environmental microbiology

Environmental Microbiology (2018) **20**(8), 2671–2685 doi:10.1111/1462-2920.14302

# Mini-review: Phytoplankton-derived polysaccharides in the marine environment and their interactions with heterotrophic bacteria

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## Summary

**Within the wealth of molecules constituting marine dissolved organic matter, carbohydrates make up the largest coherent and quantifiable fraction. Their main sources are from primary producers, which release large amounts of photosynthetic products – mainly polysaccharides – directly into the surrounding water via passive and active exudation. The organic carbon and other nutrients derived from these photosynthates enrich the 'phycosphere' and attract heterotrophic bacteria. The rapid uptake and remineralization of dissolved free monosaccharides by heterotrophic bacteria account for the barely detectable levels of these compounds. By contrast, dissolved combined polysaccharides can reach high concentrations, especially during phytoplankton blooms. Polysaccharides are too large to be taken up directly by heterotrophic bacteria, instead requiring hydrolytic cleavage to smaller oligo- or monomers by bacteria with a suitable set of exoenzymes. The release of diverse polysaccharides by various phytoplankton taxa is generally interpreted as the deposition of excess organic material. However, these molecules likely also fulfil distinct, yet not fully understood functions, as inferred from their active modulation in terms of quality and quantity when phytoplankton becomes nutrient limited or is exposed to heterotrophic bacteria. This minireview summarizes current knowledge regarding the exudation and composition of phytoplankton-derived exopolysaccharides and acquisition of these compounds by heterotrophic bacteria.**

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## Introduction

Marine primary producers are responsible for the accumulation of vast amounts of biomass. Net primary production (NPP) in oligotrophic oceans alone is comparable to that in all of the world's tropical rainforests (Field, 1998). Zooplankton grazing, viral lysis, the decay of aging phytoplankton cells and the active/passive release of photosynthetic products give rise to two distinct oceanic carbon pools: particulate and dissolved organic matter (POM and DOM respectively), with the latter defined as the < 0.2-μm fraction (Jiao *et al*., 2010). Oceanic DOM comprises an enormous carbon pool of 662 Pg, which renders it 'the largest ocean reservoir of reduced carbon' (Hansell *et al*., 2009). DOM represents more 'than 200 times the carbon inventory of marine biomass' (Hansell *et al*., 2009) and thus harbours similar amounts of carbon as the atmospheric $CO_2$ pool (Hedges, 1992). Consequently, marine DOM is the major carbon source for heterotrophic bacteria in the world's oceans (Azam *et al*., 1983).

Phytoplankton usually sequesters excess carbon in the form of storage polysaccharides, such as chrysolaminarin in diatoms (Beattie *et al*., 1961) and glycogen in cyanobacteria (Ball and Morell, 2003). These polymers also constitute the main fraction of phytoplankton exudates, exceeding the concentrations of free monosaccharides or amino acids by as much as 100-fold (Myklestad, 1995; Granum *et al*., 2002; Grossart *et al*., 2007; Grossart and Simon, 2007; Hahnke *et al*., 2013; Sarmento *et al*., 2013). Proteins are another significant component of algal exudates, whereas the contributions of lipids and acetate are small (Aluwihare *et al*., 1997; Meon and Kirchman, 2001; Grossart *et al*., 2006; Grossart and Simon, 2007; Grossart *et al*., 2007; Haas and Wild, 2010).

Using tangential flow filtration, Aluwihare and Repeta (1999) found that up to 37% of the dissolved organic

carbon (DOC) originating from phytoplankton consists of high-molecular-weight (HMW, > 1 kDa) components, mainly hydrolyzable carbohydrates. Early studies of isolated oceanic HMW-DOM obtained from different sampling sites over a wide range of depths showed that polysaccharides represent the largest fraction of HMW-DOM, with about 50% relative abundance of the DOC in surface waters and about 25% in deeper samples (Benner *et al*., 1992). On the lower end of that scale were North Atlantic samples, as also reported in recent studies of the Northeast Atlantic (~ 11% of DOC, Engel *et al*., 2012), the Norwegian Sea (~ 14.8% of DOC, Myklestad and Børsheim, 2007) and the North Pacific (~ 10.1% of DOC, Sannigrahi *et al*., 2005). However, it should be kept in mind that a share of the complex mixture of polymeric and unspecified compounds referred to as marine DOC can be of terrestrial origin (Opsahl *et al*., 1999).

Dissolved combined amino acids and proteins, about which much less is known, usually do not accumulate due to their preferential microbial utilization (e.g., Rosenstock and Simon, 2001) and hence occur at relatively low concentrations (e.g., Keil and Kirchman, 1999). The same holds true for dissolved free monosaccharides, which are generally present at low (nanomolar) concentrations although produced by phytoplankton at high rates (Kirchman *et al*., 2001 and references therein; Myklestad and Børsheim, 2007; Skoog *et al*., 1999). By contrast, polysaccharides are less rapidly metabolized by heterotrophic bacteria (e.g., Meon and Kirchman, 2001) and their standing stock is therefore larger. These molecules comprise a well-studied fraction within the otherwise highly complex mixture of polymeric and unspecified compounds that make up marine DOC (Aluwihare *et al*., 1997). Nevertheless, exudation of high and low molecular weight compounds in phytoplankton blooms also depends on the stage of the bloom, presence of bacteria and abiotic parameters (Fernández-Gómez *et al*., 2013; Thornton, 2014). The chemical composition of this DOC matrix is being slowly revealed by the application of traditional as well as modern methods, including ultra-high-resolution techniques (e.g., Dittmar and Paeng, 2009; Osterholz *et al*., 2015, 2016).

