Algal volatiles – the overlooked chemical language of aquatic primary producers

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ABSTRACT

Volatiles are important 'infochemicals' that play a crucial role in structuring life on our planet, fulfilling diverse functions in natural and artificial systems. Algae contribute significant quantities to the global budget of volatiles, but the ecological roles of aquatic volatiles are not well understood. In this review, we discuss the current knowledge of volatile compounds from freshwater and marine microalgae and marine macroalgae, with a focus on their ecological roles. We highlight the multiple reported functions of biogenic volatiles, ranging from intraspecific communication for reproduction, intra-bloom signalling and antioxidant functions, to various interspecific signal exchanges that may allow herbivores to locate them and function in defence against competitors and predators. Beyond reviewing our current understanding, we specifically highlight major knowledge gaps and emerging questions for algal volatile research. These novel perspectives have the potential to improve our understanding of aquatic ecosystems and thus need to be addressed in future research. Filling these gaps and addressing these questions will facilitate humanity's efforts to exploit aquatic volatiles in various applications.

Key words: algae, biogenic volatile organic compounds (BVOCs), chemical cues, chemical ecology, cyanobacteria, freshwater, infochemicals, marine.

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I. INTRODUCTION

Smells are ubiquitous in nature, arising from artificial and natural metabolic processes by the production of volatile organic compounds (VOCs) (see glossary in Table 1). VOCs are a group of chemicals with high volatility at ambient temperatures. VOCs of biogenic origin (BVOCs) are produced by organisms for key eco-physiological processes like thermotolerance and as antioxidants. BVOCs are also known to act as infochemicals playing crucial roles in structuring biotic interactions and regulating key ecological processes like

pollination, parasitism or predation (Dicke & Sabelis, 1988; Pohnert, Steinke & Tollrian, 2007; Saha et al., 2019).

Terrestrial plants are multifaceted chemical factories producing a complex bouquets of BVOCs (Dicke & Loreto, 2010). BVOCs are released by terrestrial plants from green leaves, flowers, fruits, vegetative tissues and from underground structures like roots (Loreto et al., 2014). It is estimated that 1000 Tg of BVOCs are emitted globally each year, exceeding total VOC emissions from human activities (Guenther et al., 2012). The most important and well-known terrestrial BVOCs include isoprene, monoterpenes and

Table 1. Glossary. The terminology of (algal) chemical ecology is complex and not always consistent. Many of the terms mentioned here, with various definitions, have appeared in previous reviews (e.g. Dicke & Sabelis, 1988; Pohnert & Boland, 2002; Pohnert et al., 2007; Saha et al., 2019; Poulin et al., 2020).

Term	Definition
Benthic	Substrate (usually bottom)-associated lifestyle in aquatic environments, referring to the benthos.
Benthos	Habitat and organismal community living on, in or near the seabed, river, lake, or stream bottom (benthic zone).
BVOCs	Volatile organic compounds of biological origin.
Chemical cues	Unintentionally released compounds that supply information.
Chemical signals	Intentionally released compounds that supply specific information.
Copepoda	Subclass of crustaceans inhabiting both pelagic and benthic habitats in all kinds of aquatic environments (marine and freshwater); due to their dominance in open ocean plankton, they are probably the most numerous group of metazoan animals on Earth and play a key role in the oceanic (and thus global) carbon cycle.
HIPVs	BVOCs released by herbivore-damaged plants. Feeding by herbivores triggers plant defence responses that lead to the systemic release of various volatiles that render the entire plant attractive to natural enemies of the herbivores.
Infochemicals	Information-conveying chemicals (semiochemicals), including allelochemicals and pheromones that mediate interspecific and intraspecific communication, and population- and ecosystem-level interactions.
Marine macroalgae	Macroscopic marine algae from the Phaeophyceae (brown algae), Rhodophyceae (red algae) and Chlorophyceae (green algae), commonly inhabiting the benthos of coastal oceans.
Microalgae	Microscopic algae (including cyanobacteria) which can be found in both freshwater and marine systems, either freely floating (pelagic) or benthic forms attached to substrates like sediment, macroalgae, and seagrass, as well as artificial structures like ship hulls.
Oxylipins	Group of low molecular weight organic compounds produced through oxidative conditions, such as a wound-activated, oxidative enzyme cascade from the lipid bilayer of biological membranes. This oxidative breakdown reduces the size of the parent molecules, forming the product molecules small enough to become volatile under ambient temperatures.
Pelagial	The open water environment in both oceans and lakes, habitat to the organisms forming the plankton.
Phycosphere	Direct surroundings of an algal cell, often rich in mucilage or other organic matter, harbouring the cell's associated microbiome (bacteria and protists) and extracellular enzymes.
Plankton	Organisms suspended in water that are unable to move actively against the major currents in the environment of the pelagial.
PUAs	Polyunsaturated aldehydes are a group of BVOCs characterized by a $\alpha,\beta,\gamma,\delta$-unsaturated aldehyde group that makes them potent Michael acceptors and thus highly reactive molecules, inducing e.g. antimitotic and embryotoxic activity in various marine animals.
Tritrophic interactions	Infochemical-mediated ecological interaction across three trophic levels, e.g. herbivory-induced plant VOC emissions that attract predators or parasitoids of the herbivores and thus indirectly serve as an activated plant defence against herbivory-related tissue loss.
Volatile organic compounds (VOCs)	Low-molecular-weight organic compounds with low to moderate hydrophilicity. Can be dissolved in water, and also dissipate into the gas phase at the air–water interface, rendering VOCs perceptible to both aquatic and terrestrial organisms.

