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Structures and functions of algal glycans shape their capacity to sequester carbon in the ocean

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Abstract

Algae synthesise structurally complex glycans to build a protective barrier, the extracellular matrix. One function of matrix glycans is to slow down microorganisms that try to enzymatically enter living algae and degrade and convert their organic carbon back to carbon dioxide. We propose that matrix glycans lock up carbon in the ocean by controlling degradation of organic carbon by bacteria and other microbes not only while algae are alive, but also after death. Data revised in this review shows accumulation of algal glycans in the ocean underscoring the challenge bacteria and other microbes face to breach the glycan barrier with carbohydrate active enzymes. Briefly we also update on methods required to certify the uncertain magnitude and unknown molecular causes of glycan-controlled carbon sequestration in a changing ocean.

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Keywords

Algal glycans, Marine carbon cycle, Polysaccharides, Carbohydrates, Microalgae, Phytoplankton, Fucoidan.

Abbreviations

FCSP, fucose-containing sulphated polysaccharide; HMWDOC, high molecular weight dissolved organic carbon; PUL, polysaccharide utilisation locus; CAZyme, carbohydrate-active enzyme.

Introduction

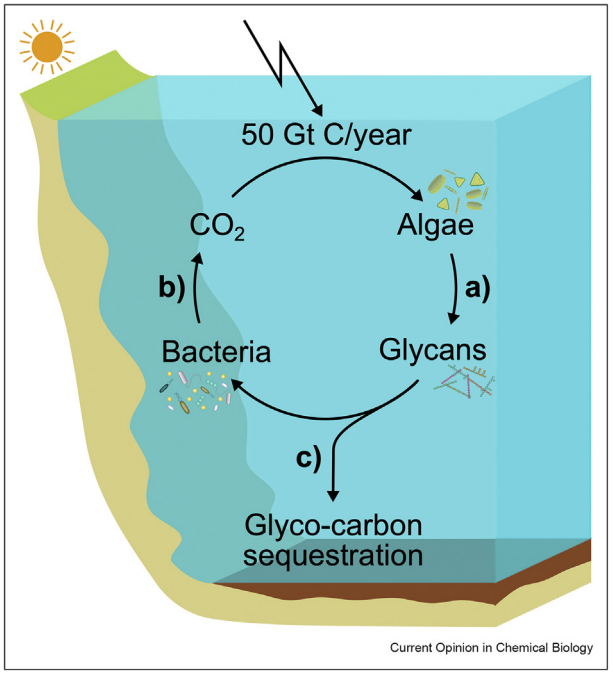
Glycan photosynthesis

Algae annually fix ~50 gigatonnes of inorganic carbon [1] via photosynthesis into glucose, the primary building block for glycans. For perspective, the combustion of fossil fuels annually adds ~10 gigatonnes to the ~900 gigatonnes of atmospheric carbon [2]. Depending on life stage, nutrient status and season, algae invest up to 80% of their organic carbon into glycans [**3]. Glycan locations and functions roughly split into three major categories. Intracellular glycans (e.g., laminarin and starch) provide rapid energy storage and release. Cell wall glycans (e.g., cellulose and hemicelluloses) confer stability and defence. Other secreted glycans (e.g., alginate and fucose-containing sulfated polysaccharides, FCSPs) form the extracellular matrix around and at the algae cell surface [4]. Among other functions matrix glycans modulate cation and water exchange and provide defence (as reviewed in [5]). While convenient, these categories do not capture the biology, complexity and dynamism of glycan distributions or solubility states. For example, alginate is composed of two building blocks, mannuronic acid (M) and guluronic acid (G) in a variable ratio. Only G units form cation bridges that promote gelling. There is significant overlap between the complex glycans in the cell wall and the extracellular matrix that are arranged along a solubility continuum from crystalline, via gel, to dissolved. Actively secreted glycans including FCSPs remain attached to the cell surface but are also detected in dissolved organic matter and so the physical and biochemical sphere of the matrix remains diffuse. Glycan structural complexity, in terms of linkage, configuration and diversity of building blocks, follows function. Intracellular storage glycans are structurally simple while extracellular matrix glycans including mammalian mucins are among the most complex [4]. This trend holds across algae, plants, animals, fungi and bacteria [6]. Glycan synthesis by algae rarely consumes nitrogen, phosphate or other limiting nutrients; glycans continue to be produced and secreted under nutrient limitation, resulting in increasing carbon-to-nitrogen ratios of organic matter during algal blooms [7]. This deviation from the Redfield ratio (C:N:P; 106:16:1) implies photosynthesis can be higher than estimated by models [8] that rely on this parameter. By secreting glycans, when alive and releasing glycans upon death, algae contribute to the oceanic pool of dissolved organic molecules [**9], which rivals in size the amount of carbon in the atmosphere [10].

