




Potential role of submerged macrophytes for oxic methane production in aquatic ecosystems

Sabine Hilt , ^{1*} Hans-Peter Grossart , ^{2,3} Daniel F. McGinnis , ⁴ Frank Keppler , ^{5,6}

¹Department of Community and Ecosystem Ecology, Leibniz Institute of Freshwater Ecology and Inland Fisheries, 12587, Berlin, Germany

²Department of Plankton and Microbial Ecology, Leibniz Institute of Freshwater Ecology and Inland Fisheries, Stechlin, Germany

³Institute for Biochemistry and Biology, Potsdam University, Potsdam, Germany

⁴Department F.-A. Forel for Environment and Aquatic Sciences, Faculty of Science, University of Geneva, Geneva, Switzerland

⁵Institute of Earth Sciences, Heidelberg University, Heidelberg, Germany

⁶Heidelberg Center for the Environment (HCE), Heidelberg University, Heidelberg, Germany

Abstract

Methane (CH₄) from aquatic ecosystems contributes to about half of total global CH₄ emissions to the atmosphere. Until recently, aquatic biogenic CH₄ production was exclusively attributed to methanogenic archaea living under anoxic or suboxic conditions in sediments, bottom waters, and wetlands. However, evidence for oxic CH₄ production (OMP) in freshwater, brackish, and marine habitats is increasing. Possible sources were found to be driven by various planktonic organisms supporting different OMP mechanisms. Surprisingly, submerged macrophytes have been fully ignored in studies on OMP, yet they are key components of littoral zones of ponds, lakes, and coastal systems. High CH₄ concentrations in these zones have been attributed to organic substrate production promoting classic methanogenesis in the absence of oxygen. Here, we review existing studies and argue that, similar to terrestrial plants and phytoplankton, macroalgae and submerged macrophytes may directly or indirectly contribute to CH₄ formation in oxic waters. We propose several potential direct and indirect mechanisms: (1) direct production of CH₄; (2) production of CH₄ precursors and facilitation of their bacterial breakdown or chemical conversion; (3) facilitation of classic methanogenesis; and (4) facilitation of CH₄ ebullition. As submerged macrophytes occur in many freshwater and marine habitats, they are important in global carbon budgets and can strongly vary in their abundance due to seasonal and boom-bust dynamics. Knowledge on their contribution to OMP is therefore essential to gain a better understanding of spatial and temporal dynamics of CH₄ emissions and thus to substantially reduce current uncertainties when estimating global CH₄ emissions from aquatic ecosystems.

It has been suggested that methane (CH₄) from aquatic ecosystems might contribute to about half of total global atmospheric CH₄ emissions (Rosentreter et al. 2021). Until recently, aquatic biogenic CH₄ production was assumed to be restricted to methanogenic archaea living under strict anoxic or suboxic conditions in sediments, bottom waters, and wetlands (Reeburgh 2007). From these environments, CH₄ can be emitted to the atmosphere via diffusion, ebullition, and transport

mediated by wetland plants (Fig. 1). Frequently detected CH₄ supersaturation (red profiles in Fig. 1) in upper oxic waters (Scranton and Brewer 1977) challenges this paradigm (review by Tang et al. 2016). Some researchers resolved this phenomenon, termed the “methane paradox” (Rogers and Whitman 1991), by assuming that anoxically produced CH₄ is physically transported to oxic waters (Peeters et al. 2019). However, since the discovery that terrestrial plants directly produce CH₄ in the presence of oxygen (Keppler et al. 2006, 2009), more studies have focused on the potential formation of CH₄ in aerobic environments and from several organisms. In this context, several recent studies provided evidence for the existence of oxic CH₄ production (OMP) in freshwater, brackish, and marine habitats, driven by various planktonic organisms such as bacteria, phytoplankton, and zooplankton (Table 1; Fig. 1).

Measured OMP rates in aquatic ecosystems are high enough to maintain CH₄ supersaturation (Reeburgh 2007;

*Correspondence: sabine.hilt@igb-berlin.de

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs](https://creativecommons.org/licenses/by-nc-nd/4.0/) License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

Author contribution statement: Idea: SH; Concept: SH, HPG, FK; Manuscript: SH, HPG, DFM, FK

Special issue: Carbon sequestration in aquatic ecosystems

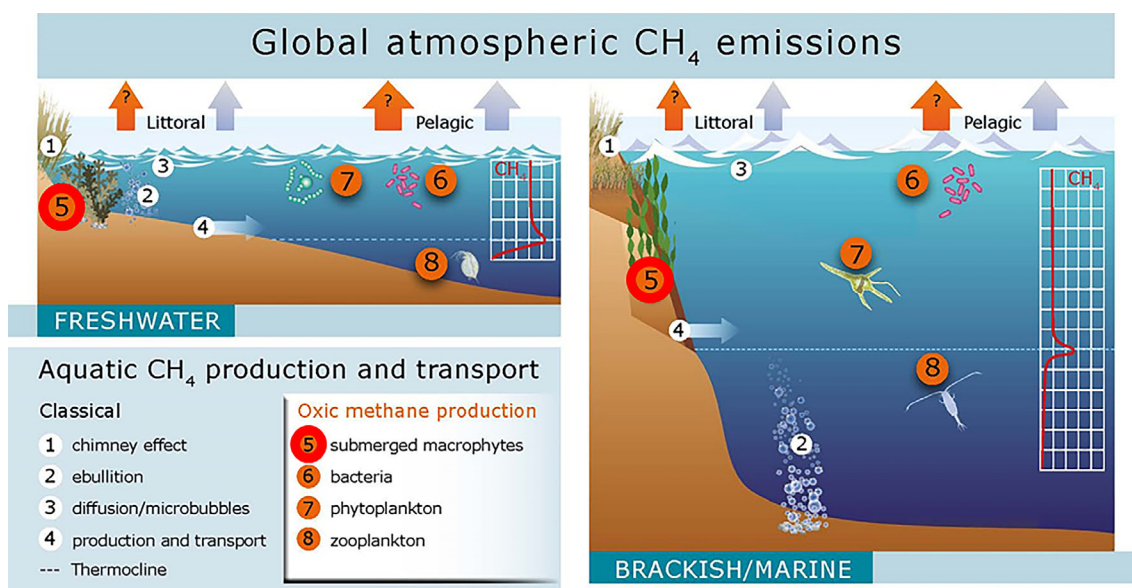


Fig. 1. CH₄ production and transport in aquatic ecosystems. CH₄ distribution (red profiles), classic CH₄ production, and transport processes from anoxic sites (1–4, gray arrows). Several planktonic organism groups have been shown to contribute to OMP (6–8, orange arrows) and thus to global CH₄ emissions from freshwater and brackish/marine ecosystems. We propose that freshwater and brackish/marine submerged macrophytes (5, red circle) also contribute to OMP.

Grossart et al. 2011; Jakobs et al. 2014; Wang et al. 2017), and thus can cause a net CH₄ flux to the atmosphere (Damm et al. 2010; Grossart et al. 2011; Gültow et al. 2013; Tang et al. 2014; McGinnis et al. 2015; Repeta et al. 2016). OMP seems to be a particularly strong CH₄ source in temperate lakes (Donis et al. 2017; Günthel et al. 2019; Hartmann et al. 2020). Preliminary studies in two mesotrophic, temperate lakes (Donis et al. 2017; Günthel et al. 2019) indicate that OMP can significantly (50–83%) contribute to total ecosystem CH₄ emissions. Recurring biogenically produced CH₄ accumulation below the thermocline, however, was also found in marine habitats (Karl et al. 2008; Ye et al. 2020) including the Baltic Sea (Jakobs et al. 2014; Schmale et al. 2018).

Various CH₄ sources and production mechanisms have been observed and identified in aquatic oxic environments which so far can be roughly divided into three major groups:

1. Classic archaeal methanogenesis in organic aggregates (Oremland 1979; Karl and Tilbrook 1994) or in anoxic microniches within zooplankton (De Angelis and Lee 1994; Schmale et al. 2018).
2. Direct metabolic CH₄ production by cyanobacteria and eukaryotic algae by processes related to the use of light as an energy source (Table 1) or by cyanobacteria and proteobacteria from either methoxyl groups present in or reduction of (bacterio)chlorophyll precursors (Perez-Coronel and Beman 2021). These observations might be linked to a common process that likely occurs in all living cells and that is based on the interplay between reactive oxygen species (ROS), iron species, and methyl donors (Ernst et al. 2022).

3. Release of CH₄ during breakdown of organic matter (Karl et al. 2008; Repeta et al. 2016; Wang et al. 2021) and methylated CH₄ precursors (Damm et al. 2010; Reisch et al. 2011; Jakobs et al. 2014), chemical conversion of methylated CH₄ precursors (Keppler et al. 2008; Althoff et al. 2014; Lenhart et al. 2016), or photochemical conversion of organic matter such as colored dissolved organic matter (cDOM) (Li et al. 2020a) or plant matter (Vigano et al. 2008; Messenger et al. 2009) to CH₄.