methanol that are emitted by plants with various biological functions like growth and ecological functions such as chemically mediated communication (Holopainen & Blande, 2013). Among ecological functions, feeding by herbivores is known to induce the emission of volatile compounds often referred to as herbivore-induced plant volatiles (HIPVs; Hare & Sun, 2011) which can increase the fitness of the emitting plant either directly or indirectly (Dicke, 2009). Along with direct defence, HIPVs are also known to play a key role in mediating tritrophic interactions in terrestrial ecosystems by attracting predators and parasitoids to plants under attack by herbivores (Turlings, Tumlinson & Lewis, 1990; Dicke & Baldwin, 2010). However, while BVOCs are widely recognized for their important functions as both intra- and interspecific infochemicals of terrestrial plants, surprisingly we know little about the ecological roles and functions of BVOCs from aquatic primary producers (macroalgae, eukaryotic microalgae, cyanobacteria). In particular, we lack information on the full 'volatilome' of algae, which limits our current ability to study their ecological roles and application potential due to a lack of appropriate bioassays for the study of BVOC perception and responses of the receiving organisms (Steinke *et al.*, 2018; Poulin *et al.*, 2020).

Like terrestrial plants, aquatic primary producers can release a wide spectrum of BVOCs, and parallels in the ecology and evolution of terrestrial and aquatic BVOC release have been proposed several times in recent literature (Saha, Gilon & Verheggen, 2021; Schmidt & Saha, 2021; Roggatz *et al.*, 2022). More than 35,000 algal species have been found to produce aquatic odours (Watson, 2004), with major odour compounds derived from algae and cyanobacteria including terpenoids, carotenoids, fatty acid derivatives and sulphur compounds (Watson, 2004). Aquatic BVOCs have been extensively studied in the context of water quality management as a primary indicator to evaluate drinking water integrity (Lee *et al.*, 2017). They are the main causes of so-called 'taste and odour' incidents in both surface and tap waters (Watson, 2004). In particular cyanobacteria are one of the principal sources of BVOCs associated with offensive taste and odour in drinking and recreational water, fish, shellfish, and other seafood. Over the past decade, advances in bioinformatics, enzymology, and applied detection technologies have greatly enhanced our understanding of the pathways, enzymes, and genetic coding for some of the most problematic BVOCs produced by cyanobacteria (Watson *et al.*, 2016). However, despite the known importance of terrestrial plant BVOCs and the management relevance of 'taste and odour algae' (which include cyanobacteria), we largely lack clear ideas regarding the ecological roles of these BVOCs (Fig. 1). It is well known that various abiotic factors such as light, temperature, nutrition and climate change-induced stressors can affect their emission. These BVOCs may enhance resistance to abiotic stressors, transfer information between algae, play allelopathic roles, and protect against predators as was summarized in a recent review on BVOCs with a focus on diatoms and cyanobacteria (Zuo, 2019). The focus of Zuo's (2019) review was mostly on algal stress responses and interactions with competitors through allelopathy, but only briefly touched on interactions with other organisms, such as bacteria and animals.
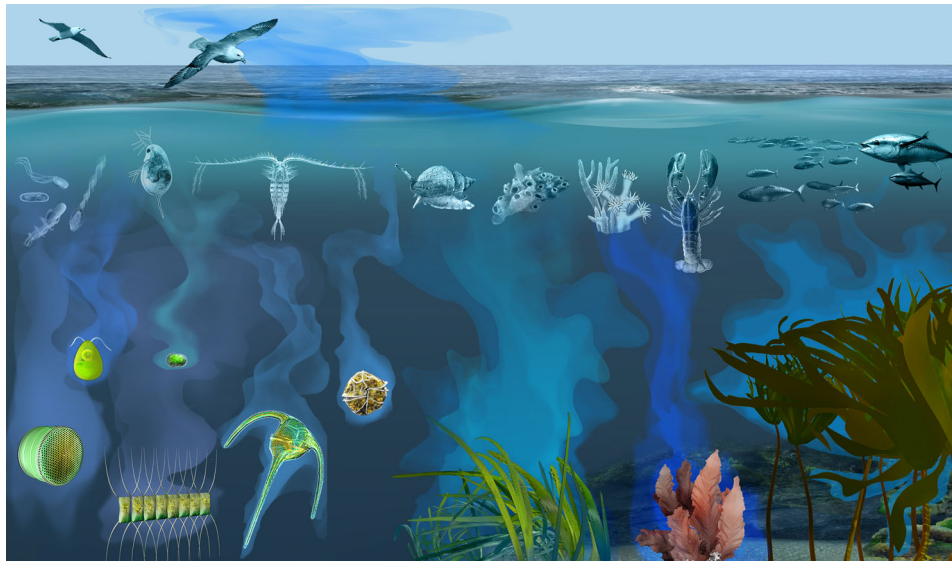
Fig. 1. Conceptual figure showing BVOC-mediated interactions between aquatic primary producers (micro- and macroalgae) and other organisms. BVOC distribution by water currents, turbulent flows, and diffusion is depicted as blue plumes with lighter shading indicating dilution at greater distances from the algal source; specific patterns of distribution will depend on the cues' chemical structure (e.g. water solubility), as well as on local hydrodynamic conditions. Anthropogenic chemicals and global change processes may alter these fine-tuned chemical interactions in unpredictable ways. Illustration by Glynn Gorick. BVOCs, volatile organic compounds of biological origin.

