbons	**Isoprene** Monoterpenes Alkanes Alkenes Benzene Toluene	C_5H_8	0.001–0.541	1.4–15.5 d	0.1–11.6 Tg C y^{-1}	Arnold et al. (2009), Dani and Loreto (2017), Hackenberg et al. (2017), Palmer and Shaw (2005), Simó et al. (2022), and Sinha et al. (2007)
Organic sulfur volatiles	**Dimethylsulfide** **Methanethiol**	C_2H_6S CH_3SH	0–316 0.02–2	Days Hours	28 Tg S y^{-1} 1.5–3.3 Tg S y^{-1}	Carpenter et al. (2012), Dani and Loreto (2017), Eyice et al. (2018), Kiene (1996), Nightingale (2003), Schlesinger and Bernhardt (2013), Simó et al. (2011, 2018), and Williams et al. (2004)
Halogenated VOCs	**Methyl bromide** **Methyl chloride** **Methyl iodide**	CH_3Br CH_3Cl CH_3I	0.001–0.13 0.08–0.23 uk	10 d uk[b] uk	0.14–0.24 Tg y^{-1} 0.761 Tg y^{-1} 0.16–0.18 Tg y^{-1}	Lu et al. (2010), Yoshida et al. (2006), and Ziska et al. (2013)
Oxygenated VOCs	**Methanol** **Acetone** **Acetaldehyde** Formaldehyde Formic acid Glyoxal	CH_3OH C_3H_6O C_2H_4O CH_2O CHO_2^- $C_2H_2O_2$	7–361 1.4–67.8 1–37	<24 h 4.5 d 3–6 h, <24 h	−14 Tg C y^{-1} −8.1 to +1.3 Tg C y^{-1} 57 Tg y^{-1}	Bates et al. (2021), Beale et al. (2013), Dixon et al. (2011a, 2011b, 2014), Millet et al. (2010), and Wang et al. (2020)
N-containing VOCs	**Monomethylamine** **Dimethylamine** **Trimethylamine** **Acetonitrile** **Alkylnitrates**	CH_3NH_2 $(CH_3)_2NH$ $(CH_3)_3N$ C_2H_3N R—O—N=O[c]	Total MAs[d]: 0.2–12 uk uk	Total MAs: 8–45 h uk Days–months	See footnote for MAs[e] 0.35 Tg N y^{-1}[f]	Fitzsimons et al. (2023), Kim et al. (2015), Van Neste et al. (1987), van Pinxteren et al. (2019), Williams et al. (2004), and Yang et al. (1994)

[a] *Emission rate is for the compound where no element is given in the units.*
[b] *uk, unknown.*
[c] *R represents an alkyl group.*
[d] *MAs, methylamines (mono-, di-, and trimethylamines) combined.*
[e] *Calculated fluxes in Van Neste et al. (1987) are −0.9–0.4 pmol m^{-2} s^{-1} for monomethylamine, −0.5–2.2 pmol m^{-2} s^{-1} for dimethylamine, and 0.2–3.2 pmol m^{-2} s^{-1} for trimethylamine for coastal seawater in Hawaii.*
[f] *Sea air emission rate of methyl and ethyl alkyl nitrates.*
Data are given for each VOC in bold. By convention, flux data that are >0 emissions from the ocean into the atmosphere, and flux data that are <0 are deposition rates from the atmosphere into the ocean.