Biological mechanisms have all been detected in or were linked to planktonic microorganisms while submerged macrophytes have been fully ignored in studies on OMP (Carmichael et al. 2014). This is surprising given the fact that aquatic plants are key components of littoral zones (Paine 2002; Hilt et al. 2017) of ponds, lakes, and coastal systems. In particular, dissolved CH₄ concentrations in lakes can be highest in zones of submerged macrophytes (Xiao et al. 2017) and CH₄ fluxes from submerged vegetation can be higher than in nonvegetated zones in lakes (Wang et al. 2006; Zhang et al. 2019) and reservoirs (Cronin et al. 2006). CH₄ emissions in a subtropical lake were directly related to macrophytes and ranged between 0.6 and 1.3 mg m⁻² h⁻¹ (Xing et al. 2006). Furthermore, CH₄ emissions by seagrass ecosystems were estimated to increase the contribution of marine global emissions by approximately 30% (Garcias-Bonet and Duarte 2017). These high concentrations and contributions to fluxes have been mainly attributed to organic substrate production by macrophytes promoting classic methanogenesis in anoxic sediments (Natchimuthu et al. 2014; Grasset

Table 1. OMP reported from freshwater and marine planktonic organisms.

Freshwater			Marine		
Organism	Domain	Reference	Organism	Domain	Reference
Methanogens, algae	Archaea, eukaryote	Grossart et al. (2011), Bogard et al. (2014)	Haptophytes	Eukaryote	Lenhart et al. (2016), Klintzsch et al. (2019, 2020), McLeod et al. (2021)
α -, γ -proteobacteria, mixed assemblages	Prokaryote	Karl et al. (2008), Yao et al. (2016), Wang et al. (2017), Donis et al. (2017), Günthel et al. (2019), Perez-Coronel and Berman (2021) Wang et al. (2021)	α -, γ -proteobacteria, mixed assemblages	Prokaryote	Damm et al. (2010), Carini et al. (2014), Repeta et al. (2016), Donis et al. (2017), Ye et al. (2020)
Cyanobacteria	Prokaryote	Khatun et al. (2019), Bižić et al. (2020)	Cyanobacteria	Prokaryote	White et al. (2010), Bižić et al. (2020)
Picoeukaryotes, green algae, diatoms, cryptophytes	Eukaryote	Hartmann et al. (2020), Leon-Palmero et al. (2020)	Alga/copepods	Eukaryote	De Angelis and Lee (1994), Florez-Leiva et al. (2013), Weller et al. (2013), Schmale et al. (2018)

et al. 2019; Zhang et al. 2019), while OMP has not been considered so far.

Existing reviews on the role of macrophytes in regulating CH₄ dynamics mainly focus on anaerobic processes and emergent species (Laanbroek 2010; Carmichael et al. 2014; Bodmer et al. 2021). Here, we propose that freshwater and marine submerged macrophytes also contribute to OMP and thus their contribution to overall CH₄ fluxes should be taken into account. We first briefly review OMP in terrestrial plants, for which evidence of OMP has been found and then assemble existing knowledge on potential direct mechanisms of aerobic production of CH₄ by freshwater and marine submerged macrophytes, their epiphytes, and herbivores. In addition, indirect mechanisms by which macrophytes and associated organisms may support OMP or CH₄ release into aerobic water columns are also considered. Finally, we discuss implications of OMP in submerged macrophytes for CH₄ emissions from aquatic ecosystems.

OMP in terrestrial plants

In early 2006, Keppler et al. reported the first evidence for direct CH₄ emissions from dead and living plant foliage of terrestrial C₃ and C₄ plants under aerobic conditions. Their initial global upscaling of emissions from living plants of 62–236 Tg CH₄ yr⁻¹ was probably an overestimate (particularly the upper end of the estimation range), but the significance on the global scale has not yet been fully addressed (Saunio et al. 2020). Initially, OMP by terrestrial plants and particularly its contribution to global emissions have been intensely debated (Dueck et al. 2007; Kirschbaum et al. 2007; Beerling et al. 2008). Several studies have suggested much lower, but still potentially important CH₄ fluxes from terrestrial vegetation (Houweling et al. 2006; Butenhoff and Khalil 2007; Bloom et al. 2010) ranging from 0.2 to 125 Tg CH₄ year⁻¹. However, a few years later Carmichael et al. (2014) estimated that direct and indirect CH₄ emissions of vegetation represent a source strength of 32–143 Tg CH₄ yr⁻¹, accounting for roughly 5–22% of the total global CH₄ budget when considering ca. 645 Tg CH₄ yr⁻¹ as total global emissions to the atmosphere. In this approach, the indirect sources of vegetation including mainly cryptic wetlands, heartwood rot, CH₄ transport through herbaceous, and woody plants represent ca. 58–75% of the total contribution of fluxes from vegetation. The remaining direct emissions of CH₄ via the aerobic CH₄ production pathways were suggested to account for ca. 25–42% (9–60 Tg CH₄ yr⁻¹) of plant-based emissions.

However, there are still large uncertainties regarding the total source strength of direct CH₄ plant emissions (but also for the indirect plant emissions) and the underlying formation processes that drive OMP in plants. This is why in recent years numerous laboratory studies and investigations are dealing with mechanisms and emission rates of OMP by terrestrial plants (e.g., see reviews by McLeod and Keppler 2010; Wang

et al. 2013; Li et al. 2020b). Initial discrepancies between some studies that did not observe OMP (Dueck et al. 2007; Beerling et al. 2008) and several others that clearly identified OMP from terrestrial plants (McLeod et al. 2008; Vigano et al. 2008; Brüggemann et al. 2009) were later resolved by considering precursors and more detailed analyses of mechanisms of CH₄ release from dead and living plant matter. Keppler et al. (2006) suggested that the methoxy groups (OCH₃) of pectin were involved in CH₄ formation, which was confirmed by a study using pectin with deuterium (²H) labeled methoxy groups (Keppler et al. 2008). Extending this idea, Vigano et al. (2008), McLeod et al. (2008), and Bruhn et al. (2009) found that release of CH₄ from plant components such as lignin, cellulose, and pectin (Fig. 2) as well as dried and fresh leaves depends on UV light (including ambient sunlight), which was excluded in studies that could not find OMP.

Next to UV radiation, there are many other environmental factors and precursor compounds involved in controlling OMP in terrestrial plants. Brüggemann et al. (2009) showed CH₄ emissions from young poplar trees grown under low-light conditions and in the absence of UV-radiation. They applied a carbon isotope (¹³C) labeling method to unambiguously demonstrate that the poplar shoot cultures grown under sterile conditions produced ¹³C-labeled CH₄. The incubation experiments showed that after exposure of the poplar plants to labeled ¹³CO₂, a rapid transfer of ¹³C from assimilated ¹³CO₂ to ¹³CH₄ occurred indicating that freshly synthesized photosynthates contribute to OMP.

The production of ROS was highlighted by Messenger et al. (2009) as an important factor that controls UV-driven

CH₄ formation from plant matter. Applying ROS generators and ROS scavengers, they demonstrated that hydroxyl radicals (•OH) and singlet oxygen are involved in the generation of CH₄ from pectin. The formation of ROS might be the key for understanding the reaction pathways of nonarchaeal CH₄ formation from vegetation and could explain the large range of observed CH₄ emission rates from terrestrial plants. Cellular signaling processes as well as biotic and abiotic induced environmental stress factors involve ROS formation (Mittler 2017). In this context, McLeod et al. (2008) demonstrated CH₄ release by tobacco leaves when using chemical generators of ROS or a bacterial pathogen. Moreover, it was reported that water stress and temperature increased CH₄ release from several terrestrial plant species (Qaderi and Reid 2009). Other parameters such as blue light, light intensity, and addition of ethene (Martel and Qaderi 2019, 2021; Martel et al. 2020) were also found to control OMP from terrestrial plants. Wang et al. (2009, 2011) demonstrated CH₄ formation when plants were physically injured. Injury or infestation by pathogens of plants induces oxidative stress that is generally accompanied by enhanced emissions of volatile organic compounds (Davison et al. 2008). Thus, terrestrial plant CH₄ emissions might be considered as an additional integral part of this defense trait.

A step toward describing the pathway of plant-derived CH₄ formation was made by Wishkerman et al. (2011). These researchers applied sodium azide (NaN₃), a chemical that is known to stop the electron transport in plant mitochondria at the cytochrome c oxidase, to cell cultures of several terrestrial

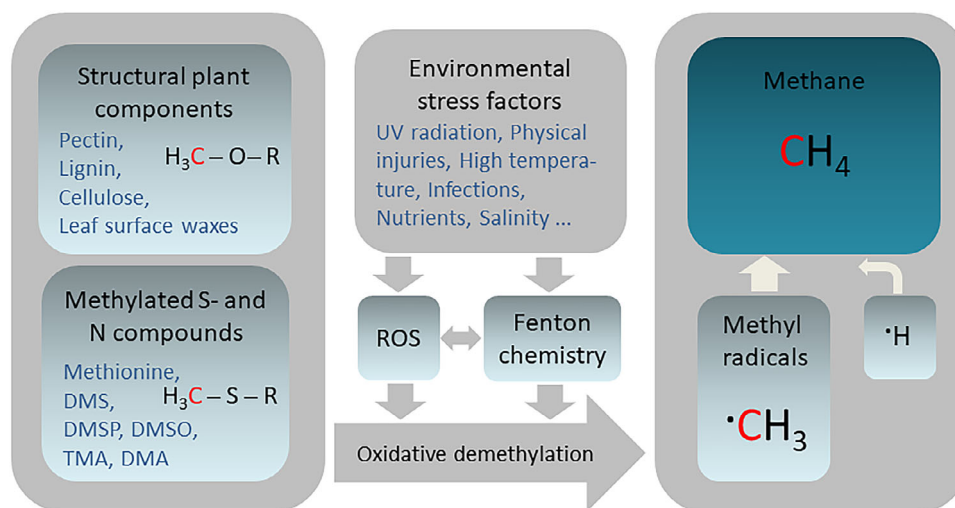


Fig. 2. Scheme of potential pathways of OMP in terrestrial plants. CH₄ can be formed under oxidative conditions from plant structural plant components such as pectin and lignin containing methoxy groups (OCH₃) or from methylated sulfur (S) or nitrogen (N) compounds such as DMSO, DMS, DMSP, TMA, or DMA. Metabolically active plant cells continuously form ROS such as H₂O₂, and in the presence of Fe(II)/Fe(III) induces Fenton chemistry which generates strong oxidants such as •OH radicals, or oxo-iron(IV) complexes ([Fe^{IV}=O]²⁺). These oxidants drive methyl radical production from hetero-bonded methyl groups. Finally, the methyl radical abstracts a hydrogen atom, most likely from an organic compound and forms CH₄. Environmental stress factors strongly affect levels of ROS and Fenton chemistry in plant cells and thus are expected to control CH₄ levels. Scheme adapted from McLeod et al. (2008), Liu et al. (2015), and Ernst et al. (2022).