Exudation of DOM by phytoplankton can be grouped into passive leakage by diffusion through the cell membrane and active exudation. Yet, why phytoplankton cells actively exude a portion of their photosynthates is not fully understood (Fig. 1). Diatoms, for example, release roughly 5% of their primary production as DOC (Wetz

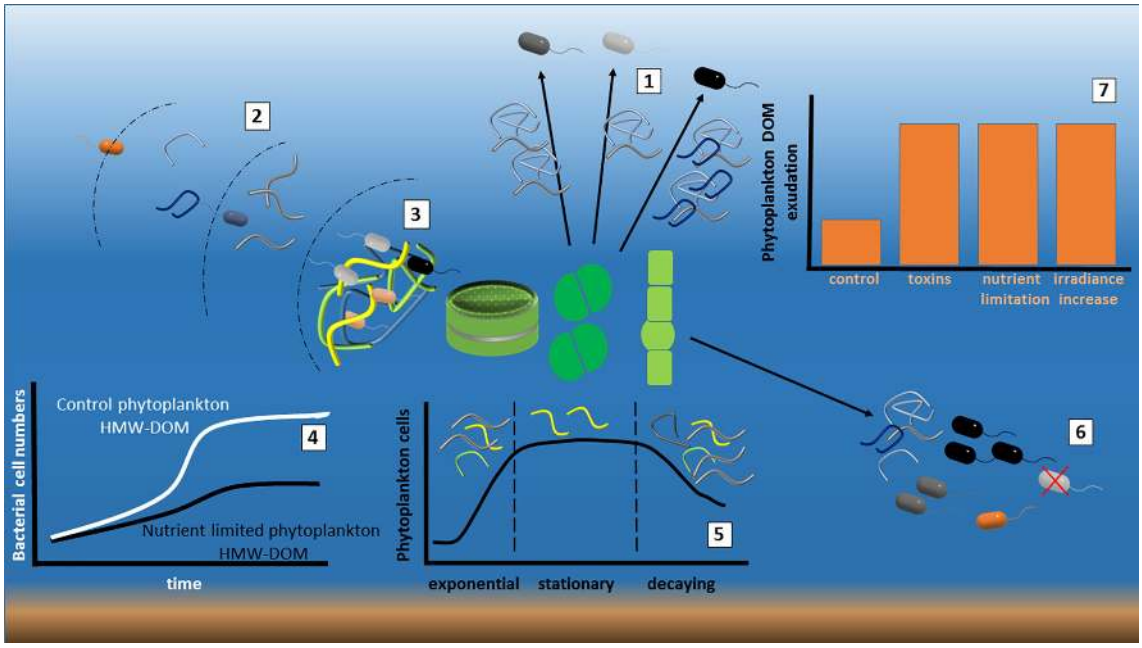


**Fig. 1.** Schematic on the influence of phytoplankton-derived polysaccharides and high-molecular-weight-dissolved organic matter (HMW-DOM) on heterotrophic bacteria. (1) Phytoplankton (diatoms, green algae and cyanobacteria as representatives for phytoplankton) specifically control their exopolysaccharide quantity depending on the bacterial strain. Polysaccharides are displayed as twisted tubes, and different bacterial strains are indicated by different colours. (2) The diffusion of DOM and polysaccharides (twisted tubes) is related to the molecular size of exudates and attracts motile bacteria toward the 'phycosphere'. Increasing distance to the phytoplankton is illustrated with dashed semi circles. (3) The restricted diffusivity of larger polymers creates microbial hotspots at the phycosphere. (4) Phytoplankton-derived HMW-DOM generated under nutrient stress conditions impacts the usage by heterotrophic bacteria. (5) The exometabolome of phytoplankton differs in its quantity and quality according to the growth phase and especially in the case of exopolysaccharides. (6) The exometabolome of phytoplankton has a distinct impact on bacterial community composition (different bacteria are illustrated by different colours). (7) Nutrient limitation and different environmental stressors increase the quantity of phytoplankton exudates. [Colour figure can be viewed at wileyonlinelibrary.com]

and Wheeler, 2007), even though this imposes a major metabolic cost for the alga. Recognition of this seemingly wasteful use of carbon quickly raised speculation concerning its true purpose (Sharp, 1977; Bjørrisen, 1988). For example, it was proposed that in return for the metabolic costs of actively exported exudates, specific functions beneficial to the phytoplankton would be fulfilled: the removal of toxic metabolites, the excretion of signalling molecules (Amin *et al*., 2012), resource acquisition of trace metals (such as iron), grazing, density reduction and host defence (reviewed by Thornton, 2014; Decho and Gutierrez, 2017). In addition, similar to the functions of dimethylsulphoniopropionate (DMSP) (Karsten *et al*., 1996), exuded compounds may act as osmolytes and cryoprotectants (Aslam *et al*., 2012). Despite the plethora of their hypothesized roles, the majority of compounds in phytoplankton-derived DOM have no known function (Thornton, 2014). Neither the reasons underlying the active release of large quantities of DOM nor the role of these substances in organism interactions are fully understood (Myklestad, 1995). Azam *et al*. (1983) were the first to report that 50% of the DOC released by phytoplankton is used by bacteria, which in turn plays a central role for microbial loop processes (Goldman *et al*., 1987). Thornton (2014) suggested that active algal exudation might also act as an overflow mechanism to prevent cell damage under stress conditions. Other authors observed that polysaccharides are an important factor influencing the community of heterotrophic bacteria that accompanies living phytoplankton (Grossart *et al*., 2005), both of which exhibit distinct seasonal succession patterns (Teeling *et al*., 2012). The abovementioned mechanisms are not mutually exclusive, but may depend on phytoplankton species, growth phase and abiotic conditions.

Here, we review the composition of phytoplankton exopolysaccharides and the possible reasons why phytoplankton actively releases large amounts of these carbohydrates. We also explore the potential role of algal exopolysaccharides in mediating and shaping phytoplankton–heterotrophic bacteria dynamics and hence in oceanic carbon cycling.