Other reviews have focused mostly on algal modulation of epiphytes and other surface-associated microbiota, but less upon BVOCs sequestered into the water column (Saha *et al.*, 2021; Schmidt & Saha, 2021). A general overview of the ecological roles and functions of BVOCs was provided 15 years ago by Fink (2007). While an emerging field at that time, it has since gained more attention in the scientific literature (e.g. Poulin *et al.*, 2020, Fig. 1). However, much of this work has taken place in a disjointed fashion with multiple independent studies that did not follow a unified concept or approach. Hence, herein we not only summarize recent progress and developments in our understanding of the ecological roles of algal BVOC emissions, but also highlight important concepts and potential directions for future research. Although we focus our review on work published since 2007, we also cite some earlier seminal or pioneering papers to provide context.

II. MICROALGAL BVOCs

Microalgal BVOCs have been an important element of studies on atmospheric chemistry for decades, details of which are beyond the scope of this review. Oceanic BVOCs influence cloud formation, rain, and planetary temperature, and potentially also climate change (CLAW hypothesis, see e.g. Ayers & Cainey, 2008). Dimethyl sulphide (DMS) and isoprene are the most abundant BVOCs emitted by marine phytoplankton, with their emission levels governed by various physical (light, temperature, salinity, wind speed) and biological factors (photosynthesis, bacterial activity; see Dani & Loreto, 2017). For example, experimental studies have demonstrated that algal (diatom, chlorophyte and chrysophyte) BVOC production depends on growth stage (Zhou *et al.*, 2017), and β-cyclocitral emissions from the cyanobacterium *Microcystis aeruginosa* depend on light and temperature conditions during growth (Zheng *et al.*, 2020). The environmental factors affecting BVOC emissions were covered extensively in a recent review (Zuo, 2019). Herein, we focus primarily on biotic interactions affecting BVOC release from microalgae and its ecological consequences for surrounding food webs and ecosystems.

(1) Microalgal BVOCs as food and habitat-finding cues for invertebrates

Fink, Von Elert & Jüttner (2006*b*,*c*) demonstrated that aquatic herbivores can utilize algal BVOCs as foraging cues, which was a novel and somewhat surprising finding considering the presumably maladaptive nature of algae releasing herbivore-attracting chemical cues (Fink, 2007). Since these early findings, our understanding of BVOC-mediated communication for food and habitat finding by aquatic invertebrates has expanded considerably, even though questions on its adaptive value for the algae remain unresolved (Moelzner & Fink, 2015*b*). Interestingly, the observed

interactions are quite similar in marine and freshwater ecosystems and operate in the pelagial as well as in the benthos.

(a) Freshwater ecosystems

Investigations in lake littoral (benthic) zones indicated that freshwater pulmonate gastropods are capable of perceiving volatile oxylipins liberated from wounded cells of benthic green algae (Fink *et al.*, 2006*c*) and diatoms (Fink *et al.*, 2006*b*). However, the scenario tested by Fink *et al.* (2006*b*,*c*) was not particularly ecologically relevant, as it only compared gastropod decision-making between algal and control BVOC extracts. In the snails' natural habitat, algal biofilms cover almost every underwater surface. Thus the snails' dilemma in terms of optimal foraging is not to distinguish between food and no food, but to choose between patches of food with potentially significantly different dietary quality [i.e. nutrient content (Fink & Von Elert, 2006; Fink, Peters & Von Elert, 2006*a*)]. Moelzner & Fink (2014) then compared the decision-making of freshwater gastropods between BVOCs extracted from equal biomasses of nutrient-rich (high quality) and nutrient-depleted (low in either phosphorus or nitrogen and hence of low dietary quality) algae. They observed that the pond snail *Lymnaea stagnalis* preferred odours associated with the high-quality food to the same extent as when choosing between food-associated odours and non-food odour controls (Moelzner & Fink, 2014). They further demonstrated that it is the snails' grazing activity itself (*via* their rasping radular 'tongue') that initiates the cell wounding and associated BVOC-liberating enzyme cascade (Moelzner & Fink, 2015*b*). While these studies were conducted in a rather artificial laboratory assay, Moelzner & Fink (2015*a*) demonstrated that the perception of algal BVOCs by pond snails can operate on environmentally realistic scales of several metres and could explain the commonly observed patchy aggregation patterns of aquatic invertebrates.

(b) Marine ecosystems

Jüttner *et al.* (2010*a*) were the first to demonstrate that, as for freshwater herbivores (Fink *et al.*, 2006*c*; Moelzner & Fink, 2015*a*), marine invertebrates show behavioural responses to microalgal (in this case diatom) BVOCs. Maibam *et al.* (2014) studied the relationship between the cue function of BVOCs and the wound-activated toxicity of diatoms on benthic invertebrates using the same model system as Jüttner *et al.* (2010*a*). Further studies in Mediterranean seagrass meadows strengthened the view that interactions mediated by BVOC cues from epiphytic algae have the potential to structure the entire seagrass ecosystem and its tightly associated algal and animal communities (Butera *et al.*, 2016; Mutalipassi *et al.*, 2020).