plants that were grown under sterile conditions. The observed increase in CH_4 was seen as evidence that disruption of the electron transport chain leads to CH_4 production in plant cells supporting the idea that generation of CH_4 is a common feature of cellular responses and changes of the oxidative status present in living plants. In this context, it has been suggested that methylated sulfur and nitrogen compounds such as methionine or phosphatidylcholine might be methyl precursors of CH_4 in both stressed plants and animals (Qaderi and Reid 2009; Wishkerman et al. 2011; Bruhn et al. 2012).

Furthermore, a novel chemical route has been proposed that CH_4 can be formed from methylated organosulfur compounds such as methionine sulfoxide (MSO) and dimethylsulfoxide (DMSO) under oxidative conditions (Althoff et al. 2014; Benzing et al. 2017). Under Fenton-type conditions, that is, in the presence of Fe(II)/Fe(III) and hydrogen peroxide, non-heme oxo-iron (IV) catalyzes the formation of methyl radicals by demethylation of the methyl sulfoxide, eventually leading to CH_4 (Fig. 2). The importance of methionine and MSO was also hypothesized for CH_4 biosynthesis in living plants (Bruhn et al. 2012). This hypothesis received support from the application of stable carbon isotope techniques to lavender plants under physical stress. CH_4 emission rates and the stable carbon isotope values greatly increased when ^{13}C position-labeled methyl groups of methionine were applied to the plants (Lenhart et al. 2015, 2016). Ernst et al. (2022) eventually established this mechanism showing that free iron and ROS, which are generated by metabolic activity and enhanced by oxidative stress, induce methyl radical formation from organic compounds containing sulfur- or nitrogen-bonded methyl groups such

as occurring in methionine, DMSO, dimethylsulfide (DMS), or trimethylamine (TMA) (Fig. 2). Terrestrial plants thus clearly contribute to CH_4 formation under oxic conditions via several carbon precursors, and various environmental factors can control these processes (Wang et al. 2013, 2020; Liu et al. 2015).

Potential of submerged macrophytes for OMP

The phenomenon of OMP is widespread across disparate taxonomic groups including fungi (Lenhart et al. 2012), phytoplankton (Table 1), and terrestrial plants (Keppler et al. 2006) and is driven by pathways that cross taxonomic boundaries as recently shown by Ernst et al. (2022). Thus, all living organisms seem to have the potential for direct OMP by a ROS-driven pathway. In addition, aquatic plants are phylogenetically well dispersed across the angiosperms and, apart from four aquatic orders, evolved from terrestrial relatives (Du et al. 2015). They contain structural components such as cellulose, lignin, and pectin and produce methylated sulfur and nitrogen compounds that have been shown to be involved in OMP in terrestrial plants (Fig. 2) and many other organisms (Ernst et al. 2022). It is thus obvious to assume that marine and freshwater macroalgae and submerged macrophytes and their epiphytes could directly or indirectly contribute to all groups of CH_4 production in oxic waters mentioned in the introduction and support the CH_4 transport into oxic environments. In the following, we review existing studies on these processes and argue why they are also likely to occur in submerged macrophytes.

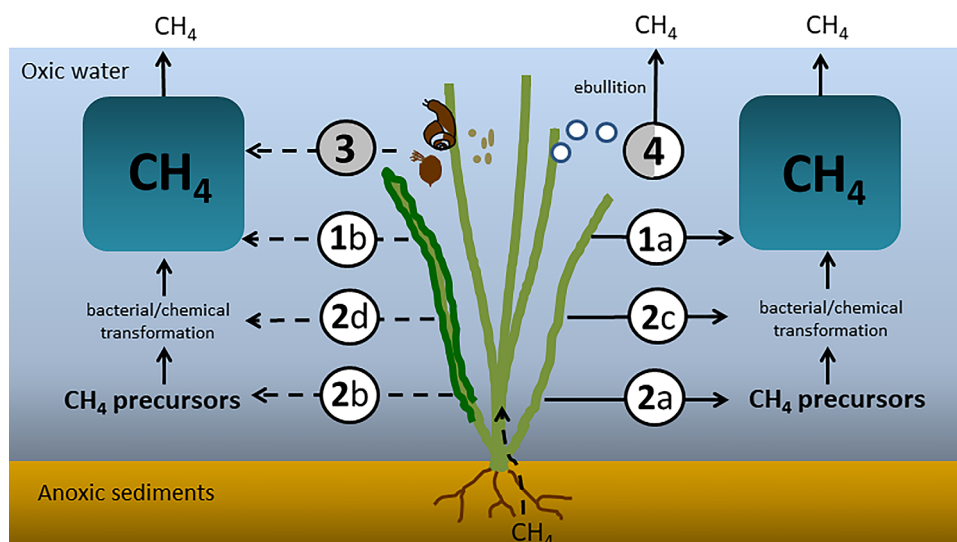


Fig. 3. Potential direct (black arrows) and indirect (dashed arrows) mechanisms by which submerged macrophytes may contribute to OMP in freshwater and marine ecosystems. 1: Direct oxic production of CH_4 by submerged macrophytes (a) and their endophytic or epiphytic archaea, algae, cyanobacteria, and proteobacteria (b); from structural components and precursors, 2: release of CH_4 precursors by submerged macrophytes (a) and their epiphytic bacteria, cyanobacteria, and algae (b) and facilitation of bacterial and chemical transformation of precursors to CH_4 by effects of macrophytes (c) or epiphytes (d) on redox conditions; 3: provision of habitat and refuge for CH_4 -producing organisms (zooplankton) and other food web related processes; 4: bubble formation at leaf surfaces and ebullition from lacunar gas transport. Gray circles indicate processes that involve anoxic CH_4 production in oxic water.

Direct CH₄ production by macrophytes and their epiphytes

Submerged macrophytes and macroalgae are hypothesized to directly contribute to CH₄ production in oxic environments by production of methylated compounds (process 1a in Fig. 3) that serve as CH₄ precursors which are transformed by a ROS-driven oxidative demethylation similar to terrestrial plants (Fig. 2).

Van Alstyne and Puglisi (2007) investigated the dimethylsulfoniopropionate (DMSP) content of 106 genera of marine macroalgae. Several red algal species of the genera *Poly-siphonia* and *Halopytis* had rather high DMSP concentrations (median \pm interquartile range: $23 \pm 123 \mu\text{mol g}^{-1}$ dry mass [DM]), while most red and brown algal species showed low DMSP concentrations (always below $3 \mu\text{mol g}^{-1}$ DM). Average DMSP concentrations in green macroalgae were higher ($41 \pm 82 \mu\text{mol g}^{-1}$ DM), especially in species of the order Ulvales, and increased with latitude in the northern hemisphere. DMSP concentrations among populations varied by an order of magnitude and were either environmentally induced or genetically determined, or affected by both (Van Alstyne and Puglisi 2007). Marine *Enteromorpha intestinalis* contained greater amounts of DMSP than freshwater conspecifics (Edwards et al. 1988). At least three different synthetic pathways used in the production of DMSP in algae and vascular plants have been reported which supports the existence of multiple evolutionary origins of DMSP production among all organisms (see review by Stefels (2000)). Dacey et al. (1994) argued that the occurrence of DMSP in three seagrass species (*Halodule wrightii*, *Syringodium filiforme*, and *Thalassia testudinum*) originates from epiphytic algae rather than the seagrass tissue. However, Borges and Champenois (2015) were able to prove that DMSP occurred in leaves of the seagrass *Posidonia oceanica*. After changing the preservation protocol of plant tissue from oven drying to freezing at -20°C , the measured DMSP content rose by two orders of magnitude, implying that freezing adequately conserves the tissue for DMSP analysis. So far, *P. oceanica* has the highest DMSP production among marine autotrophs and integrated DMSP stocks are several orders of magnitude higher than those of phytoplankton (Borges and Champenois 2017). Several methylated compounds (dimethylamine [DMA], dimethylsulfide [DMS], and methanol) were found to stimulate CH₄ production in sediment incubations vegetated by *P. oceanica* (Schorn et al. 2022).