Dissolved glycans store carbon dioxide in the ocean

Dissolved glycans account for a substantial amount of the standing stock of organic carbon in the ocean. There are ~700 gigatonnes of carbon in dissolved organic molecules, 200-fold more than in living marine biomass [2]. Glycans account for ~15–50% of the dissolved organic carbon [11–16]. Algae and cyanobacteria, the only organisms besides terrestrial plants that currently can access enough energy (sunlight) to reduce carbon dioxide on a planetary scale, are the primary source of glycans in the ocean [1,*17–19]. Diatoms, responsible for ~40% of marine carbon fixation [1], secrete as much as ~50% of their primary production as dissolved organic molecules [20]. Up to ~80–90% of these secreted molecules of diatoms and other microalgae are glycans [18]. *Phaeocystis* spp. in particular secrete large amounts of extracellular matrix glycans, which hold cells of colonies together [21]. An extracellular matrix glycan recently identified as FCSP and secreted by diatoms contributes to the dissolved glycan pool [**9]. As long as synthesis of glycans outpaces their digestion by bacteria or other organisms, glycans sequester carbon (Figure 1). This sequestration becomes apparent when considering the ~1–3 years average age of glycans in the surface ocean that contain ~10.5 gigatonnes of carbon [**22].

Figure 1



Algal glycans sequester carbon in the glyco-carbon cycle. **a)** Algae fix ~50 gigatonnes of inorganic carbon per year. A substantial fraction (up to ~80%) of this fixed carbon is converted into glycans [24]. **b)** Heterotrophic bacteria degrade glycans to CO_2. **c)** Glycans sequester carbon if they persist in dissolved form in the surface ocean or reach the deep ocean through vertical mixing and particle sinking. As long as synthesis of glycans by algae is faster than digestion by bacteria or other organisms, glycans sequester carbon in the ocean.

Older molecules of unknown structure with radiocarbon ages of ~4000–16,000 years, which also contribute to carbon storage, have been discussed elsewhere [23]. The size and age of the standing stock of dissolved glycans is surprising given removal processes such as microbial remineralisation and aggregation into sinking particles. Extracellular matrix glycans are often anionic, drawing particular interest among dissolved glycans as this chemistry promotes assembly which in turn promotes aggregation and carbon export as part of the biological carbon pump.

Particulate glycans export carbon dioxide into the deep ocean

Anionic glycans assemble into gels that promote aggregation of dissolved and particulate organic matter contributing to transfer of carbon from the sunlit surface ocean to depth. This biological carbon pump accounts for ~70% of the annual global carbon export to the deep ocean [25]. Depending on concentration dissolved sulfated and carboxylated glycans assemble into microgels [*26]. These gels coagulate and trap cells, minerals, and organic or inorganic molecules to form larger particles [**9,**27]], connecting the dissolved and particulate organic carbon pools. Glycans constitute ~8–10% of suspended and ~3–30% of sinking particulate organic matter [28–30]. Export to depth is relevant for long-term carbon sequestration because deeper remineralisation of organic matter by microorganisms delays return of carbon dioxide to the atmosphere. Carbon dioxide becomes trapped in the water depth layer where degradation takes place. The deeper remineralisation occurs, the later the water mass will equilibrate with the atmosphere. For example, sequestration of carbon for more than 100 years, considered long-term [31], is achieved by export of carbon to below 1000 m on average [32]. Up to 30% of sediment organic carbon is in the form of glycans [33], including FCSP and others [34], showing some algal glycans are resistant long enough to bacterial degradation to export carbon into the deep sea and to the ocean floor.