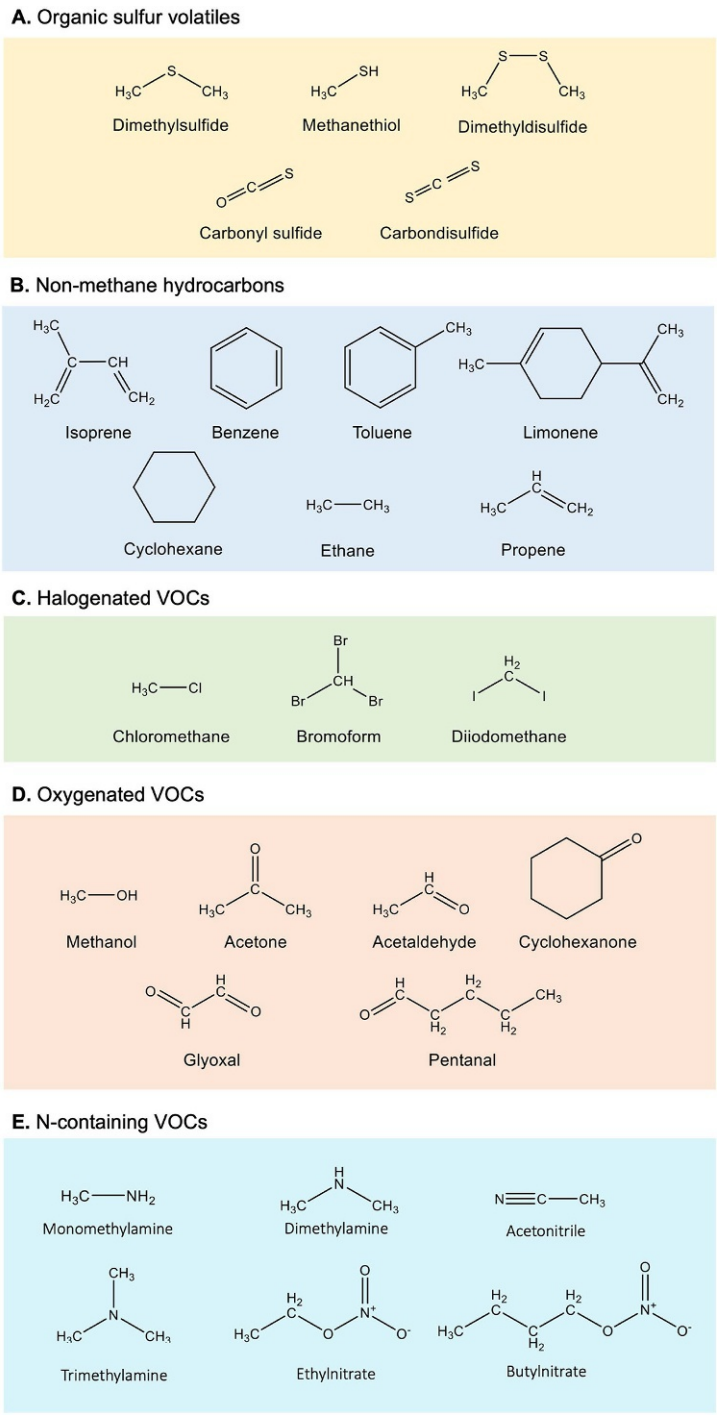

FIG. 12.2 The major classes of VOCs and the chemical structures of the most well-studied representatives.

are now recognized as major components of the global biogeochemical sulfur cycle (Kettle and Andreae, 2000; Moran and Durham, 2019). A variable fraction (i.e., 14%–77%) of DMS can be photolytically oxidized to dimethylsulfoxide (DMSO; Brimblecombe and Shooter, 1986; Hatton, 2002; Kieber et al., 1996). Methanethiol (MT) can undergo photochemical reactions releasing carbonyl sulfide (Flock and Anreae, 1996) or react with DOM, forming metal thiol complexes (Kiene and Linn, 2000; Kiene et al., 2000).

Biological sources and sinks: Dimethylsulfoniopropionate (DMSP), the precursor to DMS and methanethiol (MT), is an important and concentrated ($\sim$300 mmol L^{-1}) intracellular osmolyte in marine algae (Stefels et al., 2007; Steinke et al., 1998). Grazing of DMSP-producing algae and viral lysis release DMS (Simó et al., 2018; Malin et al., 1998). The majority of DMS is produced by catabolism of DMSP by phytoplankton and bacteria with specialized lyase or demethylation activities (Curson et al., 2018; Todd et al., 2010) or MT (Howard et al., 2006; Reisch et al., 2011), respectively. Abundant bacteria in the SAR11 clade regulate both the lyase and demethylation pathways depending on the cell's need for sulfur (Sun et al., 2016). DMS and MT can be further metabolized and assimilated into cells or diffused from cells into the seawater (Simó et al., 1995; Moran and Durham, 2019). DMS is an antioxidant that protects phytoplankton from damage caused by reactive oxygen species (ROS) (Sunda et al., 2002). DMS can also stimulate zooplankton grazing on DMS producers (Shemi et al., 2021) and has been proposed to act as an info-chemical signaling secondary metabolite production as a community-level response to active predation (Steinke et al., 2002).

12.2.2 Nonmethane hydrocarbons

Nonmethane hydrocarbons are gaseous chemicals made up solely of carbon and hydrogen. This collection of VOCs includes alkanes, alkenes, alkynes, and aromatic compounds, which are commonly known as air pollutants derived from anthropogenic activities, especially fossil fuel burning and industrial applications such as solvent use and plastics manufacturing. Nonmethane hydrocarbons are also produced from biological sources. For example, ethylene, a fruit ripening compound, and isoprene and monoterpenes, composed of chemicals built on C5 (isoprene) units, are abundant in terrestrial and marine ecosystems. Isoprenoid biosynthesis is essential in all eukaryotes and some bacteria, perhaps explaining the prominence of these compounds in environmental inventories (Dawson et al., 2021; Kesselmeier and Staudt, 1999).