## Phytoplankton exopolysaccharide composition

In oceanic DOM C:N and C:P ratios are considerably higher compared with the ambient surface water (Thornton, 2014). The specific ratios of C:N:P in phytoplankton-derived DOM depend on the phylogeny as well as on the physiological status of the phytoplankton cells (Thornton, 2014) and C:N and C:P ratios of phytoplakton-derived DOM increase if nutrient limitation occurrs (Saad *et al*., 2016). Nevertheless, the phytoplankton-derived DOM, exhibits lower C:N and C:P ratios compared with the ambient surface ocean DOM, and thus supports the preferential consumption of labile and nutrient rich phytoplankton-derived DOM by bacteria (Saad *et al*., 2016). The largest fraction of phytoplankton-derived, dissolved (< 0.2 μm) exudates is made up of polysaccharides (up to 90%) (Myklestad, 1995; Underwood *et al*., 2010), and consist of up to 10 different monomers (Rossi and De Philippis, 2016). These are mainly the neutral monosaccharides glucose, mannose, fucose, arabinose, xylose, rhamnose and galactose (Mopper *et al*., 1992; Meon and Kirchman, 2001; Grossart *et al*., 2007; Engel and Händel, 2011). In early spring, with the onset of photosynthetic activity (Kirchman *et al*., 2001), or during phytoplankton blooms (Ittekkot *et al*., 1981; Sperling *et al*., 2017), the most abundant monomer detected in exopolysaccharides is glucose, but this also depends on the phytoplankton species. For example, while glucose is one of the main neutral sugars in diatoms (Magaletti *et al*., 2004; Grossart *et al*., 2006; Grossart and Simon, 2007; Grossart *et al*., 2007; Bellinger *et al*., 2009; Gügi *et al*., 2015), arabinose makes up a greater share in both a coccolithophore and a prymnesiophyte (Hahnke *et al*., 2013).

Exopolysaccharides also include amino-sugars, such as galactosamine and glucosamine, as well as acidic sugars, such as galacturonic acid, glucuronic acid and muramic acid (Benner and Kaiser, 2003; Bhaskar *et al*., 2005; Engel *et al*., 2012; Borchard and Engel, 2015; Sperling *et al*., 2017) and chitin, a polymer of acetylglucosamin (Durkin *et al*., 2009). Acidic sugar monomers are important constituents of transparent exopolymer particles (TEP) but also colloidal exopolymer particles, both of which can be well characterized by acidic Alcian Blue staining (Alldredge *et al*., 1993; Passow, 2002). Moreover, the exopolysaccharides in diatoms can be sulfated (Dodgson and Price, 1962; Bhaskar *et al*., 2005; Helbert, 2017) and possess various combinations of monomer linkages, which gives them an enormous diversity that may be species-specific (summarized by Gügi *et al*., 2015, table 3). For example, chrysolaminarin, a storage polysaccharide mainly found in diatoms and most likely exuded, consists of β1 → 3- and ß1 → 6 linked glucose units in a ratio of 11:1 (Beattie *et al*., 1961). It does not contain mannitol residues and has a total length of 12 glucose monomers branching on average on C6 of every glucose monomer (Beattie *et al*., 1961). However, chrysolaminarin of the diatom *Thalassiosira weissflogii* consists of 5–13 glucose monomers and is not branched (Størseth *et al*., 2005) indicating species-specific chrysolaminarin features potentially impacting their degradation. Similarly, several different types of combined and linked polysaccharides are present in cyanobacteria (summarized by Pereira *et al*., 2009). Thus, according to these observations, phytoplankton-derived exopolysaccharides provide a consistent but also highly diverse class of

molecules that can be specifically used by heterotrophic bacteria as substrates for metabolic processes (Fig. 1). Recently developed, sophisticated analytical tools may increase our knowledge on the composition of phytoplankton-derived polysaccharides and their selective usage by heterotrophic bacteria. An overview of those analytical tools is beyond the scope of this minireview but can be found in Panagiotopoulos and Sempéré (2005) and, more recently, in Horňák and Pernthaler (2014) and Becker *et al*. (2017).

### Constraints of phytoplankton DOM and polysaccharide exudation

DOM is also exuded for reasons that are so far unknown (Wetz and Wheeler, 2007) and this fucntionally unkown fraction of DOM may exceed that which is exuded for specific purposes (Thornton, 2014). This may in part be because DOM exudation involves a passive diffusion process driven by a concentration gradient between the cell and its surroundings. Another reason might be a 'photosynthetic overflow', in which more carbon is fixed by photosynthesis than is needed for growth (Thornton, 2014). In combination with nutrient limitation, exudation of photosynthetically derived excess carbon may help to maintain cellular stoichiometry (e.g., the 'Redfield Ratio') (Thornton, 2014; Hansell and Carlson, 2014). In addition to the passive diffusion or active export of low-molecular-weight (LMW)-DOM, algae invest considerable energy in producing polysaccharides (Thornton, 2014), the release of which requires specific export mechanisms. This was demonstrated by Chin *et al*. (2004) for *Phaeocystis globosa,* which uses regulated exocytosis to secrete polysaccharide gels, including large polymers or particles (Verdugo *et al*., 2004; Passow, 2002; Bhaskar *et al*., 2005); however, apart from this mechanism, information about other routes of exudation is scarce. Both diatoms and green algae continuously exude organic matter, even when they are growing under balanced conditions (Myklestad, 1995). Nevertheless, the exudation rate increases when these organisms are exposed to oxidative stress, cyanobacterial toxins, heavy metals or to increases in salinity or osmotic stress (Fig. 1) (Maršálek and Rojíčkovâ, 1996; Abdullahi *et al*., 2006; Mohamed, 2008; El-Sheekh *et al*., 2012; Cherrier *et al*., 2015). While a distinct effect of UV radiation on exudation has yet to be confirmed (Pausz and Herndl, 1999; Carrillo *et al*., 2002), phytoplankton maintained in the shade for 3 days were shown to release large amounts of polysaccharides (Smith and Underwood, 2000). Conversely, Cherrier *et al*. (2015) found that extracellular release of DOM by phytoplankton was positively correlated with the amount of light in both lab and field studies. In this case, phytoplankton released higher amounts of DOM, as soon as a few hours after exposure to elevated irradiance levels. If irradiance stayed constant after an initial increase, however, exudation fell back to basal levels. Furthermore, a study from Rossi and De Philippis (2016) revealed that light and temperature had synergistic effects on polysaccharide exudation.