Interestingly, this ecological function of BVOCs does not seem to be restricted to the benthic habitat, but functions in very similar ways in the pelagic zone. In the oceans, pelagic herbivorous crustaceans of the order Copepoda are the dominant group of herbivores and probably represent the most

numerous metazoan animal on Earth (Kaiser *et al.*, 2011). Two of the most common genera of copepods, *Centropages* (Maibam *et al.*, 2015) and *Temora* (Kâ *et al.*, 2014) were found to respond behaviourally to algal BVOCs, although with somewhat contrasting results. Maibam *et al.* (2015) found *Centropages typicus* to prefer BVOCs of non-toxic dinoflagellates over those of toxic diatoms, indicating an adaptive food choice response in this copepod. By contrast, in odour-choice experiments, Kâ *et al.* (2014) reported an increase in food ingestion rates of *Temora stylifera* at low diatom BVOC (decadienal) concentrations.

(2) BVOCs involved in microalgal defence against herbivores

(a) *Freshwater ecosystems*

In fresh waters, crustacean zooplankton of the genus *Daphnia* (water fleas) are the dominant herbivores both in terms of numbers and grazing impact on phytoplankton. It is well known that eukaryotic algae are of higher dietary quality for *Daphnia* compared to cyanobacteria due to their biochemical composition (Von Elert, Martin-Creuzburg & Le Coz, 2003; Lürling, 2003). Cyanobacteria release a variety of BVOCs (β-ionone, geosmin and 2-methylisoborneol) upon cell lysis (Ozaki *et al.*, 2008). It thus appears an adaptive strategy for unselective filter-feeding zooplankton like *Daphnia* to avoid local aggregations of cyanobacteria in the pelagic environment, which may be mediated by volatile chemical cues. Watson, Jüttner & Köster (2007) showed that *Daphnia magna* could perceive and respond to the cyanobacterial BVOCs 2(E),4(E),7(Z)-decatrienal and β-cyclocitral at concentrations between 2.5 and 25 μM. Perception of these BVOCs resulted in a short-term increase in the crustaceans' swimming speed, which might be interpreted as an avoidance reaction. In a follow-up study, Jüttner *et al.* (2010*b*) demonstrated that β-cyclocitral is released from the bloomforming cyanobacterium *Microcystis* sp. While β-cyclocitral was undetectable in live *Microcystis* cells, cell damage resulted its rapid release into the surrounding water, likely as a product of the oxidative degradation of β-carotene from the cyanobacterial light-harvesting complex (Jüttner *et al.*, 2010*b*). This led to high local β-cyclocitral concentrations, which acted as a repellent (and putative signal of poorquality food) to *Daphnia magna* and thus potentially functions as a wounding-activated anti-herbivore defence through the release of cyanobacterial volatiles. This represented the first indication for an ecological function of BVOCs from a pelagic cyanobacterium. Reese *et al.* (2019) found grazing by rotiferan zooplankton to result in the release of similar volatile oxylipins (the carotenoid degradation products β-ionone and β-cyclocitral) from the alga *Microchloropsis salina*, but it is not yet clear whether these compounds serve as grazer repellents against rotifers. There is some indication that the common cyanobacterial volatile geosmin has a repellent activity against benthic herbivores (E. Von Elert & P. Fink, unpublished data).

(b) *Marine ecosystems*

The best-known example of an ecological function of microalgal BVOCs is the wound-activated release of polyunsaturated aldehydes (PUAs) by marine diatoms. These pelagic, bloom-forming algae release α,β,γ-unsaturated PUAs upon cell wounding (Pohnert, 2000), which are efficient mitosis inhibitors (Miralto *et al.*, 1999). Release of these PUAs can dramatically decrease the hatching success of pelagic copepods, the diatoms' most important predator (Ianora *et al.*, 2004). The diatom PUAs thus function as an activated chemical defence on the population level (Pohnert & Boland, 2002), although recent evidence suggests that toxicity is not restricted to the volatile fraction (Barreiro *et al.*, 2011; Ianora *et al.*, 2015). This topic was extensively covered by Pohnert & Boland (2002), and Fink (2007), and there have been regular reviews of recent developments (e.g. Schwartz *et al.*, 2016; Brown *et al.*, 2019). Marine planktonic coccolithophores are known to increase their release of DMS during zooplankton grazing (Wolfe & Steinke, 1996) as a result of mechanical damage by grazing activating the enzyme dimethylsulfoniopropionate (DMSP) lyase, which is involved in the defensive production of acrylate against herbivores (Wolfe, Steinke & Kirst, 1997).

(3) BVOCs involved in microalgal defence against competitors

The role of BVOCs in the inhibition of phototrophic competitors has been reviewed in detail previously (Poulin *et al.*, 2020; Watson, 2003; Zuo, 2019) and thus will not be discussed in detail here. For example, species in the common cyanobacterial genus *Microcystis* release a range of BVOCs (limonene, eucalyptol, β-cyclocitral, α- and β-ionone and geranylacetone) which reduce growth and photosynthetic activity in eukaryotic algae (e.g. Xu *et al.*, 2017). The mechanism involved in this BVOC-mediated allelopathic activity is probably the induction of reactive oxygen species (ROS) and resulting oxidative stress in the receiver organisms (Sun, Zhou & Zuo, 2020). Poulin *et al.* (2020) provide an excellent overview of allelopathic interactions between micro- and macroalgae and bacteria, as well as macroalgae and corals. Some of the compounds involved have been identified as volatile halogenated compounds (for details see Poulin *et al.*, 2020).