Below we focus on the nonmethane hydrocarbon example of **isoprene**.

Abiotic sources and sinks: Isoprene emitted from the global oceans is thought to have significant impacts on SOA and tropospheric ozone formation through reactions with atmospheric hydroxyl radicals (Claeys et al., 2004; Hu et al., 2013). In addition to phytoplankton production (see later), isoprene is also sourced from photochemical degradation of fatty acids that can accumulate in the sea-surface microlayer (Ciuraru et al., 2015).

Biological sources and sinks: Isoprene is ubiquitously produced by plants, including microalgae (Bonsang et al., 2010; Colomb et al., 2008; Exton et al., 2013; Halsey et al., 2017; McGenity et al., 2018; McKay et al., 1996). Isoprene is thought to serve as an antioxidant protecting cells from heat and light stress (Dani and Loreto, 2017; Exton et al., 2012;

Meskhidze et al., 2015). It appears that phytoplankton, including cyanobacteria, produce isoprene via the methylerythritol phosphate (MEP) pathway, but a second evolved pathway, mevalonic acid (MVA), functions in some plants, fungi, and bacteria (Wong et al., 2016). Both pathways produce the key precursors, dimethylallyl pyrophosphate (DMAPP) and isopentenyl diphosphate (IPP), required for terpenoid biosynthesis (Herrmann, 2011; Lichtenthaler, 2007). Isoprene synthase catabolizes DMAPP to produce isoprene. In the ocean, isoprene concentrations are often positively correlated with pigment concentrations (Broadgate et al., 1997; Hackenberg et al., 2017; Orlikowska and Schulz-Bull, 2009), reflecting high cellular requirements for isoprenoid biosynthesis in actively growing phytoplankton.

Bacterial oxidation and assimilation of isoprene were initially thought to require isoprene monooxygenase (van Hylckama Vlieg et al., 2000). Recent evidence shows that isoprene uptake in marine bacteria is widespread (Dawson et al., 2023; Johnston et al., 2017; Patel et al., 1982). Intriguingly, SAR11 bacteria take up isoprene but do not encode isoprene monooxygenase or other soluble di-iron monooxygenases (Moore et al., 2022), which have broad substrate ranges and can cometabolize isoprene (Crombie et al., 2015; Dawson et al., 2020). The search for new biochemical mechanisms involved in isoprene metabolism will be important for constraining isoprene loss terms and resolve the global isoprene budget.

12.2.3 Halogenated VOCs

Abiotic sources and sinks: Halogenated VOCs include methylhalides containing Cl, Br, or I atoms. The ocean is considered to be a major source of reactive atmospheric chlorine (Solomon et al., 1994), and bromoform ($CHBr_3$) has a significant role in stratospheric ozone destruction (Anbar et al., 1996; Barrie et al., 1988). Di- and tri-methylhalides are commonly formed by chemical reactions known as haloform and sulfohaloform reactions in seawater (Urhahn and Ballschmiter, 1998).

Biological sources and sinks: Chloromethane, bromomethane and bromoform, and iodocarbons are produced by a wide range of phytoplankton, seaweeds, and bacteria (Amachi et al., 2001; Colomb et al., 2008; Laturnus, 2001; Manley and de la Cuesta, 1997; Murphy et al., 2000; Paul and Pohnert, 2011; Scarratt and Moore, 1996; Tokarczyk and Moore, 1994). Mono-methylhalides are produced by phytoplankton (Brownell et al., 2010; Scarratt and Moore, 1996; Sœmundsdóttir and Matrai, 1998) using halide ion methyltransferase and S-adenosine methionine as the methyl donor (Itoh et al., 1997; Ohsawa et al., 2001). Haloperoxidases, especially bromoperoxidase, are widespread in phytoplankton, including cyanobacteria. These extracellular enzymes catalyze oxidation of a halide anion by peroxide, yielding a highly electron-deficient halide ion that halogenates DOM yielding complex organohalides (Paul and Pohnert, 2011). Methylhalides are also growth substrates for bacterioplankton that can cleave and oxidize the methyl group for energy production (Halsey et al., 2012) or use specialized C1 metabolism to assimilate the methyl-carbon into cell biomass (Studer et al., 2002). Haloperoxidase activity consumes peroxide, a ROS that can accumulate in phytoplankton in high light (Collén and Pedersen, 1996) or in bacteria exhibiting rapid respiration. Thus organohalide production appears to protect cells against oxidative stress. A role in grazing defense has also been suggested (Paul et al., 2006).