Phytoplankton-derived polysaccharides have unique biological properties, depending on their molecular weight, the degree of branching and ultrastructure (Rossi and De Philippis, 2016). The monomer composition of dissolved exopolysaccharides depends on the phytoplankton growth phase and group (Fig. 1) (Urbani *et al*., 2005). Indeed, exudate quality is strongly influenced by nutrient availability during growth (Grossart, 1999; Størseth *et al*., 2005; Barofsky *et al*., 2009) and differs for different limiting nutrients, such as silicate and nitrogen (Pete *et al*., 2010). Enhanced polysaccharide exudation was observed under phosphorus, sulphur and nitrogen limitation (Rossi and De Philippis, 2016). Accordingly, nutrient depletion and thus the shift from the exponential to the stationary growth phase stimulates the extracellular release of exudates (Fig. 1) (Obernosterer and Herndl, 1995; Underwood *et al*., 2004; Myklestad *et al*., 1989; Malej, 1993). A stress induced increase of polysaccharide exudation might be triggered by the production of reactive oxygen species (ROS) and/or toxins (Rossi and De Philippis, 2016).

Besides the impact of abiotic factors, both the quantity and the quality of phytoplankton exudates also seem to be actively controlled by bacteria (e.g., Bruckner *et al*., 2011; Gärdes *et al*., 2012). Moreover, the presence of bacteria can also negatively impact phytoplankton, as phytoplankton themselves are a source of bacterial nutrients. Thus, in addition to providing bacteria with a sustained carbon source (Decho and Gutierrez, 2017), phytoplankton releases polysaccharides that prevent direct bacterial colonization of the algal cell surface (e.g., Agustí and Duarte, 2013; Amin *et al*., 2012; Meyer *et al*., 2017) in the form of aggregates and particles (Passow, 2002; Verdugo *et al*., 2004; Bhaskar *et al*., 2005). This function of polysaccharides is similar to that of the surface mucopolysaccharides of *Trichodesmium* (Nausch, 1996). Vice versa, cyanobacteria may create an environment that traps nutrients provided by remineralization processes of bacteria (Guerrini *et al*., 1998). The large amounts of polysaccharides released by nutrient-limited phytoplankton (Fig. 1) (Myklestad, 1995; Wetz and Wheeler, 2007) may serve to attract bacteria that will provide important nutrients such as iron (Amin *et al*., 2009), ammonium (Amin *et al*., 2015) and vitamins (Cole, 1982; Sañudo-Wilhelmy *et al*., 2014; Durham *et al*., 2015). Some beneficial bacterial communities are capable of enhancing the dissolution of silica from the detritus of dead diatoms (Bidle and Azam, 1999). In addition, by

consuming polysaccharides, bacteria detoxify the phytoplankton phycosphere, that is, its surface and directly environed space (Bell and Mitchell, 1972), via the removal of reactive oxygen species (Morris *et al*., 2011) and other harmful metabolites (Christie-Oleza *et al*., 2017). The ability of TEP to attract and promote the growth of different bacterial strains when phytoplankton are confronted with either reduced or replete nutrient situations has been reported previously (Grossart and Simon, 2007). Conversely, bacteria can also stimulate the exudation of TEP from diatoms, which can in turn be exploited as a carbon source. Gärdes *et al*. (2012) found this to be the case for the Gammaproteobacterium *Marinobacter adhaerens* when added to a culture of *Thalassiosira weissflogii* diatoms. The authors found, however, that when under nutrient limitation, TEP production occurred independent of the presence of bacteria (Gärdes *et al*., 2012). In summary, quality and quantity of exuded polysaccharides is affected by numerous abiotic as well as biotic factors. These quality and quantity differences of released polysaccharides may reflect their ecological role and selective utilization by heterotrophic bacteria.

## Exopolysaccharides: Attraction of heterotrophic bacteria

Interactions between phytoplankton and heterotrophic bacteria range from mutualism to parasitism (reviewed by Cole, 1982; Amin *et al*., 2012) and are governed by nutrient availability via the regulation of algicidal activity (Ray and Bagchi, 2001), as well as by other environmental factors. The algal 'phycosphere' is an important basis for the interactions between algae and heterotrophic bacteria. It is largely made up of the HMW fraction of DOM (Hansell, 2013) together with other DOM fractions differing in molecular weight (Fig. 1). Since diffusion time is inversely proportional to the molecule size, HMW compounds have a higher residence time in the phycosphere (Fig. 1) (Seymour *et al*., 2017). Phytoplankton-derived exopolysaccharides are crucial attractants involved in the recruitment and retention of heterotrophic bacteria within the algal phycosphere (Bell and Mitchell, 1972; Grossart *et al*., 2001; Barbara and Mitchell, 2003; Seymour *et al*., 2010a, 2010b; Sonnenschein *et al*., 2012; Smriga *et al*., 2016).