(4) Microalgal BVOCs involved in within-bloom signalling

The freshwater green alga *Chlamydomonas reinhardtii* is a model organism for many plant physiological processes; its physiology is well characterized and multiple *Chlamydomonas* genomes have been sequenced (Sasso *et al.*, 2018). BVOC release by *C. reinhardtii* has been studied from a physiological perspective, but not with ecologically relevant scenarios. *C. reinhardtii* release BVOCs into the culture medium in response to both acetic acid (Z. Zuo *et al.*, 2012) and salt stress (Z.-J. Zuo *et al.*, 2012). When conspecific cells were exposed

to the BVOCs from stressed *Chlamydomonas* cells, the receiver cells upregulated their activity of antioxidant enzymes. It thus seems plausible that BVOCs can serve as stress signals within an algal population that allow the receiver cells to prepare physiologically against imminent oxidative stress (Z. Zuo *et al.*, 2012). Bloom processes in marine diatoms (which play an important role in the global carbon cycle) may also be regulated through volatile quorum-sensing molecules (Vardi *et al.*, 2006). Given the extensive knowledge on the molecular physiology of both *Chlamydomonas* (freshwater) and diatoms (marine), and the availability of tools for genome modification, they represent suitable model systems for further research on the genetic and enzymatic basis of BVOC synthesis in algae.

(5) Microalgal BVOC release with unknown functions

A common pattern across the ecological functions proposed for algal BVOCs is that their release is associated with cell wounding and – in most cases – with a wound-activated enzyme cascade (Pohnert, 2000). This has been observed for both unialgal (pure) cultures and natural algal blooms. It is supported by findings that marine aggregates consisting of diatom mucilage and phytodetritus release volatile iodocarbons, probably related to the degradation of algal biomass (Hughes *et al.*, 2008). BVOC release thus may serve as a cue indicating algal aggregations in the pelagic open ocean for organisms that rely on those as habitat and/or a food resource, but this hypothesis has not yet been addressed. Isoprene is a common volatile emitted from a variety of marine phytoplankton including cyanobacteria, diatoms, coccolithophorides, and chlorophytes (Colomb *et al.*, 2008; Bonsang *et al.*, 2010). Isoprene emissions depend on a variety of environmental factors such as light intensity, cell volume, and carbon content of the plankton cells (Bonsang *et al.*, 2010), but the biological significance of isoprene emissions from phytoplankton is unknown. Marine microalgae emit a wide variety of 'seafood-like' volatiles, ranging from sulfuric compounds (dimethyl disulphide, dimethyl trisulphide, and methional), to diketones, α- and β-ionone and aldehydes such as 2,4-alkadienals and 2,4,6-alkatrienals (e.g. Van Durme *et al.*, 2013). However, whether healthy or wounded cells release these BVOCs remains unclear, as BVOC extraction procedures from algal biomass (such as vacuum distillation) may induce cell lysis and thus make it impossible to distinguish between constitutive and wound-activated BVOC release (e.g. Sun, Chung & Shin, 2012). In addition, the contribution of BVOCs produced by surface-associated microbes residing in the phycosphere of microalgal cells has not been addressed. To date, investigations of BVOCs from microalgae have not distinguished between BVOCs released by the algae themselves and those released by the microbes associated with their surfaces. Hence, there remains a clear need to investigate the ecological and/or biological roles of (micro) algal chemical cues in general and of volatiles in particular (Saha *et al.*, 2019).

III. MACROALGAL BVOCs

Marine macroalgae, i.e. seaweeds, are a rich source of BVOCs, especially halogenated hydrocarbons (Paul & Pohnert, 2011) and sulphur compounds. Although the contribution of macroalgae to the global budget of these molecules and their roles in climate functioning have been well investigated (e.g. Broadgate *et al.*, 2004), reports of the production of volatiles in seaweeds have focussed largely on the chemical characterization of volatiles produced by macroalgae and on the responses of certain volatiles like DMS to environmental factors such as salinity, light, warming and ocean acidification (Kerrison *et al.*, 2012) rather than identifying their ecological roles which remain relatively underexplored. However, the few cases where the ecological roles of macroalgal BVOCs have been studied show interesting parallels to functions described from terrestrial plants (Saha *et al.*, 2021; Schmidt & Saha, 2021). Below, we draw together recent research illuminating the ecological functions of macroalgal BVOCs.

(1) Macroalgal BVOCs involved in reproduction

We do not summarise the variety of different brown algal pheromones identified to date, as this has been comprehensively covered in previous reviews (e.g. Pohnert & Boland, 2002). Pioneering work by Müller *et al.* (1971) led to the isolation of the first volatile pheromone of a cosmopolitan brown seaweed *Ectocarpus siliculosus*. Female gametes of *Ectocarpus* are known to emit ectocarpene to improve fertilization efficiency though the attraction of motile male gametes. In later work, ectocarpene was found to be the precursor of a series of C_{11} hydrocarbons used as signals in the reproduction of brown seaweeds. While macroalgae from the genus *Dictyopteris* produce such C_{11} compounds in large amounts in their thalli, for the Mediterranean *Dictyopteris membranaceae* these compounds were found to be released into the environment, potentially interfering with the chemically mediated interactions of other brown seaweeds or acting as herbivore deterrents (Zatelli, Philippus & Falkenberg, 2018). In a recent study, ectocarpene was found to induce chemotaxis of male gametes of the brown macroalgae *Mutimo cylindricus*; application of ectocarpene altered the phototaxis of these male gametes (Kinoshita-Terauchi *et al.*, 2019).