12.2.4 Oxygenated VOCs: Methanol, acetone, and acetaldehyde

Abiotic sources and sinks: Methanol, acetone, and acetaldehyde are the most well-studied marine oxygenated VOCs, because they are significant components of the total VOC in the troposphere. Formic acid, glyoxal, aldehydes, and ketones are other important products of photochemical reactions with aliphatic compounds that are enriched to $\sim 50\,\mu mol\,L^{-1}$ in the sea-surface microlayer (Fig. 12.1; Chiu et al., 2017; Mungall et al., 2017; Rossignol et al., 2016). Photochemical degradation of DOM can be a significant source of acetone and acetaldehyde (de Bruyn et al., 2011; Dixon et al., 2013; Kieber et al., 1990; Zhou and Mopper, 1997). Humics and recalcitrant DOC with long residence times in the ocean are subject to photochemical oxidation that can yield VOCs that are readily consumed by bacterioplankton (i.e., glyoxal, acetaldehyde, and formaldehyde) (Mopper and Kieber, 1991). Methanol is a product of the chemical oxidation of methylhalides (Elliott and Rowland, 1995; Zafiriou, 1975).

Biological sources and sinks: Methanol, acetone, and acetaldehyde are actively cycled in the photic zone of the ocean's water column. Phytoplankton are major sources of these VOCs, and the genetic mechanisms enabling their oxidation and assimilation in bacteria have been elucidated (Giovannoni et al., 2008; Halsey et al., 2017; Moore et al., 2022; Sun et al., 2011). Methanol is a waste product of cell wall expansion in land plants (Heikes et al., 2002), and phytoplankton cell growth may also release methanol through demethylation reactions. Methanol has been observed in a wide range of phytoplankton cell cultures (Mincer and Aicher, 2016). Phytoplankton cell division usually occurs in the late afternoon or night, offering a potential explanation for the observation that seawater methanol consumption rates are fastest at night (Dixon et al., 2011a; Halsey et al., 2012). Methanol is required for biomass production by some marine methylotrophic bacteria (Chistoserdova et al., 2009; Giovannoni et al., 2008; Morris et al., 2006), and methanol can also be oxidized by methylovorous bacterioplankton that use it for energy production but don't assimilate methanol into biomass (Sun et al., 2011). The pathways involved in acetone and acetaldehyde production in phytoplankton are not known, but both of these VOCs have been measured in axenic phytoplankton laboratory cultures (Halsey et al., 2017; Moore et al., 2020). Bacteria are also sources of acetone (Nemecek-Marshall et al., 1995), but few species have been evaluated for VOC production. An acetone/cyclohexanone monooxygenase was recently found to be highly represented in ocean transcriptome data and expressed by a wide diversity of marine bacteria (Moore et al., 2022). Acetone/cyclohexanone monooxygenase initiates oxidation of acetone and cyclohexanone and is likely a fundamental mechanism controlling concentrations of these VOCs in the ocean. Acetaldehyde oxidation is initiated by aldehyde dehydrogenase (ALDH), a superfamily of enzymes with weak to strong activity on acetaldehyde, depending on the specific ALDH involved (Halsey et al., 2017). ALDH is present in SAR11, which also oxidized acetaldehyde at rates sufficient to explain sea-air flux of that compound.

12.2.5 N-containing VOCs

N-containing VOCs, including methlyamines, acetonitrile, and alkyl nitrates, are thought to be largely produced by photolytic and biological degradation of DOM. N-containing VOCs are actively cycled in the surface ocean because they are potential sources of N and C for

bacterioplankton growth. Plankton rely on high intracellular concentrations of N-containing osmolytes to regulate cell pressures and stabilize proteins in the saline marine environment. Osmolyte degradation yields volatile methylamines that are metabolized by diverse bacterioplankton in the surface ocean (Chen, 2012; Halsey et al., 2012; Lidbury et al., 2015). Bacterial metabolism of acetonitrile, largely sourced from terrestrial biomass burning, has been hypothesized (de Gouw et al., 2003), and diatoms are the only known biological sources (Moore et al., 2020). Finally, alkyl nitrates, which are important mediators of nitrogen oxides in the atmosphere, and thus tropospheric ozone, are released during DOM photolysis and bacterial growth (Kim et al., 2015).