Within the phycosphere (Bell and Mitchell, 1972; Seymour *et al*., 2017), the bacteria attracted by the high concentration of nutritional substrates (Kiørboe and Thygesen, 2001; Stocker, 2012) can perform several beneficial functions for phytoplankton, such as remineralization of nutrients (Seymour *et al*., 2017). Because phytoplankton increase polysaccharide exudation toward the end of their exponential growth phase (Aslam *et al*., 2012), bacterial colonization of phytoplankton cells also reaches a maximum during this phase (Grossart *et al*., 2006).

## Acquisition of polysaccharides by heterotrophic bacteria

Carbohydrates with a size of ~ 600 Da can either diffuse freely into gram-negative bacterial cells (Decad and Nikaido, 1976) or be channelled into the cells via porins (Weiss *et al*., 1991). Consequently, these mono- and oligo-saccharide or amino acid substrates have high turnover rates (Hansell, 2013) and cannot sustain the continued presence of bacteria, although they may act as important signalling molecules (Seymour *et al*., 2017). Bacterial growth is instead maintained by HMW polysaccharides within the semi-labile fraction of DOM (Fig. 1). These compounds diffuse away more slowly and are therefore available for bacterial consumption for longer periods (Smriga *et al*., 2016). Large polysaccharides must first be broken down by hydrolytic exo-enzymes to generate the oligo- or monomers that can then be readily taken up by the cells by the above-described mechanisms (e.g.,Traving *et al*., 2015). However, only a few bacterial taxa and less than half of the tested bacterial communities possess the enzymes and uptake mechanisms that enable access to carbon-rich exopolysaccharides (Elifantz *et al*., 2007; Alderkamp *et al*., 2007), even though recent studies pointed out that almost half of all bacterial genomes possess genes for exoenyme production (Zimmerman *et al*., 2013). Consequently, the enzymatic degradation products of fungi and other microorganisms (Rojas-Jimenez *et al*., 2017) play important roles in providing nutrients for heterotrophic bacteria. So far, two groups of organisms capable of polysaccharide uptake have been identified: (i) organisms that exude extracellular enzymes for hydrolysis and (ii) those that take advantage of the hydrolyzed products, that is, oligosaccharides. The production of a product by a bacterium that can be used by another auxotrophic bacterium is referred as 'cross-feeding' (e.g., Garcia *et al*., 2017), and degradation of polysaccharides is thereby accompanied by succession of bacterial communities (Datta *et al*., 2016). For extracellular enzymes, two scenarios exist, which balance substrate encounter rate with energy costs for maintenance of the enzymatic apparatus. In one scenario, enzymes are bound to the cell surface – a situation that may pay off energetically for solitary cells at low substrate concentrations. In the second, enzymes are released into the environment, which might only be favourable under high substrate concentrations (Traving *et al*., 2015).

A third model with a 'selfish-uptake' mechanism was recently evidenced in human gut bacteria, whereby

bacteria directly scavenge polysaccharides for hydrolysis. In this strategy, a long α-mannan polymer is bound at the cell surface, where it is partially hydrolyzed and the resulting oligosaccharides are then taken up and further hydrolyzed in the periplasm (or paryphoplasm in *Planctomycetes*) (Cuskin *et al*., 2015). This same principle was recently shown in marine systems with laminarin, xylan and chondroitin sulphate polysaccharides (Reintjes *et al*., 2017). When processed via this pathway, the uptake of the glucan laminarin is rapid, occurring in ≤ 30 min (Reintjes *et al*., 2017).

The degradation of algal polysaccharides is catalyzed by carbohydrate-active enzymes (CAZymes, Lombard *et al*., 2014, http://www.cazy.org/). Abundances of CAZymes follow bacterioplankton community succession patterns during phytoplankton blooms, and high enzyme levels have been detected in Gammaproteobacteria and *Flavobacteriia*, whose abundances follow phytoplankton blooms (Teeling *et al*., 2012; 2016; Sperling *et al*., 2017). By allowing for the hydrolysis of diverse polymers, CAZymes of the Gammaproteobacterium *Alteromonas macleodii* strain 83–1 allow for growth on a broad spectrum of exudates (Neumann *et al*., 2015). Other Gammaproteobacteria that rely on CAZymes include several *Vibrio* species, which express laminarases (Alderkamp *et al*., 2007). *Flavobacteriia* are among the genera of *Bacteroidetes* frequently found during diatom blooms (Pinhassi *et al*., 2004; Teeling *et al*., 2012) and they are important polymer degraders (e.g., Fernández-Gómez *et al*., 2013; Kabisch *et al*., 2014; Tang *et al*., 2017). In the algae-associated *Flavobacterium Zobellia galactanivorans*, the highest number of glycoside hydrolases and polysaccharide lyases compared with 125 other marine bacterial genomes were found, and thus its adaptation to the associated lifestyle and specialization to algae derived polysaccharides (Barbeyron *et al*., 2016). Flavobacterial SusD-like TonB-dependent receptors couple with SusC-like TonB-dependent transporter porins, whose abundances increase significantly during phytoplankton blooms (Teeling *et al*., 2012, 2016). In *Bacteroidetes* CAZymes are co-localized within clusters referred to as polysaccharide utilization loci (PUL), which often harbour several sulfatases (Grondin *et al*., 2017; Helbert, 2017).