A release of CH₄ from structural components of terrestrial plants such as cellulose, lignin, and pectin has been shown in several studies (see above). A similar process seems likely for submerged macrophytes and macroalgae. Submerged macrophytes have variable cellulose and lignin concentrations ($104\text{--}387 \text{ mg g}^{-1}$ dry weight and $3\text{--}192 \text{ mg g}^{-1}$ dry weight, respectively, were measured in 10 macrophyte species by Schoelynck et al. 2010). Pectin containing substances can also be found in freshwater angiosperms (Popov et al. 2007) and charophytes (Cherno et al. 1976) as well as in marine seagrasses (Gloaguen

et al. 2010; Khotimchenko et al. 2012). For terrestrial vegetation, UV light was considered an important environmental factor that controls OMP from the plant components lignin and pectin. However, UV light is strongly attenuated in natural waters depending on water depth (McLeod et al. 2021) and the concentration of cDOM (Bricaud et al. 1981). The UV-driven pathway of CH₄ formation might thus be less important in aquatic ecosystems as compared to terrestrial systems (see above). However, other environmental factors might also be important (Fig. 2). In an experiment with sediment and lake water in bottles that were incubated in the dark for 20 h, the addition of submerged macrophyte biomass (*Elodea nuttallii*) doubled the potential CH₄ production rates (Harpenslager et al. In press) and direct CH₄ production by the macrophytes is a potential explanation.

Submerged macrophytes provide substantial surface for epiphyton growth, on average $1000 \text{ cm}^2 \text{ g dry weight}^{-1}$ (Fischer and Pusch 2001). Several recent studies demonstrate a direct CH₄ production by cyanobacteria and eukaryotic algae during photosynthesis (Table 1; see also Bižić-Ionescu et al. 2018), which might be linked to the ROS-induced oxidative methylation of methyl donors (Fig. 2; Ernst et al. 2022). These organism groups can also be abundant in the epiphyton on macrophyte surfaces (Laugaste and Reunanen 2005) and thus potentially contribute to OMP in macrophyte stands (process 1b in Fig. 3).

Release of precursors by macrophytes and epiphyton and facilitation of their transformation to CH₄

Submerged macrophytes and their epiphyton are also hypothesized to contribute to CH₄ production in oxic environments by a release of CH₄ precursors and a facilitation of their bacterial and/or chemical breakdown into CH₄ (processes 2c,d in Fig. 3).

Submerged macrophytes release 1–10% of the amount of C they fix photosynthetically as dissolved organic carbon (Carpenter and Lodge 1986; Paine et al. 2021), including cDOM (Zhang et al. 2013). DOC release rates of up to $157 \mu\text{g C}\cdot\text{g dw}^{-1}\cdot\text{h}^{-1}$ were measured from macrophyte epiphyte complexes by Demarty and Prairie (2009). Several methylated compounds, among others methylated sulfur compounds such as DMSP and DMS (Sunda et al. 2002; Neufeld et al. 2008), can be used by bacteria for methylotrophic methanogenesis (Sowers and Ferry 1983; Damm et al. 2010). Abiotic CH₄ photoproduction from cDOM has been found to significantly contribute to oceanic OMP (Li et al. 2020) and macrophytes could significantly contribute to this process by their cDOM release. However, cDOM also limits the penetration of UV light into the water column (Bricaud et al. 1981; Zhang et al. 2013) and thus might counteract direct UV-driven OMP from macrophytes (see above).

Submerged macrophytes and their epiphyton are hypothesized to facilitate the bacterial and chemical transformation of precursors into CH₄ by photosynthesis and by respiration that

can lead to anoxic conditions within dense stands (Vilas et al. 2017). Anoxic conditions allow for the conversion of methylated organic compounds to CH_4 via methylotrophic methanogens, which also use the classic methyl-coenzyme A mediated pathway to convert the methyl-group to CH_4 in the absence of oxygen (Yin et al. 2019).

Facilitation of classic methanogenesis inside of macrophytes and macrophyte stands

Similar to trees (Covey and Megonigal 2019; Yip et al. 2019), submerged macrophytes may support CH_4 production by endophytic methanogenic archaea in anaerobic microsites inside of the plants. Macrophyte stands also provide a habitat for several aquatic organism groups that produce CH_4 via classic methanogenesis in an otherwise aerobic water column. Marine zooplankton produces CH_4 in anoxic microzones (De Angelis and Lee 1994; Schmale et al. 2018) and snails have been shown to promote CH_4 release from freshwater lakes (Xu et al. 2014). Provision of shelter for zooplankton and macroinvertebrates has been observed for marine kelps (Pakhomov et al. 2002), seagrass stands (Robertson et al. 1988), and freshwater submerged macrophytes (Timms and Moss 1984). We thus infer that an increased abundance of zooplankton and snails in macrophyte stands indirectly facilitates the production of CH_4 in oxic zones close to the water surface and hence atmospheric CH_4 emissions (process 3 in Fig. 3). However, *Daphnia* sp. has also been shown to feed on CH_4 oxidizing bacteria, and a reduced zooplankton density by top-down effects of fish increased the abundance of methanotrophic bacteria, which in turn reduced CH_4 efflux rates by roughly 10 times (Devlin et al. 2015). Such effects could be offset by the positive effects of submerged vegetation on piscivorous pike (*Esox lucius*) providing top-down control on planktivorous fish (Chapman and Mackay 1984). The different effects of submerged macrophytes on aquatic food web dynamics may thus lead to an increase or reduction of CH_4 production and emission from oxic zones. Anoxic conditions in dense macrophyte stands at night should also allow for classic methanogenesis by archaea, that is, hydrogenotrophic and acetoclastic (Conrad 2005 and references therein).

Facilitation of bubble formation and ebullition

Emission of photosynthetically produced oxygen in submerged macrophytes can be found as bubbles released from either the stomata or from openings originating from herbivory or other injuries. A short single sound pulse which can be measured acoustically is emitted by the bubble of oxygen during escape (Kratochvil and Pollirer 2017; Ballard et al. 2020). These bubbles could also contain CH_4 which would be released by ebullition (process 4 in Fig. 3) and thus escape CH_4 oxidation in the water column. In addition, most of the internal volume of macrophyte stems and roots is composed of a network of enlarged intercellular airspaces known as gas

lacunae or aerenchyma. In many emergent and floating-leaved macrophyte species, convective flow is an important mechanism of lacunar gas transport. Heilman and Carlton (2001b) measured an ebullitive release of sediment-produced CH_4 from submerged floral spikes of two pondweed species. Herbivores such as waterfowl, fish, or invertebrates (Bakker et al. 2016) could facilitate CH_4 ebullition from submerged macrophytes by injuries. For example, Dingemans et al. (2011) found significantly higher CH_4 release from grazed helophytes. Winton and Richardson (2017) reported an inhibition of CH_4 oxidation by herbivory in wetlands and thus increased emissions due to a lower belowground biomass and thus retardation of aerenchymous stems transporting oxygen into wetland soils. Yet, studies on herbivores affecting OMP in submerged macrophyte stands are still lacking.

Additional indirect mechanisms and macrophyte-related processes that counterbalance OMP

Many other processes potentially affecting macrophyte-related CH_4 emissions are still largely unknown, but should be considered in the future to better understand greenhouse gas dynamics in the large variety of macrophyte stands in fresh, brackish, and marine waters. Examples include physical effects of submerged macrophytes on stratification (Herb and Stefan 2005) and wind-induced mixing (Andersen et al. 2017) which might affect bubble formation and ebullition. Phenolic substances produced by several marine and freshwater macrophytes (Gross 2003) may differentially influence CH_4 producers and oxidizers in the plants, epiphyton, and the open water and thus may indirectly affect OMP. Grutters et al. (2017) did not find any inhibitory effect of polyphenol-rich submerged macrophytes on diffusive CH_4 emissions.

OMP by submerged macrophyte stands may have been overlooked in previous studies due to subsequent methanotrophy or other parallel CH_4 oxidation processes that counterbalance OMP. The balance between OMP and CH_4 oxidation may depend on the presence of specific environmental conditions and may show diurnal and seasonal changes, which needs to be taken into account for overall CH_4 flux estimates. Disentangling these counteracting processes still requires some methodological development. A higher temporal-spatial resolution of data, omic approaches and methods such as bottle incubations and mass budgets incorporating CH_4 stable carbon and hydrogen isotope data allow detecting different CH_4 sources (Günthel et al. 2021) but have not yet been applied in combination.

Heilman and Carlton (2001a) showed that epiphytic CH_4 -oxidizing bacteria play an important role in the regulation of CH_4 emissions from submerged macrophytes. Sorrell et al. (2002) also found methanotrophic bacteria associated with root and shoot tissues of 8 out of 13 tested submerged macrophytes. Methanotrophic activity was highest in plants from eutrophic habitats. The possibility of harboring methanotrophs inside of plant tissues has been reported for

Sphagnum mosses (Kostka et al. 2016). Yoshida et al. (2014) measured CH₄ consumption activities in several submerged macrophyte species which were up to a hundred times higher than activities measured in roots of rice.

Potential consequences of macrophyte OMP for global CH₄ emissions of aquatic systems

Macrophyte vegetation (angiosperms and macroalgae) has a vast global distribution and is very productive. The global abundance of seagrass was recently estimated to range from a mapped area of at least 160,387 km² (McKenzie et al. 2020) to a modeled area of 1.6 million km² (Jayatilake and Costello 2018; Dunic et al. 2021). Macroalgae dominate in coastal ecosystems and contribute 5–10% of global primary production (Mann 1973; Smith 1981; Charpy-Roubaud and Sournia 1990). Similar estimations are lacking for freshwater submerged macrophytes, but they often dominate the primary production of abundant water bodies such as shallow lakes (Brothers et al. 2013) or lowland rivers (Hilt et al. 2011).