12.3 VOC–taxonomy relationships

Early evidence indicates that the VOC "fingerprints" of phytoplankton—the diversity and amounts of VOC compounds produced—are taxonomically correlated (Christie-Oleza et al., 2017; Kuntzel et al., 2018; Steinke et al., 2018). Some VOCs may be ubiquitously produced by phytoplankton. For example, acetaldehyde is commonly observed in phytoplankton cultures, likely because it is a central molecule in the dark reactions of photosynthetic metabolism, (Laothawornkitkul et al., 2009; Lees and Jago, 1978). Taxonomic relationships might be associated with VOC functional roles. Phytoplankton experiencing environmental stress appear to produce either isoprene or DMS, but not both, as their primary antioxidant (Dani and Loreto, 2017). Cyanobacteria and green algae are stronger emitters of isoprene than diatoms (Bonsang et al., 2010; Shaw et al., 2010), and haptophytes, dinoflagellates, and prymnesiophytes are strong DMS producers (Archer et al., 2010; Meskhidze et al., 2015). The abundance of cyanobacteria and diatoms in the surface oceans makes them important producers of halogenated VOCs and aromatic nonmethane hydrocarbons (Brownell et al., 2010; Colomb et al., 2008; Lovelock and Maggs, 1973; Rocco et al., 2021).

Five dinoflagellates in the Symbiodiniaceae family, which are obligate endosymbionts of reef-building corals, all produced a set of six VOCs that included three of the four major VOC classes (organosulfur and halogenated VOCs, nonmethane hydrocarbons). These six VOCs represented half to a quarter of the total number of measured VOCs in each species, suggesting species-specific production of VOCs may contribute to Symbiodiniaceae functional diversity and, possibly, stress resistance in the coral holobiont (Lawson et al., 2021). Balanced carbon and nitrogen exchange between corals and their Symbiodiniaceae endosymbionts facilitates their stable symbiosis (Matthews et al., 2018; Rosset et al., 2021), and some VOCs may influence the thermal tolerance of the coral holobiont by serving as antioxidants or as direct or indirect defense signals within the holobiont or to predators (Saha and Fink, 2022; Steinke et al., 2018). Corals and the anemone-dinoflagellate model system, *Aiptasia*, are producers of DMS (Franchini and Steinke, 2017). The suite of VOCs produced by the *Aiptasia* holobiont differed from that produced by either the dinoflagellate symbiont grown alone or by the anemone growing without the symbiont, and 35 of the 152 detected VOCs were produced in all three bionts (Wuerz et al., 2022). Many outstanding questions remain about how Symbiodiniaceae taxonomic relationships impact holobiont physiology and symbiosis and whether VOC metabolism plays a role in holobiont stability.

At the core of VOC–taxonomy relationships are evolved cell metabolisms encoded by the genome. VOC-producing metabolic pathways that are shared between closely related cells, or homologous pathways in more distantly related cells, would be expected to give rise to the same VOCs. For example, stress response regulation leading to VOC production might be a phylogenetically linked trait. Furthermore, VOC production associated with metabolite accumulation, for example, via central carbon metabolism (i.e., acetaldehyde) or pathways leading to aromatic amino acids (i.e., benzene), could be regulated by similar strategies. End product induction might require similar substrate concentrations, and enzymes using VOCs as substrates might have similar K_m values. The first step to determining whether VOC production is associated with taxonomic relationships will be to systematically evaluate VOC production within and across the diversity of phytoplankton clades. A key challenge in this approach is that physiological status will alter the collections of VOCs produced by an individual species. Another open question is whether physiological shifts in VOC production are taxonomically related.

12.4 VOC production and photosynthetic metabolism

VOC production is typically positively associated with photosynthesis (Halsey et al., 2017; Meskhidze et al., 2015; Shaw et al., 2003), exhibiting maxima coincident with midday peaks in light intensity (Davie-Martin et al., 2020; Gali et al., 2013; Royer et al., 2016). EDOC was often maximal at midday in the Southern Ocean when carbon fixation rates become saturated (Ruiz-Halpern et al., 2014). Photosynthetic metabolism leads to accumulation of VOCs during daylight hours, but acetone, methanol, DMS, and EDOC sometimes exhibit a second peak in concentration during the night (Davie-Martin et al., 2020; Omori et al., 2017; Ruiz-Halpern et al., 2014). Nighttime VOC production may be associated with cell division processes that, for most phytoplankton, occur at or after dusk. Volatile end products associated with stages of cell division may be released, as in the case of methanol production during cell wall synthesis. Diel patterns in VOC production may also be caused by food web processes, such as zooplankton that migrate to the surface at night to graze on phytoplankton before returning to depths during the day. VOCs are released during active grazing of phytoplankton either as stress response signals (Sauer et al., 2021; Wolfe and Steinke, 1996) or as a consequence of sloppy feeding (Fink, 2007; Møller, 2005).