PULs are operons/regulons of genes that encode the machinery for polysaccharide detection, hydrolysis and uptake. They always include an outer membrane transport protein, which is homologous to SusC, and operates as receptor for the TonB uptake system (e.g., Martens *et al*., 2011). For different polysaccharides, different PULs are present, as shown for *Gramella forseti* KT0803 (*Bacteroidetes*) whose specific PULs were activated by laminarin and alginate respectively (Kabisch *et al*., 2014). Also the marine *Bacteroidetes Gramella flava* reveals high abundances of glycoside hydrolase genes that are organized in PULs or PUL-like systems that enable the usage of diverse algae-derived polysaccharides (Tang *et al*., 2017). For *Bacteroidetes*, habitat adaptations of PULs were shown with populations specialized in peptides and bacterial- and animal-derived polysaccharide degradation on the one hand, and algae- and plant-derived polysaccharide degradation on the other (Bennke *et al*., 2016). Similar enzyme complexes are known for *Pseudoalteromonas haloplanktis*, a marine Gammaproteobacterium, whose enzyme fusion may reduce substrate and enzyme loss and thus represent an adaptation to its aquatic habitat (Hehemann *et al*., 2017). However, ecophysiolocial differentiation in the degradation of an algal-derived polysaccharide of closely related *Vibrionaceae* populations (also Gammaproteobacteria) was achieved by horizontal gene transfer (Hehemann *et al*., 2016).

However, phytoplankton is not the only source of polysaccharides, because bacteria exude polysaccharides themselves (Thornton, 2014; Zhang *et al*., 2015). Mostly, bacterial polysaccharides consist of mannose, rhamnose, glucose, galactose and galacturonic acid, and are characterized by their high proportion of uronic acid (20%–50%), which tend to form complexes with transition metals due to its negative charge (Zhang *et al*., 2015). Compared with phytoplankton polysaccharides, polysaccharides of bacterial origin have a higher resistence against mineralization by microbes and thus longer residence times. Nevertheless, bacterial polysaccharides can also be utilized by dinstinct bacteria, which mostly belong to the *Bacteroidetes* (Zhang *et al*., 2015). Such secondary usage of polysaccharides (after the primary utilization of phytoplankton-derived polysaccharides) yields humic-like components that contribute to the formation of refractory DOC in the oceans.

In summary, heterotrophic bacteria may aquire polysaccharides with diverse uptake systems (exoenzymes for polysaccharide degradation to oligo-saccharides, uptake mechanisms for oligo-saccharides, 'selfish' uptake system) which might be species specific, but are not necessarily mutually exclusive.

### Effects of algal exopolysaccharide release on the metabolism and community composition of heterotrophic bacteria

Phytoplankton-derived polysaccharides and other substances like DMSP, attract heterotrophic bacteria (Bell and Mitchell, 1972; Kiørboe *et al*., 2002; Grossart *et al*., 2001; Seymour *et al*., 2010a, 2010b; Smriga *et al*., 2016), and appear to be species-specific (Barofsky *et al*., 2009; Hahnke *et al*., 2013; Becker *et al*., 2014; Gügi *et al*., 2015). Thus, the nature of the phytoplankton and

therefore of its largest fraction of exudates, polysaccharides, strongly determine the phytoplankton-associated bacterial community composition (Pinhassi *et al*., 2004; Grossart *et al*., 2005; Haynes *et al*., 2007; Sapp *et al*., 2007; Baker and Kemp, 2014; Baker *et al*., 2016; Bohórquez *et al*., 2017), and shape the interactions between phytoplankton and bacteria (Fig. 1). Preference for specific phytoplankton polysaccharide exudates was also shown for *Planktotalea frisia.* This *Roseobacter* species is highly selective since it prefers the exudate of some types of diatoms over that of other species: It yielded high growth rates if cultured together with *Phaeocystis globosa* and *Thalassiosira rotula*, whereas only marginal growth was observed in culture with *Leptocylindrus danicus* (Hahnke *et al*. 2013). These experimental growth rates matched those found in natural populations occurring in and after diatom blooms, respectively, and could be attributed to differences in the released polysaccharides of the diatoms (Hahnke *et al*. 2013).

Differences in polysaccharide exudate composition reflect the seasonal occurrence of various phytoplankton species and thus influence bacterial abundances, including distinct bacterial species that accompany phytoplankton blooms (Schäfer and Abbas, 2002; Grossart *et al*., 2005; Sison-Mangus *et al*., 2014; Baker *et al*., 2016). Conversely, low phytoplankton abundances during winter corresponded with low abundances of *Flavobacteriia* and their CAZymes (Kopf *et al*., 2015). Teeling *et al*. (2012) proposed that seasonality in the composition of the main phytoplankton polysaccharides in the North Sea reflects the abundances of specific phytoplankton species. Phytoplankton blooms were accompanied by a relatively conserved bacterioplankton community composition characterized by high abundances of *Flavobacteriia*, Gammaproteobacteria and *Roseobacter* (Buchan *et al*., 2014; Teeling *et al*., 2016).

At a higher phylogenetic resolution, bacterial species with specific metabolic traits are supported by specific 'exudate-regimes' of photosynthetic products and thus may form species-specific associations with phytoplankton species (Grossart *et al*., 2005; Sapp *et al*., 2007). Contrary, a gene expression analysis demonstrated a rather broad spectrum of polysaccharides utilized by a single *Flavobacterium* isolate (Thomas *et al.,* 2017) indicating a low substrate specificity of algae-associated bacteria. However, *Zobellia galactanivorans* responded both to a single type of polysaccharide and to several others, as long as they originated from the same taxon (Thomas *et al*., 2017). This finding indicated a tight and species-specific association of *Z. galactanivorans* to macroalgae. Similarly, *Bacillus weihaiensis*, a brown-algae-associated *Firmicutes*, produces enzymes that enable the complete degradation of alginate and laminarin, which are major components of brown algae polysaccharides (Zhu *et al*., 2016). In this case, the same heterotrophic bacterium was responsible for a succession of degradation processes: First, alginate was degraded and thus the cell wall destructed, and subsequently the released laminarin and mannitol utilized (Zhu *et al*., 2016). These, at a first glance, contradictory observations of low and high substrate specificity can be explained by different bacterial lifestyles, and thus associations of copiotroph and oligotroph bacterial species to phytoplankton. Further, a recent study on niche partitioning indicated that bacterial populations tend to be more generalistic in their carbon utilization when provided with increasing substrate quantities, regardless of the quality of those substrates (Sarmento *et al*., 2017).