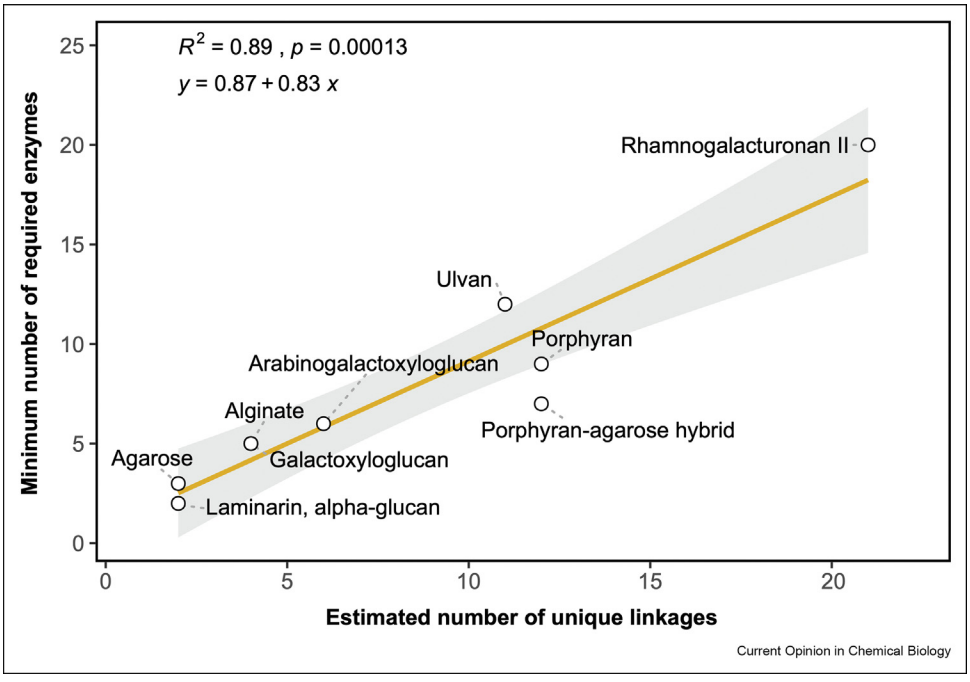
Bacterial degradation of glycans

With extensive glycan synthesis by algae comes extensive potential for glycan degradation by bacteria and other microbes. Hundreds of carbohydrate-active enzymes (CAZymes) [35,36] are encoded within the genomes of bacteria that thrive during microalgae blooms [e.g., the studies by Avcı et al., Kappelmann et al. [37,38]]. Bacteroidetes, Alphaproteobacteria, Gammaproteobacteria and Verrucomicrobia are common responders to algal blooms [**9,39]. These phyla contain genes for glycan degradation uptake and metabolism within polysaccharide utilisation loci (PULs) [*40,41]. Sets of expressed endo- (mid-chain cut) and exo-acting (end-chain cut) CAZymes within PULs enact stepwise cascades of glycan depolymerisation. Recent examples of

algal glycans targeted by PULs are laminarin [42], agar [*43], alginate [44,45], ulvan [46], carrageenan [47] and porphyran [*48]. PULs targeting storage glycans are common in heterotrophs. Laminarin and starch PULs for these energy glycans encode at least one enzyme for the same chemical bond plus proteins to sense, bind and import the glycan oligosaccharides [49]. More enzymes are required for degradation and catabolic utilization of structural glycans such as xylans and mannans [37]. The degradation potential for structural glycans is less frequent in microorganisms compared to energy glycans. Extracellular matrix such as FCSP, rhamnogalacturonan II (plants), agars and aforementioned cell wall glycans shape bacterial niches [37,38]. Degradation of FCSPs is confined to specialist bacteria with hundreds of expressed enzyme genes required to degrade variants of FCSPs from different algae [**50]. To completely degrade a glycan, bacteria must have at least one unique enzyme for each unique chemical bond between the building blocks. This requirement leads to complicated glycan-degrading cascades, where the number of enzymes scales with target glycan structural complexity (Figure 2).