12.4.1 Photosynthetic carbon partitioning

Emerging evidence indicates that VOCs comprise a significant pool of carbon produced through photosynthesis. Direct sea-air emissions are frequently reported, and the number of VOCs that are substrates for bacterioplankton metabolism continues to increase with our deepening understanding of bacterioplankton metabolism. The view has changed since the early 2000s from niche interest in a handful of phototroph-derived molecules to a large collection of reactive molecules ubiquitously and constitutively produced in all photosynthetically based ecosystems. Recent results suggest a strong VOC flux from a diatom to abundant SAR11 bacteria. When grown in coculture with SAR11, the rate of CO_2 fixation in the model diatom, *Thalassiosira pseudonana*, increased 18%–20% compared to the axenic *T. pseudonana* control culture (Moore et al., 2020). Substituting a hydrocarbon trap as the VOC consumer

in the place of SAR11 yielded the same increase in carbon fixation. Those results were interpreted as evidence that VOCs produced by diatoms are used by SAR11 as carbon and energy sources, and that VOC sinks in their environment force diatoms to increase CO_2 fixation to replace lost VOCs. This interpretation implies that VOCs are not simply dead-end metabolites that diffuse from primary producers but are instead necessary metabolic intermediates that phytoplankton cannot control because of their diffusivity. In this perspective, VOCs are significant agents of the classical microbial loop concept, providing a conduit of carbon and energy flow that leads straight from phytoplankton to prokaryoplankton without transiting the animal and viral components of food webs.

Excretion and/or passive release of organic carbon from phytoplankton has long been recognized (Baines and Pace, 1991) (see Chapter 5). Despite the awareness that VOCs are components of the pool of extracellular products released by phytoplankton (Myklestad, 2000) (see Chapter 3), systematic evaluations of DOC production do not yet include the discussion of VOCs (Moran et al., 2022). Carbon actively excreted or passively lost from phytoplankton cells has important consequences in biogeochemical cycles. Both VOCs and DOC are important growth substrates for bacterioplankton, and their biological, photochemical, and chemical conversions can produce nonvolatile chemicals (Kiene et al., 2000) that could contribute to the much larger reservoir of longer-lived DOC in the ocean (Walker et al., 2016). A clear difference in the VOC and DOC pools is their turnover rates in the surface ocean, which are hours for acetaldehyde, DMS, and isoprene (Beale et al., 2015; de Bruyn et al., 2021, 2017; Dixon et al., 2013; Jian et al., 2017; Mopper and Stahovec, 1986; Simó et al., 2022) compared to days for the most labile form of DOC (Table 12.3; Carlson and Hansell, 2015; see Chapter 5).

VOCs are a component of primary production (Fig. 12.3). Phytoplankton are by far the most important primary producers in the open ocean. Using photosynthesis, phytoplankton