It is also possible that phytoplankton, by modulating the concentration and quality of its polysaccharide exudates, are able to attract selectively heterotrophs. Amin *et al*. (2012) suggest that phytoplankton 'cultivates' heterotrophic bacteria by offering specific signalling molecules (Gram *et al*., 2002; Seymour *et al*., 2017), which are then preferentially metabolized only by the bacteria capable of perceiving them. In fact, Amin *et al*. (2012) show that diatoms selectively react to the presence of heterotrophic bacteria by drastically changing the quantity of polysaccharides in their exudates (Fig. 1) depending on the strain they were co-cultured with. Bacteria rely on these signals and, in the case of diatom exudates, are able to rapidly take up these complex compounds within 30 h (Taylor *et al*., 2013).

A considerable amount of marine labile DOM can be remineralized by a single bacterial strain (Pedler *et al*., 2014), and many bacterial species possess genes for several exo-enzymes (Zimmerman *et al*., 2013). As an example, approximately half of the examined bacterial genomes possess genes for alkaline phosphatase, glucosaminidase and/or chitinase (Zimmerman *et al*., 2013); chitin production might be a common trait in diatoms, as suggested by Durkin *et al*. (2009). Bulk DOM turnover, however, likely requires several groups of bacteria (Cottrell and Kirchman, 2000; Datta *et al*., 2016). The concerted action of the three dominant groups *Roseobacter*, *Flavobacteriia* and Gammaproteobacteria (potentially with the aid of fungi) in particular drive the interdependence with their metabolic traits (Garcia *et al*., 2017). The exo-enzymes expressed by *Roseobacter* enable polymer degradation (Christie-Oleza *et al*., 2015), with the resulting oligomers and monomers taken up by the bacteria via a sophisticated set of uptake systems (Buchan *et al*., 2014; Klindworth *et al*., 2014).

Thus, a bacterial assemblage may develop with a temporal succession pattern that allows the incremental degradation of algal polymers and a resource partitioning of polysaccharides with coordinated cooperative activities of specialized bacteria (Datta *et al*., 2016). Hence, even

bacteria lacking certain exo-enzyme capabilities benefit from the hydrolysis products of others (McCarren *et al*., 2010; Alderkamp *et al*., 2007; Datta *et al*., 2016). Support for the requirement for bacteria with multiple enzymatic capabilities stems from a co-culture study, in which the axenic strain alone was unable to complement the metabolism of the diatom (Christie-Oleza *et al*., 2017). The authors suggested that the co-culture instead relied on a mutual metabolite exchange that served to enhance the long-term stability of both organisms. However, much remains to be learned about the dynamics of these bacterial groups with respect to the overall fate of marine carbon cycling.

## Role of algal polysaccharides in marine carbon cycling

Marine phytoplankton supplements the water column with large amounts of organic carbon. However, the fate of DOM and its impact on the biological pump and microbial loop is highly dependent on degradation activities of heterotrophic bacteria and the composition of the DOM (Azam *et al*., 1983; Jiao *et al*., 2010; Letscher and Moore, 2015). Whereas LMW-DOM is essentially undetectable due to its high turnover by bacteria (Kirchman *et al*., 2001 and references therein; Skoog *et al*., 1999; Saad *et al*., 2016), the large HMW-DOM fraction consists of semi-labile polysaccharides with turnover times as long as weeks. Ambient pools of marine DOM in contrast might be thousands of years old, especially in deep waters (Saad *et al*., 2016). In general, a net accumulation of polysaccharides occurs with the onset of summertime stratification, whereas a net removal takes place with deep winter mixing (McCarren *et al*., 2010), which is the largest vertical export of carbon in the sea (Hansell, 2013; Aluwihare and Repeta, 1999; Mari *et al*., 2017). The vertical transport also depends on the type of exuded polysaccharides: If the exuded polysaccharides attract particles and bacteria, the formation of marine snow is very likely, resulting in higher sinking velocities and downward fluxes of carbon. If the exuded polysaccharides repel bacteria, the lower density of the exudates compared with seawater may result in an upward flux (Berman-Frank *et al*., 2007).

The ability of marine microorganisms to utilize polysaccharides may reflect the conflict posed by the metabolic costs of its uptake versus the energy gained from its metabolism (Arrieta *et al*., 2015). However, based on the frequent clustering of the bacterial community into preferential consumers of either LMW- or HMW-DOM (e.g., Fernández-Gómez *et al*., 2013), it is likely that phytoplankton-derived polysaccharides are almost completely remineralized and that heterotrophic bacteria are generators of recalcitrant DOM in the ocean (e.g., Jiao *et al*., 2010; Zhang *et al*., 2015). DOM of bacterial origin is especially rich in uronic acid and humic-like components, which increases its resistance against mineralization by microbes (Zhang *et al*., 2015). Nevertheless, some of the bacterial EPS can be consumed, for example, by *Flavobacteria*, and phytoplankten are themselves a source of partly recalcitrant DOM (Landa *et al*., 2014). The presence of specific phytoplankton-derived refractory substrates could also be explained with concentrations below a threshold, which impedes their biological utilization (Traving *et al*., 2015), or by rapid successions of bacterial communities, where secondary consumers are not capable of polysaccharide breakdown (Datta *et al*., 2016).