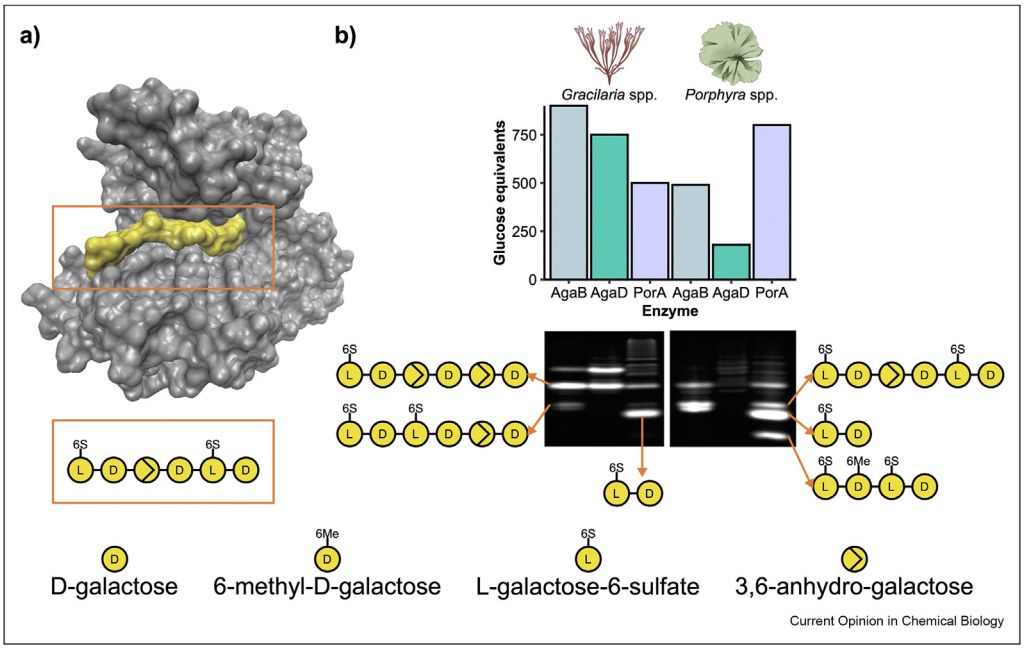
The abundance of glycan-degrading enzymes results from the specificity of CAZymes in glycan binding and chemical bond cleavage. This specificity is reflected in the conservation of active site residues involved in glycan recognition and catalysis [54]. For example, the endo-acting, porphyran-degrading GH86 hydrolase from *Bacteroides plebeius* binds to and cleaves a distinct monomer sequence in porphyran (Figure 3a). A change in the glycan structure, such as the addition or removal of a sulfate group, blocks binding of glycoside hydrolases (Figure 3b). Thus, binding is strongly influenced by sulfate and other modifications, which are targeted by specific accessory enzymes (e.g., sulfatases, esterases, glycosidases …) [*56]. Another example illustrating the sensitivity of CAZymes to their substrate comes from the red algae epibiont *Zobellia galactanivorans*. The presence of a sulfate group on C6 of the L-galactose, which is enriched in porphyran compared to other agars, selected for a *Z. galactanivorans* with four agarases plus five porphyranases of family GH16 [57]. Similarly, the addition of a methyl group on the C6 of the D-galactose in agars inhibits binding in the −1 subsite of some GH16 porphyranases [58]. These methyl groups are removed in an energy consuming reaction by oxidative P450 demethylases [59]. Metabolism of monosaccharides which contain methyl groups, including fucose, generates toxic aldehyde intermediates [**50,59]. Methylated and deoxy carbohydrates accumulate enough to become detectable in seawater [60], indicating methyl groups are

Figure 2



The number of carbohydrate-active enzymes (CAZymes) required by bacteria for degradation of glycans scales linearly with structural complexity. Estimated numbers of unique linkages (i.e., unique disaccharide units) in glycans and minimum numbers of enzymes required for degradation based on elucidated pathways for laminarin [51], agarose [*43], alpha−glucan [52], alginate [44,45], galactoxyloglucan, arabinogalactoxyloglucan [53], ulvan [46], porphyran−agarose hybrid [*48], porphyran [54] and rhamnogalacturonan II [*55]. Note that enzymes can recognise epitopes of >2 monomers so the calculated number of unique linkages may not accurately reflect the number of unique recognised epitopes. The linear correlation (y = 0.87 + 0.83x; R^2 = 0.89; P = <0.001) between the minimum number of unique linkages and required enzymes is shown in yellow. The grey area represents the 95% confidence interval.