Macrophytes have experienced major dynamics in terms of large-scale decline in keystone species (Waycott et al. 2009; Araújo et al. 2016; Zhang et al. 2017) and blooms of opportunistic species (Hussner et al. 2017; Vadeboncoeur et al. 2021) due to various stressors. The associated effects on CH₄ emissions are largely unknown (Hilt et al. 2017), but are even more important to be quantified given their potential role for OMP. Macrophytes also play a major role in carbon sequestration (Macreadie et al. 2021) and the quantification of their role in CH₄ production is also important for better evaluation of the net carbon sequestration of macrophyte-dominated ecosystems.

Summary and outlook

Our review suggests that freshwater and marine submerged macrophytes and macroalgae directly and indirectly contribute to OMP (Fig. 3) by:

1. (a) Direct ROS driven CH₄ production from methylated sulfur and nitrogen compounds such as DMSO, DMSP, DMS, TMA, and DMA and structural components such as cellulose, lignin, and pectin.
(b) Facilitation of direct OMP by endophytic or epiphytic archaea, algae, cyanobacteria, and proteobacteria.
2. (a) Release of CH₄ precursors and colored organic matter for bacterial breakdown or chemical conversion.
(b) Facilitation of production and release of CH₄ precursors and colored organic matter by epiphytic algae, cyanobacteria, and proteobacteria.
(c) Facilitation of bacterial breakdown of CH₄ precursors and colored organic matter as well as their chemical conversion by modifying oxygen conditions.
(d) Increased bacterial breakdown of CH₄ precursors and colored organic matter by providing surface for attached bacteria.
3. Facilitation of classic methanogenesis by providing anoxic conditions for archaea inside the plants and in the biofilm;

and habitat as well as shelter for zooplankton producing CH₄ and snails promoting CH₄ emissions.

4. Facilitation of CH₄ (produced in macrophytes or by microbes in sediments) ebullition by lacunar gas transport and bubble formation at macrophyte leaf surfaces.

Changes in the spatial and temporal abundance of submerged macrophytes will substantially impact CH₄ emissions from aquatic areas with high abundance of submerged vegetation such as wetlands, ponds, shallow lakes, and littoral zones of deeper lakes and reservoirs, shallow brackish habitats, and coastal zones of oceans. Yet, we need specific laboratory and field measurements for direct evidence of OMP in submerged vegetation through our suggested mechanisms leading to CH₄ formation in oxic waters. Addition of labeled ¹³C to macrophytes grown under sterile conditions and subsequent determination of released ¹³C-labeled CH₄ can be carried out similar to the methods applied to detect OMP in terrestrial plants. In a similar way, supplementation of isotopically labeled methylated sulfur and nitrogen compounds might help with identifying and constraining potential CH₄ precursors from macrophytes. In addition, field measurements are needed to determine the role of submerged vegetation in the delicate balance between physical, chemical, and biological mechanisms affecting OMP and oxidation. Understanding the role of submerged macrophytes for aquatic OMP is thus essential to reduce current uncertainties in global assessments of CH₄ emissions from aquatic ecosystems to allow for improved mitigation measures and more sustainable ecosystem management.

References

- Althoff, F., K. Benzing, P. Comba, C. McRoberts, D. R. Boyd, S. Greiner, and F. Keppler. 2014. Abiotic methanogenesis from organosulphur compounds under ambient conditions. *Nat. Commun.* **5**: 4205.
- Andersen, R. M., K. Sand-Jensen, I. Woolway, and I. D. Jones. 2017. Profound daily vertical stratification and mixing in a small, shallow, wind-exposed lake with submerged macrophytes. *Aquat. Sci.* **79**: 395–406.
- Araújo, R. M., and others. 2016. Status, trends and drivers of kelp forests in Europe: An expert assessment. *Biodivers. Conserv.* **25**: 1319–1348.
- Bakker, E. S., K. Wood, J. F. Pages, G. F. Veen, M. J. A. Christianen, L. Santamaria, B. Nolet, and S. Hilt. 2016. Herbivory on freshwater and marine macrophytes: A review and perspective. *Aquat. Bot.* **135**: 18–36.
- Ballard, M. S., K. M. Lee, J. D. Sagers, G. R. Venegas, A. R. McNeese, P. S. Wilson, and A. F. Rahman. 2020. Application of acoustical remote sensing techniques for ecosystem monitoring of a seagrass meadow. *J. Acoust. Soc. Am.* **147**: 2002–2019.

- Beerling, D. J., T. Gradiner, G. Leggett, A. McLeod, and W. P. Quick. 2008. Missing methane emissions from leaves of terrestrial plants. *Glob. Change Biol.* **14**: 1–6.
- Benzing, K., P. Comba, B. Martin, B. Pokrandt, and F. Keppler. 2017. Nonheme iron-oxo-catalyzed methane formation from methyl thioethers: Scope, mechanism, and relevance for natural systems. *Chem. A Eur. J.* **23**: 10465–10472.
- Bižić-Ionescu, M., D. Ionescu, M. Günthel, K. W. Tang, and H. P. Grossart. 2018. Oxic methane cycling: New evidence for methane formation in oxic lake water. *In* A. J. M. Stams and D. Z. Sousa [eds.], *Biogenesis of hydrocarbons, handbook of hydrocarbon and lipid microbiology*. Springer International Publishing.
- Bižić, M., and others. 2020. Aquatic and terrestrial cyanobacteria produce methane. *Sci. Adv.* **6**: eaax5343.
- Bloom, A. A., J. Lee-Taylor, S. Madronich, D. J. Messenger, P. I. Palmer, D. S. Reay, and A. R. McLeod. 2010. Global methane emission estimates from ultraviolet irradiation of terrestrial plant foliage. *New Phytol.* **187**: 417–425.
- Bodmer, P., R. Vroom, T. Stepina, P. del Giorgio, and S. Kosten. 2021. Methane fluxes of vegetated areas in natural freshwater ecosystems: Assessments and global significance. *EarthArXiv*.
- Bogard, M., P. A. del Giorgio, L. Boutet, M. C. Garcia Chaves, Y. T. Prairie, A. Merante, and A. M. Derry. 2014. Oxic water column methanogenesis as a major component of aquatic CH₄ fluxes. *Nat. Commun.* **5**: 5350.
- Borges, A. V., and W. Champenois. 2015. Seasonal and spatial variability of dimethylsulfonio-propionate (DMSP) in the Mediterranean seagrass *Posidonia oceanica*. *Aquat. Bot.* **125**: 72–79.
- Borges, A. V., and W. Champenois. 2017. Preservation protocol for dimethyl-sulfoniopropionate and dimethylsulfoxide analysis in plant material of the Mediterranean seagrass *Posidonia oceanica*, and re-evaluation of dimethylsulfoniopropionate leaf content. *Aquat. Bot.* **143**: 8–10.
- Bricaud, A., A. Morel, and L. Prieur. 1981. Absorption by dissolved organic matter of the sea (yellow substance) in the UV and visible domains. *Limnol. Oceanogr.* **26**: 43–53.
- Brothers, S., S. Hilt, S. Meyer, and J. Köhler. 2013. Plant community structure determines primary productivity in shallow, eutrophic lakes. *Freshw. Biol.* **58**: 2264–2276.
- Brüggemann, N., R. Meier, D. Steigner, I. Zimmer, S. Louis, and J. P. Schnitzler. 2009. Nonmicrobial aerobic methane emission from poplar shoot cultures under low-light conditions. *New Phytol.* **182**: 912–918.
- Bruhn, D., T. N. Mikkelsen, J. Øbro, W. G. T. Willats, and P. Ambus. 2009. Effects of temperature, ultraviolet radiation and pectin methyl esterase on aerobic methane release from plant material. *Plant Biol.* **11**: 43–48.
- Bruhn, D., I. M. Moller, T. N. Mikkelsen, and P. Ambus. 2012. Terrestrial plant methane production and emission. *Physiol. Plant.* **144**: 201–209.
- Butenhoff, C. L., and M. A. K. Khalil. 2007. Global methane emissions from terrestrial plants. *Environ. Sci. Technol.* **41**: 4032.
- Carmichael, M. J., E. S. Bernhardt, S. L. Bräuer, and W. K. Smith. 2014. The role of vegetation in methane flux to the atmosphere: Should vegetation be included as a distinct category in the global methane budget? *Biogeochemistry* **119**: 1–24.
- Carini, P., A. White, E. Campbell, and S. J. Giovannoni. 2014. Methane production by phosphate-starved SAR11 chemoheterotrophic marine bacteria. *Nat. Commun.* **5**: 4346.
- Carpenter, S. R., and D. M. Lodge. 1986. Effects of submersed macrophytes on ecosystem processes. *Aquat. Bot.* **26**: 341–370.
- Chapman, C. A., and W. C. Mackay. 1984. Versatility in habitat use by a top aquatic predator, *Esox lucius*. *J. Fish Biol.* **25**: 109–115.
- Charpy-Roubaud, C., and A. Sournia. 1990. The comparative estimation of phytoplanktonic, microphytobenthic and macrophytobenthic production in the oceans. *Mar. Microb. Food Webs* **4**: 31–57.
- Cherno, N. K., M. S. Dudkin, and I. V. Areshidze. 1976. Pectin substances of *Chara aculeolata*. *Khim. Prir. Soedin.* **6**: 702–705.
- Conrad, R. 2005. Quantification of methanogenic pathways using stable carbon isotopic signatures: A review and a proposal. *Org. Geochem.* **36**: 739–752.
- Covey, K. R., and J. P. Megonigal. 2019. Methane production and emissions in trees and forests. *New Phytol.* **222**: 35–51.
- Cronin, G., W. M. Lewis Jr., and M. A. Schiehsler. 2006. Influence of freshwater macrophytes on the littoral ecosystem structure and function of a young Colorado reservoir. *Aquat. Bot.* **85**: 37–43.
- Dacey, J. W. H., G. M. King, and P. S. Lobel. 1994. Herbivory by reef fishes and the production of dimethylsulfide and acrylic acid. *Mar. Ecol. Prog. Ser.* **112**: 67–74.
- Damm, E., E. Helmke, S. Thoms, U. Schauer, E. Nothig, K. Bakker, and R. P. Kiene. 2010. Methane production in aerobic oligotrophic surface water in the central Arctic Ocean. *Biogeosciences* **7**: 1099–1108.
- Davison, B., A. Brunner, C. Ammann, C. Spirig, M. Jocher, and A. Neftel. 2008. Cut-induced VOC emissions from agricultural grasslands. *Plant Biol.* **10**: 76–85.
- De Angelis, M. A., and C. Lee. 1994. Methane production during zooplankton grazing on marine phytoplankton. *Limnol. Oceanogr.* **39**: 1298–1308.
- Demarty, M., and Y. T. Prairie. 2009. In situ dissolved organic carbon (DOC) release by submerged macrophyte-epiphyte communities in southern Quebec lakes. *Can. J. Fish. Aquat. Sci.* **66**: 1522–1531.
- Devlin, S. P., J. Saarenheimo, J. Syväranta, and R. I. Jones. 2015. Top consumer abundance influences lake methane efflux. *Nat. Commun.* **6**: 8787.