In long-term mesocosm experiments lasting months to almost 3 years, ~ 30% of algal exudates remained recalcitrant to microbial remineralization, even though the water still contained polysaccharides (Fry *et al*., 1996; Meon and Kirchman, 2001; Osterholz *et al*., 2015). Meon *et al*. (2001) reported that despite the apparent species specificity of algal-derived polysaccharides, these substrates are only partially metabolized by bacteria, such that recalcitrant polysaccharides of relatively uniform composition are left behind. Those observations are supported by the recalcitrant behaviour of dissolved combined neutral sugars, based on their molar composition (Goldberg *et al*., 2009, 2011), and by the relatively uniform patterns of aldose derived from dissolved combined carbohydrates (McCarthy *et al*., 1996; Aluwihare *et al*., 1997; Borch and Kirchman, 1997). In another study, 'fresh' polysaccharides in the surface waters were found to contain high galactose and mannose/xylose concentrations, whereas in 'aged' and more recalcitrant polysaccharides, the contribution of glucose was larger than that of other sugars (Goldberg *et al*., 2009, 2011). Other studies demonstrated that neutral sugars, acetate and lipids account for the major fractions of macromolecules, with residence times < 3 years (Aluwihare *et al*., 1997; Repeta and Aluwihare, 2006). Thus, microbial activities may also modify the chemical structure of polysaccharides, such that enzymatic cleavage or the uptake of molecules controlling resilience to further microbial utilization are either hampered or induced.

For bacterial polysaccharide breakdown, different bacterial strategies exist, which also affect the fate of the released DOM. These different acquisition strategies accompany microbial lifestyle strategies and therewith phylogeny. For solitary cells facing low substrate densities, surface attached enzymes might be the most effective approach, whereas the release of enzymes might yield higher effectiveness for high cell and substrate concentrations (Traving *et al*., 2015, see also chapter 'Acquisition of polysaccharides by heterotrophic bacteria'). Oligotrophic bacteria possess uptake systems for a broad

substrate spectrum and streamlined genomes, and mostly lack motility and therefore preferentially use membrane bound enzymes, whereas copiotrophic bacteria that mostly exhibit motility, chemotaxis, fast growth and the potential of high uptake rates under high substrate concentrations, may release their extracellular enzymes (Traving *et al*., 2015). One example for this copiotrophic lifestyle is the Gammaproteobacterium *Alteromonas,* who often reaches high abundances in and after phytoplankton blooms (Zhang *et al*., 2015), and many *Bacteroidetes* are specialists for POM degradation (Puddu *et al*., 2003). The degradation of phytoplankton derived polysaccharides is a concert of different bacterial species and groups with synergistic interactions and population dynamics in time spans of hours to days (McCarren *et al*., 2010). Gammaproteobacteria may degrade LMW polysaccharides, whereas *Bacteroidetes* degrade more the HMW fraction and Methylotrophs utilize C1 compounds that decorate the polysaccharides (McCarren *et al*., 2010; Sosa *et al*., 2015). Together, polysaccharide-degrading bacterial taxa and species involved in sequential polymer degradation may produce a wealth of molecules differing in their chemical formulas and characteristics.

However, there are several other factors that affect the fate of released polysaccharides. As example, the locality of polysaccharide degradation also impacts the degradation, because different bacteria capable of polysaccharide degradation occur at different places in the oceans. Thus, different biomes may harbour different hydrolytic potentials (Wietz *et al*., 2015). Furthermore, polysaccharides produced under phosphate limitation support a different microbial communities compared with polysaccharides produced under phosphate replete conditions (Saad *et al*., 2016). Accompanied with different microbial communities, polysaccharides exuded into phosphate-depleted conditions reveal a longer persistence if compared with nutrient replete conditions (Puddu *et al*., 2003).

Another important factor for the fate of phytoplankton derived polysaccharides is the mortality pathway of the phytoplankton. Autocatalytic programmed cell death, for example, was highly coupled to POM release in aquatic ecosystems (Berman-Frank *et al*., 2007). The complexity of phytoplankton-derived polysaccharides, its microbial turnover and the nature of the co-existence of algae and bacteria are important areas of research that will provide insights into oceanic carbon cycling and the potential for the production of recalcitrant DOM.

## Summary and conclusions

Exudates of phytoplankton include mono-, oligo- and polysaccharides that can be broken down and consumed by heterotrophic bacteria. Therefore, (exo)polysaccharides are an important link between marine heterotrophic bacteria and marine primary producers. Accordingly, following the fate and role of dissolved marine carbohydrates can reveal the interactions and interdependencies of the different microbes in the pelagic zone. Moreover, carbohydrates have an extensive impact on carbon export by controlling organic matter aggregation and particle transport from the surface to the deep ocean and sediments. However, much needs to be learned from the types of interactions, the involved partners and the modulation of phytoplankton exudates by the presence of bacteria or changing environmental conditions. Recent 'omics' approaches allow for a better insight into the mutual interactions between phytoplankton and heterotrophic bacteria, with metagenomes that reveal the partners in associations, and transcripts that resolve the different physiological processes executed by the different partners. Proteomes may further reveal species-specific exudates in multispecies assemblages, as well as the response to the presence of specific bacteria. Furthermore, mass spectrometry at the nanoscale level (NanoSIMS) may resolve the fate of exudates in interactions at the cellular level. Combinations of these approaches may help to define the partners in and the type of interactions between phytoplankton and heterotrophic bacteria, as for example, the association of generalist and specialist bacteria to phytoplankton. A better understanding of the microscale relationship between phytoplankton and bacteria will then help us to untangle important aspects of oceanic carbon fluxes, which provides an important feedback to global climate changes.

## Acknowledgements

The authors thank Wendy Rhan and Sarah Weber for language improvement and three anonymous reviewers for valuable input for the manuscript. This work was supported by a grant of the Human Frontiers Science Program (RGP0020/2016).

The authors have no conflict of interest.

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