Figure 3



Carbohydrate-active enzymes (CAZymes) specifically fit glycan substrates, which renders enzymes inactive when glycan structures change. **a)** Crystal structure of GH86 porphyranase from *Bacteroides plebeius* in complex with a sulfated hybrid galactan from its substrate porphyran (PDB ID: 4AW7). The image was generated with VMD [61]. **b)** Substrate specificity shown for three GH16 enzymes (AgaB, AgaD, PorA) from *Zobellia galactanivorans*. Each enzyme creates, akin to a restriction enzyme, a distinct oligosaccharide fragment pattern when degrading the structurally related extracellular matrix galactans agar from *Gracilaria* spp. and porphyran from *Porphyra* spp. The three enzymes have different selectivity for the presence of the C6 sulfate group in the –2 subsite of their active sites. AgaD is specific for non-sulfated parts, AgaB can accept sulfation on the non-reducing end of the galactan, and PorA requires the galactan to be sulfated. This high substrate specificity for sulfated/non-sulfated regions enables their use as bioanalytic tools for quantitative and qualitative measurements of glycans in algae and the environment. The oligosaccharide fragments created by the enzymes were labelled with a fluorophore and separated by polyacrylamide gel electrophoresis. Their quantity shown above the gel was measured using a reducing sugar assay (Hehemann, unpublished results). D-galactose and 6-methyl-D-galactose monomers are beta-1,4-linked to the next monomer. L-galactose-6-sulfate and 3,6-anhydro-galactose are alpha-1,3-linked.

protective in and outside of the test tube. Applying this knowledge to glycans as variable and complex in structure as FCSPs explains why few specialised bacteria carry hundreds of genes for FCSP degradation [**50].

Resource- and energy-limitation constrain the amount of CAZymes encoded within the genomes of heterotrophic microorganisms and the levels of enzyme expression. The more enzyme homologues a bacterium encodes and expresses to target the linkages within a glycan, the faster it degrades that glycan. The inverse is also true [62]. Possession of CAZymes for various glycan substrates broadens the niche of a bacterium. Thus, in the absence of constraining factors, the optimal strategy for bacteria would be to express high levels of many CAZymes for high rates of glycan degradation and a broad substrate range. However, expansion of CAZyme repertoires increases energy, nitrogen and phosphorus demand for genome duplication. Moreover, CAZyme expression requires energy and CAZyme secretion for glycan degradation consumes nitrogen and reduces growth rate in the absence of the glycan [63]. Even in the absence of the glycan a baseline expression and secretion of CAZymes is required for detection of the glycan [64]. Bacteria must balance the nutrient and energy demands for possession and expression of CAZymes with the energy they provide. Ecological constraints manifest as strategies where some bacteria tether enzymes to their surface or internalise digestion [65], while others increase the amount of secreted, free enzymes [62]. In a resource limited world ecology, energy, nutrients, and other unknown factors shape the repertoire, cellular location and expression levels of bacterial CAZymes.

Extracellular matrix glycans as antimicrobials

The structure and complexity of extracellular matrix glycans confer resistance against enzyme-catalysed invasion. Extracellular matrix glycans on cell surfaces in contact with microbiomes form a barrier against bacteria, fungi and viruses [5]. Despite independent evolution in separate algal phyla and structural variation across species and seasons, matrix glycans share common features

that offer protection [5,66]. Matrix glycans physically protect cells, for example, through cation bridging between carboxyl groups which form a gel that controls the diffusion of proteins including proteases or other enzymes [67,68]. The cations trapped by carboxyl groups include iron and copper [69], which depending on concentration can be crucial trace elements or antimicrobials [70]. The chemical complexity of matrix glycans requires invaders to express a multitude of CAZymes (Bacterial degradation of glycans, Figure 2), slowing their growth rate. By integrating monosaccharides that contain methyl groups (e.g., fucose, rhamnose, 6-O-methyl-galactose) extracellular matrix glycans become less favourable substrates. Adding sulfate groups interferes with protein binding and therefore requires degraders to carry and express genes for additional enzymes that remove sulfate groups or accommodate sulfate in the active site [57]. In fact, sulfate groups mask almost all hydroxyl groups in *Laminaria hyperborea* FCSP fucoidan [71]. FCSP fucoidan is a broad-acting antimicrobial with activity against bacteria, viruses, and human cancer cells [72]. Importantly, FCSP fucoidan structures change. This structural change makes them challenging to degrade for microbes, to resolve their structures, to assign names to the molecules, to uncover their antagonistic reaction mechanisms and to certify them as drugs for humans. This 'unruly' disorder is no mistake, it is a feature. Akin to increased mucus synthesis during infection of the nasal and lung airways, algae secrete extracellular matrix glycans in the presence of bacteria and viruses [73,74].