- Dingemans, B. J. J., E. S. Bakker, and P. L. E. Bodelier. 2011. Aquatic herbivores facilitate the emission of methane from wetlands. *Ecology* **92**: 1166–1173.
- Donis, D., S. Flury, A. Stöckli, J. E. Spangenberg, D. Vachon, and D. F. McGinnis. 2017. Full-scale evaluation of methane production under oxic conditions in a mesotrophic lake. *Nat. Commun.* **8**: 1661.
- Du, Z. Y., Q. F. Wang, and China Phylogeny Consortium. 2015. Phylogenetic tree of vascular plants reveals the origins of aquatic angiosperms. *J. Syst. Evol.* **54**: 342–348.
- Dueck, T. A., and others. 2007. No evidence for substantial aerobic methane emission by terrestrial plants: A ^{13}C -labelling approach. *New Phytol.* **175**: 29–35.
- Dunic, J. C., C. J. Brown, R. M. Connolly, M. P. Turschwell, and I. M. Côté. 2021. Long-term declines and recovery of meadow area across the world's seagrass bioregions. *Glob. Chang. Biol.* **27**: 4096–4109.
- Edwards, D. M., R. H. Reed, and W. D. P. Stewart. 1988. Osmoacclimation in *Enteromorpha intestinalis*: Long-term effects of osmotic stress on organic solute accumulation. *Mar. Biol.* **98**: 467–476.
- Ernst, L., and others. 2022. Methane formation driven by reactive oxygen species across all living organism. *Nature* **603**: 482–487.
- Fischer, H., and M. Pusch. 2001. Comparison of bacterial production in sediments, epiphyton and the pelagic zone of a lowland river. *Freshw. Biol.* **46**: 1335–1348.
- Florez-Leiva, L., E. Damm, and L. Farias. 2013. Methane production induced by dimethylsulfide in surface water of an upwelling ecosystem. *Prog. Oceanogr.* **112–113**: 38–48.
- Garcias-Bonet, N., and C. M. Duarte. 2017. Methane production by seagrass ecosystems in the Red Sea. *Front. Mar. Sci.* **4**: 340.
- Gloaguen, V., and others. 2010. Structural characterization and cytotoxic properties of an apiose-rich pectic polysaccharide obtained from the cell wall of the marine phanerogam *Zostera marina*. *J. Nat. Prod.* **73**: 1087–1092.
- Grasset, C., G. Abril, R. Mendonca, F. Roland, and S. Sobek. 2019. The transformation of macrophyte-derived organic matter to methane relates to plant water and nutrient content. *Limnol. Oceanogr.* **64**: 1737–1749.
- Gross, E. M. 2003. Allelopathy of aquatic autotrophs. *Crit. Rev. Plant Sci.* **22**: 313–339.
- Grossart, H. P., K. Frindte, C. Dziallas, W. Eckert, and K. W. Tang. 2011. Microbial methane production in oxygenated water column of an oligotrophic lake. *PNAS* **108**: 19657–19661.
- Grutters, B. M. C., R. C. H. Aben, S. Kosten, and E. S. Bakker. 2017. Impact of native and non-native aquatic plants on methane emission and phytoplankton growth. *Aquat. Invasions* **12**: 371–383.
- Gülzow, W., G. Rehder, J. S. von Deimling, T. Seifert, and Z. Toth. 2013. One year of continuous measurements constraining methane emissions from the Baltic Sea to the atmosphere using a ship of opportunity. *Biogeosciences* **10**: 81–99.
- Günthel, M., D. Donis, G. Kirillin, D. Ionescu, M. Bizic, D. F. McGinnis, H. P. Grossart, and K. W. Tang. 2019. Contribution of oxic methane production to surface methane emission in lakes and its global importance. *Nat. Commun.* **10**: 5497.
- Günthel, M., D. Donis, G. Kirillin, D. Ionescu, M. Bizic, D. F. McGinnis, H. P. Grossart, and K. W. Tang. 2021. Reply to 'Oxic methanogenesis is only a minor source of lake-wide diffusive CH_4 emissions from lakes'. *Nat. Commun.* **12**: 1205.
- Harpenslager, S. F., K. Thiemer, C. Levertz, B. Misteli, K. Sebola, S. C. Schneider, S. Hilt, and J. Köhler. Forthcoming. Short-term effects of macrophyte removal on emission of CO_2 and CH_4 in shallow lakes. *Aquat. Bot.*
- Hartmann, J. F., M. Günthel, T. Klintzsch, G. Kirillin, H. P. Grossart, F. Keppler, and M. Isenbeck-Schröter. 2020. High spatiotemporal dynamics of methane production and emission in oxic surface water. *Environ. Sci. Technol.* **54**: 1451–1463.
- Heilman, M. A., and R. G. Carlton. 2001a. Methane oxidation associated with submersed vascular macrophytes and its impact on plant diffusive methane flux. *Biogeochemistry* **52**: 207–224.
- Heilman, M. A., and R. G. Carlton. 2001b. Ebullitive release of lacunar gases from floral spikes of *Potamogeton angustifolius* and *Potamogeton amplifolius*: Effects on plant aeration and sediment CH_4 flux. *Aquat. Bot.* **71**: 19–33.
- Herb, W. R., and H. G. Stefan. 2005. Dynamics of vertical mixing in a shallow lake with submersed macrophytes. *Water Resour. Res.* **41**: W02023.
- Hilt, S., J. Köhler, H. P. Kozerski, M. Scheffer, and E. van Nes. 2011. Abrupt regime shifts in space and time along rivers and connected lakes systems. *Oikos* **120**: 766–775.
- Hilt, S., S. Brothers, E. Jeppesen, A. Veraart, and S. Kosten. 2017. Translating regime shifts in shallow lakes into changes in ecosystem functions and services. *Bioscience* **67**: 928–936.
- Houweling, S., T. Rockmann, I. Aben, F. Keppler, M. Krol, J. F. Meirink, E. J. Dlugokencky, and C. Frankenberg. 2006. Atmospheric constraints on global emissions of methane from plants. *Geophys. Res. Lett.* **33**: L15821.
- Hussner, A., and others. 2017. Management and control methods of invasive alien freshwater aquatic plants: A review. *Aquat. Bot.* **136**: 112–137.
- Jakobs, G., P. Holtermann, C. Berndmeyer, G. Rehder, M. Blumenberg, G. Jost, G. Nausch, and O. Schmale. 2014. Seasonal and spatial methane dynamics in the water column of the central Baltic Sea (Gotland Sea). *Cont. Shelf Res.* **91**: 12–25.
- Jayathilake, D. R., and M. J. Costello. 2018. A modelled global distribution of the seagrass biome. *Biol. Conserv.* **226**: 120–126.
- Karl, D. M., and B. D. Tilbrook. 1994. Production and transport of methane in oceanic particulate organic matter. *Nature* **368**: 732–734.