Ethylene (or ethene) is a volatile 'aging' hormone present in land plants that promotes ripening, fruit abscission and regulates many aspects of growth and development throughout the life cycle of the plant, thus playing a critical role in plant morphogenesis (Iqbal *et al.*, 2017). Ethylene production is known from a variety of red, brown and green macroalgae (Broadgate *et al.*, 2004). García-Jímenez & Robaina (2012) first tested the effect of ethylene on tetrasporogenesis in the red macroalgae *Pterocladiella capillacea*. They exposed immature tetrasporophytic thalli to ethylene for different periods and observed maximum maturation of tetrasporangia at 7 days post exposure in thalli exposed to ethylene for 15 min, concluding that ethylene may have a role as a

physiological regulator of tetrasporogenesis in *P. capillacea*. Production of ethylene was found to be 60-fold higher than that observed from the green alga *Ulva intestinalis* (Plettner, Steinke & Malin, 2005), although it must be noted that different measurement techniques were used. Ethylene production from *P. capillacea* was comparable to that of terrestrial plants such as *Solanum lycopersicum* (tomato) and *Galium aparine* (cleavers) (Hansen & Grossmann, 2000). Upon exogenous treatment with the ethylene precursor 1-aminocylopropane-1-carboxylic acid (ACC), the red seaweed *Pyropia yezoensis* formed spermatia and zygotospores (Uji *et al.*, 2016). Ethylene was also found to be released by the red macroalga *Gelidium arbuscula*, but its ecological or biological role was not tested (García-Jímenez, Brito-Romano & Robaina, 2013).

In terrestrial plants, jasmonic acid and its derivatives are known to regulate a variety of physiological processes such as the maturation and germination of pollen grains (Avanci *et al.*, 2010). A burst of jasmonates was reported from the cystocarp-bearing thalli of the red macroalgae *Grateloupia imbricata* compared to infertile thalli (Pilar, Olegario & Rafael, 2016). Treating *G. imbricata* thalli with external methyl jasmonate lead to 7.5-fold greater production of cystocarps than in untreated thalli, and maturation was completed within 48 h compared to the typical >3 week maturation period and included the opening of cystocarps and the presence of dehiscent cavities.

(2) Macroalgal BVOCs in chemical defence

Seaweeds, in particular rhodophytes, are rich sources of halogenated metabolites (reviewed by Paul & Pohnert, 2011). The roles of seaweed BVOCs in defence against epibacteria and in structuring epimicrobial communities have recently been reviewed by Saha *et al.* (2021), and are not discussed further herein.

Laurencia dendroidea, a common intertidal and shallow subtidal seaweed of the Brazilian coast produces the sesquiterpene elatol, which has anti-fouling and anti-herbivory activity (Sudatti *et al.*, 2008). Elatol was produced more at higher temperatures by *Laurencia rigida* and its production varies according to small-scale environmental fluctuations (Oliveira *et al.*, 2013). Halogenated BVOCs produced by *Gracilaria* sp. and *Gracilaria chilensis* are known to have antibacterial activity (Weinberger *et al.*, 2007, 2011). Volatile C6 and C9 aldehydes play an important role in wound healing and pest resistance in land plants. Similar to the volatile PUAs produced by diatoms and other plankton as defence chemicals (see Section II.2.*b*) and stress alarm systems, long- and short-chain aldehydes produced by brown macroalgae may function as signalling chemicals in their natural environment. The kelp *Laminaria digitata* releases aldehydes in response to biotic and abiotic stressors (Goulitquer *et al.*, 2009). Treatment of algae with oligoguluronate to mimic a biotic stress (attack by pathogenic microbes) induces an oxidative burst. Upon challenge with oligoguluronate, *L. digitata* plantlets release a suite of more than 11 compounds ranging in chain length from hexanal to 4-hydroxydodeca-

2,6-dienal compared to control *L. digitata* sporophytes. Aldehyde fingerprints were also obtained from tidal pools colonized by *L. digitata* subjected to environmental stresses such as ultraviolet exposure, ozone exposure, desiccation and rapid fluctuations of temperature and salinity. Goulitquer *et al.* (2009) suggested that some aldehydes may induce the synthesis of oxylipins in algae and therefore act as inducers of metabolic responses, and thus that aldehyde release may act as an external or internal cue in *L. digitata* exposed to biotic and abiotic stressors. *L. digitata* is also known to transmit a warning message to neighbouring conspecifics (Thomas *et al.*, 2011). *L. digitata* can integrate waterborne cues present in the kelp bed and/or released from elicited neighbouring *L. digitata*. Exposure to elicited conspecifics changed the patterns of oxidative burst and volatile emissions and potentiated faster induction of genes specifically regulated in response to oligoguluronates. Methyl jasmonate is also known to trigger oxidative bursts inducing resistance in *L. digitata* against infection by the brown endophyte *Laminariocolax tomentosoides* (Küpper *et al.*, 2009). Macroalgae were also found to deter herbivores with halogenated terpenoids (Paul & Pohnert, 2011). However, long chain aldehydes in the oils of the green seaweed *Ulva pertusa* were found to be feeding attractants for the turbinid gastropod *Lunella coronate coreensis* (Akakabe & Kajiwara, 2008).

In land plants, jasmonic acid and related phytohormones are known to be crucial for the mediation of induced chemical defences. Although this hormone is abundant in the marine environment, it was found to play no role in defence induction for seven brown seaweeds (*Dictyota dichotoma*, *Colpomenia peregrina*, *Ectocarpus fasciculatus*, *Fucus vesiculosus*, *Himanthalia elongata*, *Saccharina latissima*, and *Sargassum muticum*) against the amphipod *Ampithoe longimana* and the isopod *Paracerceis caudata* (Wiesemeier, Jahn & Pohnert, 2008).