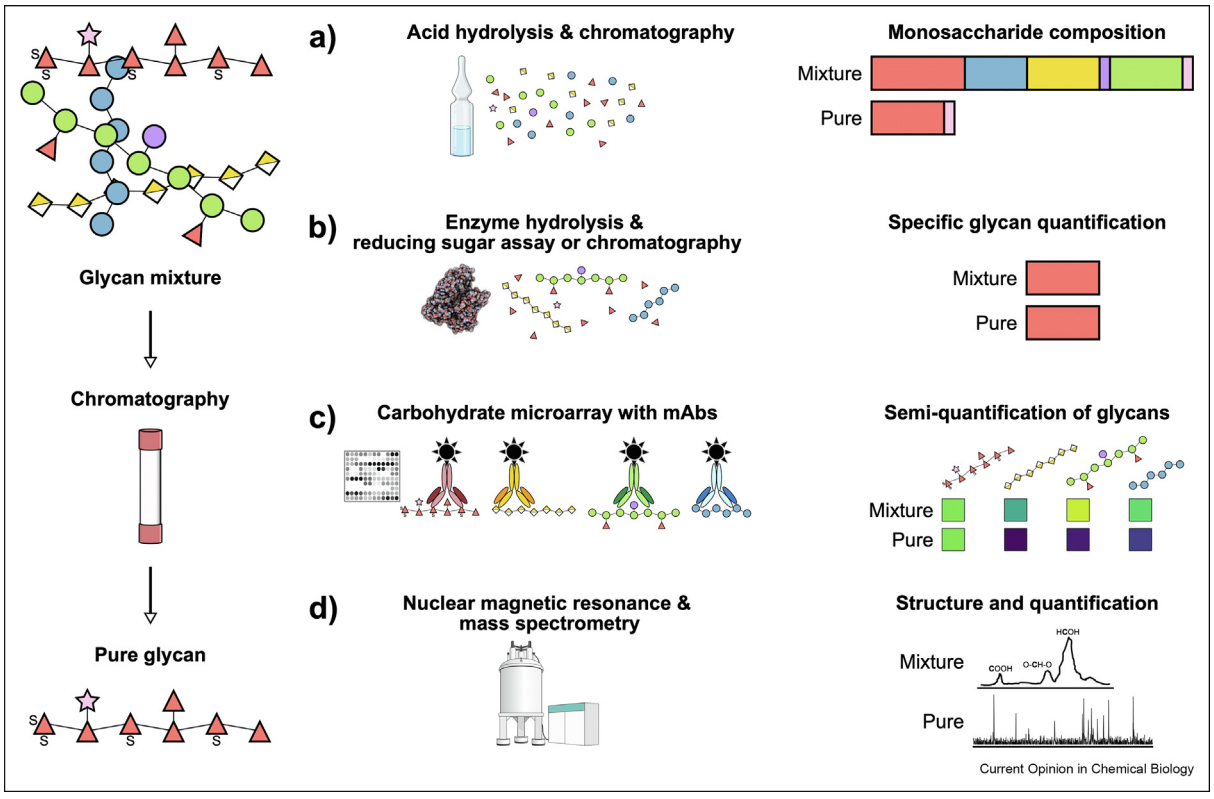
Glycan synthesis does not adhere to the central dogma (DNA–RNA–protein). Instead, the structures of glycans are made by and encoded in enzymes, enabling combinatorial change of structural diversity and complexity theoretically exceeding other organic molecules in nature [75]. The glycan 'alphabet' of monosaccharides is, unlike the genetic code, not universal [*76]. Bacteria adapt to changes in algal glycan structures by birth, duplication, transfer and loss of CAZyme genes [62] that assemble complicated glycan-degrading pathways. A question relevant for carbon sequestration is: Who will be faster in this arms race? Products of defensive glycans released during degradation upregulate expression of virulence factors in pathogenic bacteria [**77]. Degradation of algal cells by bacteria invokes defence reactions of algae which induce a stress response in bacteria [**78]. Horizontal gene transfer, which appears pervasive in nature, provides bacteria with CAZymes [79]. Eukaryotes control the virulence of bacteria and the transfer of PULs that are directed against their defensive glycans. Mucin glycans, secreted by mammalian epithelial cells exposed to microbiomes, interact with the protein machineries involved in the transfer of genes among microbes [**80] and can attenuate the virulence of potential pathogens [**81]. Thus, the same glycan that shields against invasion may simultaneously limit the flow of genes involved in its own degradation. Structural glycan diversity combined with unknown antimicrobial mechanisms may enable algae to stay ahead in this arms race. The evolution of extracellular matrix glycans protects organic carbon from bacterial degradation in and beyond algal cells.