- Karl, D. M., L. Beversdorf, K. M. Bjorkman, M. J. Church, A. Martinez, and E. F. Delong. 2008. Aerobic production of methane in the sea. *Nat. Geosci.* **1**: 473–478.
- Keppler, F., J. T. G. Hamilton, M. Braß, and T. Röckmann. 2006. Methane emissions from terrestrial plants under aerobic conditions. *Nature* **439**: 187.
- Keppler, F., J. T. G. Hamilton, W. C. McRoberts, I. Vigano, M. Braß, and T. Röckmann. 2008. Methoxyl groups of plant pectin as a precursor of atmospheric methane: Evidence from deuterium labelling studies. *New Phytol.* **178**: 808–814.
- Keppler, F., M. Boros, C. Frankenberg, J. Lelieveld, A. R. McLeod, A. M. Pirtilä, T. Röckmann, and J. P. Schnitzler. 2009. Methane formation in aerobic environments. *Environ. Chem.* **6**: 459–465.
- Khatun, S., and others. 2019. Aerobic methane production by planktonic microbes in lakes. *Sci. Total Environ.* **696**: 133916.
- Kirschbaum, M. U. F., U. Niinemets, D. Bruhn, and A. J. Winters. 2007. How important is aerobic methane release by plants? p. 138–145. *In* Functional plant science and biotechnology. Global Science Books.
- Klitzsch, T., G. Lange, A. Wieland, H. Geisinger, K. Lenhart, G. Nehrke, and F. Keppler. 2020. Effects of temperature and light on methane production of widespread marine phytoplankton. *Eur. J. Vasc. Endovasc. Surg.* **125**: e2020JG005793.
- Klitzsch, T., G. Langer, G. Nehrke, A. Wieland, K. Lenhart, and F. Keppler. 2019. Methane production by three widespread marine phytoplankton species: Release rates, precursor compounds, and potential relevance for the environment. *Biogeosciences* **16**: 4129–4144.
- Khotimchenko, Y., E. Khozhaenko, V. Kovalev, and M. Khotimchenko. 2012. Cerium binding activity of pectins isolated from the seagrasses *Zostera marina* and *Phyllospadix watensis*. *Mar. Drugs* **10**: 834–848.
- Kostka, J. E., D. J. Weston, J. B. Glass, E. A. Lilleskov, A. J. Shaw, and M. R. Turetsky. 2016. The *Sphagnum* microbiome: New insights from an ancient plant lineage. *New Phytol.* **211**: 57–64.
- Kratochvil, H. G., and M. Pollirer. 2017. Acoustic effects during photosynthesis of aquatic plants enable new research opportunities. *Sci. Rep.* **7**: 44526.
- Laanbroek, H. J. 2010. Methane emission from natural wetlands: Interplay between emergent macrophytes and soil microbial processes. A mini-review. *Ann Bot.* **105**: 141–153.
- Laugaste, R., and M. Reunanen. 2005. The composition and density of epiphyton on some macrophyte species in the partly meromictic Lake Verevi. *Hydrobiologia* **547**: 137–150.
- Lenhart, K., and others. 2012. Evidence for methane production by saprotrophic fungi. *Nat. Commun.* **3**: 1046.
- Lenhart, K., F. Althoff, M. Greule, and F. Keppler. 2015. Technical note: Methionine, a precursor of methane in living plants. *Biogeosciences* **12**: 1907–1914.
- Lenhart, K., T. Klitzsch, G. Langer, G. Nehrke, M. Bunge, S. Schnell, and F. Keppler. 2016. Evidence for methane production by the marine algae *Emiliania huxleyi*. *Biogeosciences* **13**: 3163–3174.
- Leon-Palmero, E., A. Contreras-Ruiz, A. Sierra, R. Morales-Baquero, and I. Reche. 2020. Dissolved CH₄ coupled to photosynthetic picoeukaryotes in oxic waters and to cumulative chlorophyll a in anoxic waters of reservoirs. *Biogeosciences* **17**: 3223–3245.
- Li, Y., C. G. Fichot, L. Geng, M. G. Scarratt, and H. Xie. 2020a. The contribution of methane photoproduction to the oceanic methane paradox. *Geophys. Res. Lett.* **47**: e2020GL088362.
- Li, L., S. Wei, and W. Shen. 2020b. The role of methane in plant physiology: A review. *Plant Cell Rep.* **39**: 171–179.
- Liu, J., H. Chen, Q. Zhu, Y. Shen, X. Wang, M. Wang, and C. Peng. 2015. A novel pathway of direct methane production and emission by eukaryotes including plants, animals and fungi: An overview. *Atmos. Environ.* **115**: 26–35.
- Macreadie, P. I., and others. 2021. Blue carbon as a natural climate solution. *Nat. Rev. Earth Environ.* **2**: 826–839.
- Mann, K. H. 1973. Seaweeds: Their productivity and strategy for growth. *Science* **182**: 975–981.
- Martel, A. B., and M. M. Qaderi. 2019. Unravelling the effects of blue light on aerobic methane emissions from canola. *J. Plant Physiol.* **233**: 12–19.
- Martel, A. B., and M. M. Qaderi. 2021. Exogenous ethylene increases methane emissions from canola by adversely affecting plant growth and physiological processes. *Botany* **99**: 421–431.
- Martel, A. B., A. E. Taylor, and M. M. Qaderi. 2020. Individual and interactive effects of temperature and light intensity on canola growth, physiological characteristics and methane emissions. *Plant Physiol. Biochem.* **157**: 160–168.
- McGinnis, D. F., G. Kirillin, K. W. Tang, S. Flury, P. Bodmer, C. Engelhardt, P. Casper, and H. P. Grossart. 2015. Enhancing surface methane fluxes from an oligotrophic lake: Exploring the microbubble hypothesis. *Environ. Sci. Tech.* **49**: 873–880.
- McKenzie, L. J., L. M. Nordlund, B. L. Jones, L. C. Cullen-Unsworth, C. Roelfsema, and R. K. Unsworth. 2020. The global distribution of seagrass meadows. *Environ. Res. Lett.* **15**: 074041.
- McLeod, A. R., S. C. Fry, G. J. Loake, D. J. Messenger, D. S. Reay, K. A. Smith, and B. W. Yum. 2008. Ultraviolet radiation drives methane emissions from terrestrial plant pectins. *New Phytol.* **180**: 124–132.
- McLeod, A. R., and F. Keppler. 2010. Methane from vegetation, p. 74–96. *In* D. Reay, P. Smith, and A. van Amstel [eds.], Methane and climate change. Earthscan Ltd.
- McLeod, A. R., T. Brand, C. N. Campbell, K. Davidson, and A. D. Hatton. 2021. Ultraviolet radiation drives emission of climate-relevant gases from marine phytoplankton. *JGR. Biogeosciences* **126**: e2021JG006345.

- Messenger, D. J., A. R. McLeod, and S. C. Fry. 2009. The role of ultraviolet radiation, photosensitizers, reactive oxygen species and ester groups in mechanisms of methane formation from pectin. *Plant Cell Environ.* **32**: 1–9.
- Mittler, R. 2017. ROS are good. *Trends Plant Sci.* **22**: 11–19.
- Natchimuthu, S., B. P. Selvam, and D. Bastviken. 2014. Influence of weather variables on methane and carbon dioxide flux from a shallow pond. *Biogeochemistry* **119**: 403–413.
- Neufeld, J. D., R. Boden, H. Moussard, H. Schäfer, and J. C. Murrell. 2008. Substrate-specific clades of active marine methylotrophs associated with a phytoplankton bloom in a temperate coastal environment. *Appl. Environ. Microbiol.* **74**: 7321–7328.
- Oremland, R. S. 1979. Methanogenic activity in plankton samples and fish intestines: A mechanism for in situ methanogenesis in oceanic surface waters. *Limnol. Oceanogr.* **24**: 1136–1141.
- Paine, R. T. 2002. Trophic control of production in a rocky intertidal community. *Science* **296**: 736–739.
- Paine, E. R., M. Schmid, P. W. Boyd, G. Diaz-Pulido, and C. L. Hurd. 2021. Rate and fate of dissolved organic carbon release by seaweeds: A missing link in the coastal ocean carbon cycle. *J. Phycol.* **57**: 1375–1391.
- Pakhomov, E. A., S. Kaehler, and C. D. McQuaid. 2002. Zooplankton community structure in the kelp beds of the sub-Antarctic Prince Edward Archipelago: Are they a refuge for larval stages? *Polar Biol.* **25**: 778–788.
- Peeters, F., E. J. Fernandez, and H. Hofmann. 2019. Sediment fluxes rather than oxic methanogenesis explain diffusive CH₄ emissions from lakes and reservoirs. *Sci. Rep.* **9**: 243.
- Perez-Coronel, E., and J. M. Beman. 2021. Biogeochemical and omic evidence for multiple paradoxical methane production mechanisms in freshwater lakes. Preprint at bioRxiv.
- Popov, S. V., G. Y. Popova, N. M. Paderin, O. A. Koval, R. G. Ovodova, and Y. S. Ovodov. 2007. Preventive anti-inflammatory effect of Potamogeton, a pectin from the common pondweed *Potamogeton natans*. *Phytother. Res.* **21**: 609–614.
- Qaderi, M. M., and D. M. Reid. 2009. Methane emissions from six crop species exposed to three components of global climate change: Temperature, ultraviolet-B radiation and water stress. *Physiol. Plant.* **137**: 139–147.
- Reeburgh, W. S. 2007. Oceanic methane biogeochemistry. *Chem. Rev.* **107**: 486–513.
- Reisch, C., M. Moran, and W. Whitman. 2011. Bacterial catabolism of dimethylsulfonio-propionate (DMSP). *Front. Microbiol.* **2**: 172.
- Repeta, D. J., S. Ferron, O. A. Sosa, C. G. Johnson, L. D. Repeta, M. Acker, E. F. DeLong, and D. M. Karl. 2016. Marine methane paradox explained by bacterial degradation of dissolved organic matter. *Nat. Geosci.* **9**: 884–887.
- Robertson, A. I., P. Dixon, and P. Daniel. 1988. Zooplankton dynamics in mangrove and other nearshore habitats in tropical Australia. *Mar. Ecol. Progr. Ser.* **43**: 139–150.
- Rogers, J. E., and W. B. Whitman. 1991. Microbial production and consumption of greenhouse gases: Methane, nitrogen oxides, and halomethanes. *Am. Soc. Microbiol.*: 219–235.
- Rosentreter, J. A., and others. 2021. Half of global methane emissions come from highly variable aquatic ecosystem sources. *Nat. Geosci.* **14**: 225–230.
- Saunois, M., and others. 2020. The global methane budget 2000–2017. *Earth Syst. Sci. Data* **12**: 1561–1623.
- Scranton, M. I., and P. G. Brewer. 1977. Occurrence of methane in the near-surface waters of the western subtropical North-Atlantic. *Deep-Sea Res.* **24**: 127–138.
- Schmale, O., J. Wäge, V. Mohrholz, N. Wasmund, U. Gräwe, G. Rehder, M. Labrenz, and N. Loick-Wilde. 2018. The contribution of zooplankton to methane supersaturation in the oxygenated upper waters of the central Baltic Sea. *Limnol. Oceanogr.* **63**: 412–430.
- Schoelynck, J., K. Bal, H. Backx, T. Okruszko, P. Meire, and E. Struyf. 2010. Silica uptake in aquatic and wetland macrophytes: A strategic choice between silica, lignin and cellulose? *New Phytol.* **186**: 385–391.
- Schorn, S., and others. 2022. Diverse methylotrophic methanogenic archaea cause high methane emissions from seagrass meadows. *PNAS* **119**: e2106628119.
- Smith, S. V. 1981. Marine macrophytes as a global carbon sink. *Science* **211**: 838–840.
- Sorrell, B. K., M. T. Downes, and C. L. Stanger. 2002. Methanotrophic bacteria and their activity on submerged aquatic macrophytes. *Aquat. Bot.* **72**: 107–119.
- Sowers, K. R., and J. G. Ferry. 1983. Isolation and characterization of a methylotrophic marine methanogen, *Methanococcoides methylutens*, gen. nov., sp. nov. *App. Environ. Microbiol.* **45**: 684–690.
- Stefels, J. 2000. Physiological aspects of the production and conversion of DMSP in marine algae and higher plants. *J. Sea Res.* **43**: 183–197.
- Sunda, W., D. J. Kieber, R. P. Kiene, and S. Huntsman. 2002. An antioxidant function for DMSP and DMS in marine algae. *Nature* **418**: 317–320.
- Tang, K. W., D. F. McGinnis, K. Frindte, V. Brüchert, and H. P. Grossart. 2014. Paradox reconsidered: Methane oversaturation in well-oxygenated lake waters. *Limnol. Oceanogr.* **59**: 275–284.
- Tang, K. W., D. F. McGinnis, D. Ionescu, and H. P. Grossart. 2016. Methane production in oxic lake waters potentially increases aquatic methane flux to air. *Environ. Sci. Technol. Lett.* **3**: 227–233.
- Timms, R. M., and B. Moss. 1984. Prevention of growth of potentially dense phytoplankton populations by zooplankton grazing, in the presence of zooplanktivorous fish, in a shallow wetland ecosystem. *Limnol. Oceanogr.* **29**: 472–486.
- Vadeboncoeur, Y., and others. 2021. Blue Waters, green bottoms: Filamentous attached algal blooms (FABs) are an emerging threat to clear lakes worldwide. *Bioscience* **71**: 1011–1021.