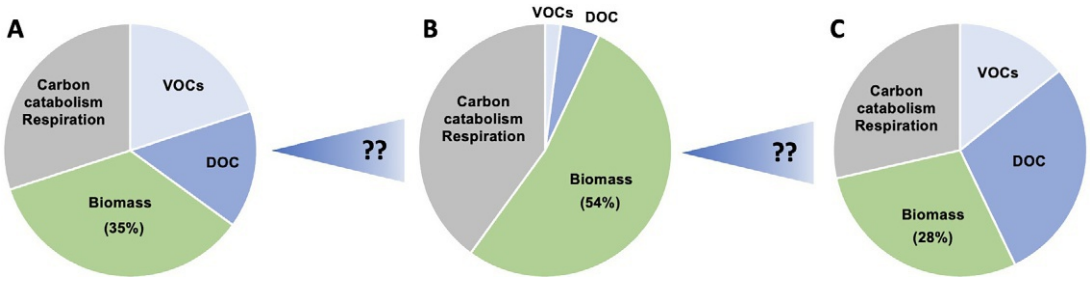

FIG. 12.3 VOC contributions to gross primary production and phytoplankton growth efficiency. VOC losses from cells cause growth efficiency to decline and provide a direct conduit for carbon flux to heterotrophic VOC consumers. Biological and abiotic processes that influence VOC production and growth efficiency are not well understood (wedges between pie charts with ?? indicating outstanding questions causing shifts in carbon allocation). (A) Under moderate light and nutrient availability, diatoms catabolize about 30% of fixed carbon (gray wedge) for energy production (ATP) and generation of biochemically reduced metabolites (i.e., lipids, nucleic acids, amino acids). About 35% of fixed carbon is retained in biomass (green wedge). The remaining carbon is either actively released or passively lost from the cell as VOCs (light blue wedge) and DOM (dark blue wedge) into the surrounding medium (Halsey et al., 2010, 2013; Moore et al., 2020). (B) If we next adjust the VOC pool such that it is one-tenth the size of the experimentally estimated pool in "A," and the DOC pool is the low end of the measured range (Moran et al., 2022), growth efficiency increases to 54%. (C) If we assume the VOC pool is half the size of the experimentally estimated pool in "A," and the DOC pool is the high end of the measured range (Moran et al., 2022), the resulting photosynthetic growth efficiency is only 28%.

collect light energy for the purpose of converting CO_2 into organic compounds for growth. About 30%–40% of the organic compounds are catabolized via glycolysis and respiration. A variable fraction of the total amount of organic carbon produced through photosynthesis, ranging from 5% to 50%, is excreted from the cell as DOC (Moran et al., 2022). It is reasonable to expect that the amount of photosynthetic production emitted from cells as VOCs is also variable (see Section 12.4.2). The magnitudes of the VOC and DOC pools have important consequences on quantifying phytoplankton carbon production in situ and the standing stock of phytoplankton carbon available for export to ocean depths and consumption by higher trophic levels. Phytoplankton growth efficiency is described by the fraction of harvested light energy that is retained in biomass following a full cell division cycle. Several major groups of eukaryotic phytoplankton appear to share similar carbon partitioning strategies, resulting in 30%–35% growth efficiencies, but a full accounting of photosynthetic carbon that includes VOCs and DOC has only been done for *T. pseudonana* (Fig. 12.3; Halsey et al., 2013; Moore et al., 2020).

12.4.2 Factors influencing VOC production

Fig. 12.3 shows how variation in VOC production impacts the efficiency of phytoplankton biomass production. VOC production may vary with taxonomy (as in the case of DMS and isoprene released as antioxidants, discussed earlier in Section 12.3). Shifts in the types and amounts of VOCs produced will also change as phytoplankton adjust their physiology in response to the environment. The impact of nutrient concentrations on VOC production is still uncertain. However, the positive correlation between nutrients and growth rate will increase phytoplankton standing stocks, which may also increase VOCs (Dani and Loreto, 2017). On the other hand, nutrient-replete conditions may favor higher phytoplankton growth efficiencies, constraining VOC release (Fig. 12.3, panel B).

Oxidative stress: DMS and acetaldehyde are produced in response to high light and UV exposure (Halsey et al., 2017; Sunda et al., 2002). Phytoplankton employ a variety of strategies to tolerate periodic exposure to light levels that force cells into physiological imbalance. DOC release is considered to be an effective sink for excess photosynthetic reductant. VOCs, including DMS, could function similarly in energy dissipation (Stefels, 2000). In fact, VOC diffusivity across cell membranes may make them even more favorable reductant sinks than DOC. Oxidative stress associated with iron limitation might explain the lower-than-expected amounts of methyl iodide following the Southern Ocean Iron Enrichment Experiments (Wingenter et al., 2004).

Growth rate: There are many observations that associate VOC production with rapid phytoplankton growth. The linkage between methanol production and cell wall expansion suggests that methanol production increases with growth rate, as was observed in the North Atlantic Ocean (Davie-Martin et al., 2020). DMS, isoprene, and halogenated VOCs were highest during periods of peak phytoplankton productivity (Davie-Martin et al., 2020; Orlikowska and Schulz-Bull, 2009; Reese and Anderson, 2009). Similarly, high monoterpene concentrations (700–1400 pmol L^{-1}) were measured in the southern Atlantic Ocean during an active phytoplankton bloom (Yassaa et al., 2013). Bloom termination is caused by viral lysis or grazing pressure that slows phytoplankton accumulation, even when phytoplankton growth

rates are high (Behrenfeld and Boss, 2014). Sauer et al. (2021) showed that C_4H_7N increased during the initial phases of ciliate grazing on *Synechococcus elongatus*, suggesting the algae produced the VOC as a deterrent. Other studies show DMS production during algal grazing (Wohl et al., 2023), which appears to signal other predators to the availability of abundant prey (Shemi et al., 2021). The mechanisms underlying the production of other VOCs during grazing remain unknown, but some VOCs may be compounds accumulated intracellularly that are released during cell breakage or by-products of grazer metabolism.