DMSP (the precursor to DMS) is a common metabolite present in marine organisms including microalgae (see Section II.2.*b*), seaweeds (Lyons, Scheibling & Van Alstyne, 2010) and invertebrates (Van Alstyne, Schupp & Slattery, 2006), in salt marsh bacteria (Williams *et al.*, 2019) and is also produced by terrestrial plants (Otte *et al.*, 2004). Despite the importance of DMS as a climate-active gas and contributor to the global sulphur cycle, its ecological roles have been underexplored for marine macroalgae. DMS was first described from the red macroalgae *Polysiphonia fastigiata* and *Polysiphonia nigrescens* (Haas, 1935). The first direct evidence that DMS produced in response to damage by grazers can inhibit feeding by marine herbivores was from a multi-choice feeding preference experiment in which two DMSP-producing green macroalgae *Enteromorpha linza* and *Ulva fenestrata* were among the least preferred (Van Alstyne & Houser, 2003). Feeding-activated chemical defence is also common among dictyoalean brown seaweeds (Cetrulo & Hay, 2000). Metabolic profiling of intact *Dictyota dichotoma* compared to wounded algal tissue revealed the presence of trace gases as active compounds. In behavioural assays in which *Amphithoe longimana* were fed on artificial diets, mixtures of volatile trimethylamine and DMS and non-

volatile acrylate reduced the association of these herbivores with treated food pellets (Wiesemeier *et al.*, 2008). To our knowledge this is the only study investigating the role of seaweed sulphur-containing gases in mediating ecological interactions in recent years.

Volatile terpenoids play an important role as defences against biotic stressors in terrestrial plants (Abbas *et al.*, 2017). Marine macroalgae are also rich sources of terpenoids. Three dolabelane diterpenes isolated from the Brazilian brown macroalgae *Canistrocarpus cervicornis* inhibited mussel byssus formation (Bianco *et al.*, 2009). Dictyol C, a pachydictiane diterpene obtained from a Mediterranean brown macroalgae *Dictyota* sp. was found to inhibit growth of biofilm-forming bacteria at a low concentration (Rubiano-Buitrago *et al.*, 2019). Surface-associated compounds gleenol and trans-calamenene isolated from the brown macroalga *Taonia atomaria* were found to exhibit anti-adhesion properties against five marine bacterial strains isolated from different artificial marine surfaces (Othmani *et al.*, 2016). However, these compounds were found to be inactive against epibiotic bacteria from the macroalga itself. Othmani *et al.* (2016) also showed that *T. atomaria* was able to release gleenol and trans-calamenene into the surrounding sea water.

(3) Macroalgal BVOCs as antioxidants

Ectocarpus is a genus of filamentous brown macroalgae with a worldwide distribution along temperate coastlines and is a common fouling organism on substrates in the sea including both living substrates like kelp and artificial substrates. Küpper *et al.* (2018) demonstrated that *Ectocarpus* has an active bromine and iodine metabolism and is a significant producer of methyl iodide, especially under oxidative stress conditions. Additionally, dehalogenase enzymes were detected in the genome of *Ectocarpus* and Küpper *et al.* (2018) speculated that such enzymes may protect *Ectocarpus* against halogenated defence compounds produced by kelps, enabling *Ectocarpus* to grow on the thalli of kelps as an epiphyte or endophyte.

IV. ISSUES AND EMERGING RESEARCH QUESTIONS

In a recent opinion paper, we highlighted the immense and not yet fully developed potential of marine infochemicals (including both volatile and non-volatile compounds) for applied and fundamental research on aquatic ecosystems (Saha *et al.*, 2019). Here we extend this by specifically exploring promising concepts and directions for future research on algal BVOCs. For example, while complex, tritrophic interactions mediated by BVOCs are well studied in terrestrial plant–herbivore systems, these have only been hypothesized but not yet well explored for aquatic ecosystems (Steinke, Malin & Liss, 2002; Fink, 2007). An exception is the use of DMS as a foraging cue by procellariiform seabirds to locate

phytoplankton grazers (Nevitt & Haberman, 2003). Future studies should investigate how micro- and macroalgal BVOCs released to function in chemical defence (towards grazers or foulers) or in response to other biotic stressors may act as a cue to other nearby micro- (viruses, fungi, and diatoms) and macro-organisms (e.g. bryozoans, mussels, grazers). In a context of potential multifunctionality of BVOCs, it is essential to study not only a few selected compounds, but also to assess the full 'volatilome' (Steinke *et al.*, 2018). Without the full set of compounds, the context dependence of their production and emission, as well as appropriate bioassays to study these responses, investigations of BVOC-mediated ecological interactions will remain anecdotal (e.g. Mutalipassi *et al.*, 2022).

It has been repeatedly hypothesized that anthropogenic chemicals could interfere with the fine-tuned chemical communication processes that have evolved between organisms (Lürling & Scheffer, 2007; Klaschka, 2008; Lürling, 2012). This has been termed 'info-disruption' or an 'infochemical effect' although this terminology lacks precision. Such interference by micropollutants has the potential for large-scale, but easily overlooked effects on aquatic ecosystems, as it could act at environmental pollutant concentrations far below the classically determined thresholds for toxicity (Lürling, 2012). Recently, several such cases involving aquatic chemosensory interactions have been investigated in both pelagic (Lürling & Beekman, 2002; Lürling, 2006; Von Elert, Preuss & Fink, 2016) and benthic aquatic systems (Fink *et al.*, 2017; Fink & Von Elert, 2017). None of the chemical cues tested to date was a volatile, but it is reasonable to assume that this process could also interfere with natural BVOC-mediated chemical communication processes in aquatic algae, which warrants further investigation.