- Van Alstyne, K. L., and M. P. Puglisi. 2007. DMSP in marine macroalgae and macroinvertebrates: Distribution, function, and ecological impacts. *Aquat. Sci.* **69**: 394–402.
- Vigano, I., H. van Weelden, R. Holzinger, F. Keppler, and T. Röckmann. 2008. Effect of UV radiation and temperature on the emission of methane from plant biomass and structural components. *Biogeosci. Discuss.* **5**: 243–270.
- Vilas, M. P., C. L. Marti, M. P. Adams, C. E. Oldham, and M. R. Hipsey. 2017. Invasive macrophytes control the spatial and temporal patterns of temperature and dissolved oxygen in a shallow lake: A proposed feedback mechanism of macrophyte loss. *Front. Plant Sci.* **8**: 2097.
- Wang, H. J., J. W. Lu, W. D. Wang, L. Y. Yang, and C. Q. Yin. 2006. Methane fluxes from the littoral zone of hypertrophic Taihu Lake, China. *J. Geophys. Res. Atmos.* **111**: D17109.
- Wang, Z., P. J. Gullledge, J. Q. Zheng, W. Liu, L. H. Li, and X. G. Han. 2009. Physical injury stimulates aerobic methane emissions from terrestrial plants. *Biogeosciences* **6**: 615–621.
- Wang, Z. P., F. Keppler, M. Greule, and J. T. G. Hamilton. 2011. Non-microbial methane emissions from fresh leaves: Effects of physical wounding and anoxia. *Atmos. Environ.* **45**: 4915–4921.
- Wang, Z. P., S. X. Chang, H. Chen, and X. G. Han. 2013. Widespread non-microbial methane production by organic compounds and the impact of environmental stresses. *Earth Sci. Rev.* **127**: 193–202.
- Wang, Q., J. E. Dore, and T. R. McDermott. 2017. Methylphosphonate metabolism by *Pseudomonas* sp. populations contributes to the methane oversaturation paradox in an oxic freshwater lake. *Environ. Microbiol.* **19**: 2366–2378.
- Wang, N., D. Huang, C. Li, Y. Deng, W. Li, Y. Yao, and W. Liao. 2020. Regulatory roles of methane in plants. *Sci. Hortic.* **272**: 109492.
- Wang, Q., and others. 2021. Aerobic bacterial methane synthesis. *PNAS* **118**: e2019229118.
- Waycott, M., and others. 2009. Accelerating loss of seagrasses across the globe threatens coastal ecosystems. *PNAS* **106**: 12377–12381.
- Weller, D. I., and others. 2013. Temporal variation of dissolved methane in a subtropical mesoscale eddy during a phytoplankton bloom in the Southwest Pacific Ocean. *Prog. Oceanogr.* **116**: 193–206.
- White, A. E., D. M. Karl, K. M. Björkman, L. J. Beversdorf, and R. M. Letelier. 2010. Phosphonate metabolism by *Trichodesmium* IMS101 and the production of greenhouse gases. *Limnol. Oceanogr.* **55**: 1755–1767.
- Winton, R. S., and C. J. Richardson. 2017. Top-down control of methane emission and nitrogen cycling by waterfowl. *Ecology* **98**: 265–277.
- Wishkerman, A., S. Greiner, M. Ghyczy, M. Boros, T. Rausch, K. Lenhart, and F. Keppler. 2011. Enhanced formation of methane in plant cell cultures by inhibition of cytochrome c oxidase. *Plant Cell Environ.* **34**: 457–464.
- Xiao, Q. T., and others. 2017. Spatial variations of methane emission in a large shallow eutrophic lake in subtropical climate. *Eur. J. Vasc. Endovasc. Surg.* **122**: 1597–1614.
- Xu, X., W. Zhao, M. Xiao, J. Huang, C. Fang, B. Li, and M. Nie. 2014. Snails promote methane release from a freshwater lake ecosystem. *Front. Environ. Sci.* **2**: 12.
- Yao, M., C. Henny, and J. A. Maresca. 2016. Freshwater bacteria release methane as a byproduct of phosphorus acquisition. *Appl. Environ. Microbiol.* **82**: 6994–7003.
- Ye, W. W., X. L. Wang, X. H. Zhang, and G. L. Zhang. 2020. Methane production in oxic seawater of the western North Pacific and its marginal seas. *Limnol. Oceanogr.* **65**: 2352–2365.
- Xing, Y. P., P. Xie, H. Yang, A. P. Wu, and L. Ni. 2006. The change of gaseous fluxes following the switch of dominant producers from macrophytes to algae in a shallow subtropical lake of China. *Atmos. Environ.* **40**: 8034–8043.
- Yin, X., and others. 2019. CO₂ conversion to methane and biomass in obligate methylotrophic methanogens in marine sediments. *ISME J.* **13**: 2107–2119.
- Yip, D. Z., A. M. Veach, Z. K. Yang, M. A. Cregger, and C. W. Schadt. 2019. Methanogenic archaea dominate mature heartwood habitats of eastern cottonwood (*Populus deltoides*). *New Phytol.* **222**: 115–121.
- Yoshida, N., H. Iguchi, H. Yurimoto, A. Murakami, and Y. Sakai. 2014. Aquatic plant surface as a niche for methanotrophs. *Front. Microbiol.* **5**: 30.
- Zhang, J., X. Liu, M. Wang, and B. Qin. 2013. Compositional differences of chromophoric dissolved organic matter derived from phytoplankton and macrophytes. *Org. Geochem.* **55**: 26–37.
- Zhang, Y., E. Jeppesen, X. Liu, B. Qin, K. Shi, Y. Zhou, S. M. Thomaz, and J. Deng. 2017. Global loss of aquatic vegetation in lakes. *Earth Sci. Rev.* **173**: 259–265.
- Zhang, M., and others. 2019. Methane flux dynamics in a submerged aquatic vegetation zone in a subtropical lake. *Sci. Total Environ.* **672**: 400–409.

Acknowledgments

The authors acknowledge the very valuable contributions of an anonymous reviewer and Pat Megonigal that substantially helped improving an earlier version of the manuscript. Open access funding enabled and organized by Projekt DEAL. HPG and FK were supported by German Research Foundation (GR 1540/21/2, GR 1540/35/1, KE 884/16/2) and DFM by Swiss National Science Foundation (grant 200021/169899). Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

None declared.

Submitted 14 November 2021

Revised 08 March 2022

Accepted 15 April 2022

Associate editor: Dorte Krause-Jensen