Other VOCs have been observed when phytoplankton exhibit slow growth. Acetone was in higher amounts in the low light conditions of deep convective mixing in the Indian Ocean (Warneke and de Gouw, 2001). Nonmethane hydrocarbons, ethane, ethene, propane, and propene, have been associated with phytoplankton bloom decline (McKay et al., 1996). Reports such as threefold increases in ethane, propane, and n-C_4H_{10} following iron fertilization in the subarctic Pacific (Broadgate et al., 1997), and depth-dependent production of methylated VOCs (Moore and Webb, 1996), highlight the contrasting impacts of specific factors mediating VOC production. The complexity of the task of identifying the full range of VOC species in the ocean, their roles, and the factors influencing their production is large and full of opportunity.

12.4.3 VOC contributions to the photosynthetic quotient

Although carbon mass is the primary currency of carbon cycle science, photosynthetic production of organic carbon is often captured by measuring changes in dissolved oxygen concentrations, which can be measured continuously by remote instruments. The photosynthetic quotient (PQ) is an important value used to convert oxygen production rates to carbon production rates. At the cell level, PQ is the molar ratio of O_2 produced to CO_2 assimilated into phytoplankton biomass. PQ and growth efficiency, discussed before, are related, but PQ considers non-CO_2 sinks for electrons, which mainly are forms of nitrogen. PQ values ranging from 1.0 to 2.25 have been reported (Laws, 1991; Williams and Robertson, 1991), but values higher than 1.4 are difficult to explain, even after accounting for carbon excretion as nonvolatile DOM. DOM excretion was calculated to maximally increase PQ to 1.6 after accounting for the average C:N ratio of DOM fluxed from the photic zone (Laws, 1991). PQ increases with increasing requirements for biochemical reduction. For example, a PQ of 1.4 is commonly used when nitrate is the primary nitrogen source, and PQ is closer to 1.1 when ammonia is assimilated.

VOC production has not yet been considered in quantitative calculations of PQ, but from a theoretical perspective, this is an obvious omission that should be corrected. We propose that VOC production could be an important component of the missing "reductant sink" that causes PQ values >1.4. Many VOCs are highly reduced, saturated, or methylated compounds. VOCs containing N will further increase PQ. VOC flux from phytoplankton cells into the environment, in principle, causes the elevation of PQ, just as it decreases the related metric, growth efficiency. Increasing VOC flux would cause oxygen production to become increasingly decoupled from biomass accumulation. A caveat is that if the released VOCs (or nonvolatile DOM) were instantaneously reoxidized, the apparent PQ would remain unchanged, while energy would be transferred from photoautotrophs to heterotrophic VOC consumers. Oceanographic conversions using PQ values

that are lower than actuality for natural phytoplankton communities will overestimate carbon production in situ.

Knowledge of VOCs in marine systems is expanding rapidly but we remain on the steep part of the learning curve, with some VOC compounds only recently detected in marine systems and for others that are more well known, large uncertainties about their quantitative impacts on geochemical cycles or their roles in plankton metabolism. Marine VOC cycling is likely to remain a rich topic for research exploration that has the potential to alter models that simulate the global carbon cycle and atmospheric chemistry and predict future impacts of changing climate.

12.5 Summary points

1. VOCs are being recognized as a diverse collection of molecules that comprise an important but not well-constrained fraction of DOC, with estimates ranging from 6.7% to 67%.
2. VOCs arise from a wide variety of abiotic and biotic processes. Some VOCs result directly from the metabolic activities of phytoplankton or are products produced by microbial degradation of nonvolatile compounds produced by phytoplankton.
3. VOC production and consumption are correlated with taxonomic diversity in the sense that individual cell types can have characteristic VOC "fingerprints."
4. The metabolic roles of VOCs are poorly understood, but some appear to be intermediates in metabolic pathways, suggesting they might be "common goods," a biological concept emphasizing the sharing of dissolved metabolites by members of microbial communities.
5. Some bacterioplankton taxa have specialized metabolic pathways for oxidizing specific classes of VOC compounds to produce energy and supply carbon for metabolism.
6. VOC concentrations in seawater, which impact air-sea transfer rates, likely result from imbalances between production and consumption.
7. VOC production by photosynthetic cells is a loss of fixed carbon that is not accounted for in traditional measurements of particulate and dissolved organic carbon and, in principle, lowers photosynthetic growth efficiency and elevates photosynthetic quotient PQ. Thus variability in VOC production might partially explain variability in estimates of PQ.

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