Outlook

Uncertainties in residence time [**22] and proportion of dissolved and particulate organic carbon in form of glycans [11–15,30] remain intriguing. Due to the scale of carbon cycling in the ocean, even seemingly small uncertainties in measurements propagate to significantly different interpretations of impact [82]. Quantifying specific glycans separately, elucidating their (algal) sources and tracing their fate is key [**9]. This glyco-carbon accounting will require a combination of methods (Figure 4). Monoclonal antibody-based approaches, especially in combination with fluorescent imaging, can track specific glycans from algae to dissolved and particulate organic matter and even sediment in a semi-quantitative manner [**9,34]. Nuclear magnetic resonance [83] and mass spectrometry of oligosaccharides derived from glycans can achieve molecular-level resolution of glycan structures [*84]. Quantification of the total hydrolysable carbohydrate carbon [30] and glycan-specific quantification with enzymatic assays [**3,52] will inform on mass balances and relative importance of different glycans in terms of carbon sequestration. The available wealth of genomic and proteomic data can be used to design future enzyme assays quantifying ecologically significant glycans. Finally, compound-specific radiocarbon ages will constrain timescales of glycan cycling and potential for carbon sequestration [**22].

Constraining biological roles of algal glycans and their contribution to carbon sequestration in the ocean will require study from algal, microbial, zoological, and biogeochemical perspectives. This effort includes structural elucidation and quantification of glycans, algal, and bacterial community composition and abundance, and transcriptomics and proteomics of glycan producers and degraders. Laboratory biochemical and microbiological experiments are central to uncover the molecular mechanisms of carbon sequestration that make sense of biogeochemical and ecological observations in the environment. Once biochemically and ecologically relevant glycans are detected and quantified, uncovering molecular mechanisms of their biology will be facilitated with new tools: genetic engineering of bacteria [64] and algae [85], enzyme inhibitors [86] and fluorescent [87,88] and defined synthesised model glycans [89]. Only combined approaches from molecular to ocean basin scales can expose if and why the synthesis of matrix glycans and their ability to sequester carbon is changing in the Anthropocene.

Figure 4



Multiple methods are needed for detection, quantification and structural characterisation of glycans. Glycans can be measured either as a bulk mixture extracted from marine samples or individually after purification with, for example, anion-exchange chromatography (AEX). Mock results are shown for both glycan mixtures and a fucose-containing sulfated polysaccharide (FCSP). **a)** Monosaccharide quantification is achieved by acid hydrolysis and high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). **b)** Specific glycans can be quantified by quantification of monosaccharides (e.g., with reducing sugar assays as per [**3]) released by enzyme digestion. FCSP quantification is represented here. Note that the mixture and pure glycan theoretically give the same result unlike in A. **c)** Specific glycans in samples are profiled in a semi-quantitative manner with monoclonal antibodies (mAbs) on carbohydrate microarrays [**9] or in plate-based assays (enzyme-linked immunosorbent assay, ELISA, not shown). Colours of boxes indicate signal intensity after detection with an enzyme-conjugated secondary antibody (viridis colour scale). **d)** Nuclear magnetic resonance (NMR) quantifies functional groups characteristic of glycans in mixtures and also elucidates structures of pure glycans. In the 'mixture' spectrum, each peak represents a functional group (e.g., COOH). In the 'pure' spectrum, each peak represents a specific carbon (e.g., reducing end C1). Mass spectrometry can be used for structural characterisation [*84].