There is tremendous potential for the study of coevolutionary processes related to BVOC-mediated chemical communication in aquatic algae, which compared to terrestrial plant–insect interactions (Dicke & Baldwin, 2010) are relatively unexplored. For example, intricate predator–prey communication processes are mediated by algal volatiles with varying costs and benefits to the emitters and receivers (Karban, 2011). Hence, signalling mediated *via* algal BVOCs would represent an excellent system within which to investigate coevolutionary Red Queen dynamics, in particular with respect to signal–receiver coevolution, exploitation of honest/dishonest signals, quorum sensing, and host–parasite dynamics. This could shed light on the seemingly maladaptive attraction of grazers by algae (e.g. Fink, 2007; Moelzner & Fink, 2015*b*,*a*) and potential tritrophic interactions (Coleman *et al.*, 2007). For example, a co-adaptation (coevolution) in seaweed–bacteria interactions may be prevented by chemical communication *via* BVOCs (M. Saha, unpublished data).

Algal BVOC research has additional implications beyond fundamental research. Sustainable aquaculture of fish, shellfish and macroalgae is an industry with massive economic and ecological impacts (Ahmed, Thompson & Glaser, 2019). Analogous to terrestrial 'push–pull' applications of volatile

signal compounds (Khan *et al.*, 2016), BVOC research has potential for applications in the context of sustainable aquaculture (Saha *et al.*, 2019). For example, significant parasites in fish aquaculture use BVOCs as host-finding cues (Ingvarsdóttir *et al.*, 2002; Bailey *et al.*, 2006) and it is possible that a directed application of attractive (odour traps) and repellent BVOC sources may allow aquaculture systems with lower economic costs due to reduced requirements for pharmaceutical control of parasites (Saha *et al.*, 2019). Similar approaches may prove promising for the growing industry of macroalgae farming, where BVOCs that deter fouling organisms may be exploited. Given that the initial microbial colonizers are known to regulate further colonization by macrofoulers (reviewed by da Gama, Plouguerné & Pereira, 2014; Saha, Goecke & Bhadury, 2017) and act as a 'protective coat' against macrofoulers (Nasrolahi *et al.*, 2012), manipulation of the initial biofilm community *via* macroalgal BVOCs could be employed to reduce deleterious fouling, thereby improving macroalgal biomass yields.

Finally, it can be expected that climate change-induced stressors will not only impact the BVOCs released by micro and macroalgae (influencing atmospheric chemistry and climate), but also the fine-tuned ecological and biological interactions mediated by algal BVOCs (Roggatz *et al.*, 2022). Our planet is experiencing a simultaneous increase in atmospheric CO_2 concentrations and surface temperature as a consequence of human actions (IPCC, 2007). These changes have been demonstrated to affect insect behaviour, semiochemistry and populations in terrestrial plant–insect interactions (Blanchard *et al.*, 2019). In marine ecosystems, seawater pH levels that have remained stable for millennia started to decrease rapidly during the last century as a consequence of anthropogenic CO_2 emissions (Orr *et al.*, 2005). This has had consequences for underwater chemical communication processes among fishes (Munday *et al.*, 2009; Dixson, Munday & Jones, 2010), although the relevant cues are probably not volatile and the exact modes of interference remain unclear (Leduc *et al.*, 2013; but see Roggatz *et al.*, 2016). Recent studies indicate that BVOC-mediated communication processes can also be affected by ocean acidification: a reduction of seawater pH altered invertebrate behavioural responses to their volatile food- and habitat-finding cues (Zupo *et al.*, 2016; Mutalipassi *et al.*, 2020, 2022). Similarly, marine copepod zooplankton that use algal BVOCs to evaluate diet suitability show altered and potentially maladaptive responses to algal BVOCs under artificially acidified conditions mimicking future atmospheric CO_2 levels (Maibam *et al.*, 2015). This highlights that global change is likely to have subtle, but significant effects on chemical communication processes (*via* BVOCs and other factors) that require urgent investigation (Roggatz *et al.*, 2022).

V. CONCLUSIONS

(1) There is increasing evidence for the ecological importance of BVOCs not only among terrestrial, but also aquatic primary producers (Fig. 1). However, our current understanding is still sketchy and incomplete. For example, a role in complex tritrophic food web interactions has been hypothesized for aquatic ecosystems (Steinke *et al.*, 2002; Fink, 2007), but still requires detailed investigation.

(2) A deeper understanding of BVOC-mediated interactions in aquatic ecosystems/primary producers has huge potential to further our understanding of food-web interactions in globally changing environments (Roggatz *et al.*, 2022) and of the possible effects of interference by anthropogenic chemicals (Lürling & Scheffer, 2007).

(3) BVOC-mediated interactions of aquatic primary producers with their conspecifics, competitors, pathogens, and predators may serve as excellent models for the study of coevolutionary processes.

(4) Understanding the volatile 'chemical language' of algae (Saha *et al.*, 2019), as well as their entire 'volatilomes' (Steinke *et al.*, 2018) offers opportunities for improving sustainable exploitation of aquatic natural resources and for applications in aquaculture.

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VII. AUTHOR CONTRIBUTIONS

Both authors conceived the idea, designed, planned and wrote the paper. Both authors approved the final version.

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