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Declaration of competing interest

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

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References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest
** of outstanding interest

1. Field CB, Behrenfeld MJ, Randerson JT, Falkowski P: **Primary production of the biosphere: integrating terrestrial and oceanic components**. *Science* 1998, **281**:237–240, https://doi.org/10.1126/science.281.5374.237.

2. Friedlingstein P, Jones MW, O'Sullivan M, Andrew RM, Bakker DCE, Hauck J, le Quéré C, Peters GP, Peters W, Pongratz J, *et al.*: **Global carbon budget 2021**. *Earth Syst Sci Data* 2022, **14**:1917–2005, https://doi.org/10.5194/essd-14-1917-2022.

3. ** Becker S, Tebben J, Coffinet S, Wiltshire K, Iversen MH, Harder T, Hinrichs KU, Hehemann JH: **Laminarin is a major molecule in the marine carbon cycle**. *Proc Natl Acad Sci U S A* 2020, **117**:6599–6607, https://doi.org/10.1073/pnas.1917001117.
Using an enzyme-based biocatalytic assay to quantify the algal glycan laminarin in particulate organic matter along transects in the Arctic, Atlantic, and Pacific oceans and during time series in the North Sea. The measurements revealed that laminarin plays a major role in the marine carbon cycle with an estimated annual production of ~12 gigatonnes. This study shows components of particulate organic matter can be identified and quantified with enzymes at a molecular resolution.

4. Stiger-Pouvreau V, Bourgougnon N, Deslandes E: **Carbohydrates from seaweeds**. In *Seaweed in Health and Disease Prevention*. Edited by Fleurence J, Levine I, Elsevier; 2016: 223–274, https://doi.org/10.1016/B978-0-12-802772-1.00008-7.

5. Kloareg B, Badis Y, Cock JM, Michel G: **Role and evolution of the extracellular matrix in the acquisition of complex multicellularity in eukaryotes: a macroalgal perspective**. *Genes* 2021, **12**, https://doi.org/10.3390/genes12071059.

6. Varki A: **Biological roles of glycans**. *Glycobiology* 2017, **27**: 3–49, https://doi.org/10.1093/glycob/cww086.

7. Engel A, Goldthwait S, Passow U, Alldredge A: **Temporal decoupling of carbon and nitrogen dynamics in a mesocosm diatom bloom**. *Limnol Oceanogr* 2002, **47**:753–761, https://doi.org/10.4319/lo.2002.47.3.0753.

8. Geider RJ, la Roche J: **Redfield revisited: variability of C:N:P in marine microalgae and its biochemical basis**. *Eur J Phycol* 2002, **37**:1–17, https://doi.org/10.1017/S0967026201003456.

9. ** Vidal-Melgosa S, Sichert A, Francis T, Bartosik D, Niggemann J, Wichels A, Willats WGT, Fuchs BM, Teeling H, Becher D, *et al.*: **Diatom fucan polysaccharide precipitates carbon during algal blooms**. *Nat Commun* 2021, **12**:1–13, https://doi.org/10.1038/s41467-021-21009-6.
Using monoclonal antibodies and carbohydrate microarrays, the scientists discovered a fucose-containing sulphated polysaccharide (FCSP) secreted by diatoms that accumulated and aggregated during a diatom bloom in the North Sea. This FCSP is the first candidate glycan identified to contribute to carbon sequestration in the ocean.

10. Carlson CA, Hansell DA: **DOM sources, sinks, reactivity, and budgets**. In *Biogeochemistry of Marine Dissolved Organic Matter*. Edited by Hansell DA, Carlson CA: Academic Press; 2015: 65–126, https://doi.org/10.1016/B978-0-12-405940-5.00003-0.

11. Benner R, Palulski JD, McCarth M, Hedges JI, Hatcher PG: **Bulk chemical characteristics of dissolved organic matter in the ocean**. *Science* 1992, **255**:1561–1564, https://doi.org/10.1126/science.255.5051.1561.

12. Hung C-C, Guo L, Santschi PH, Alvarado-Quiroz N, Haye JM: **Distributions of carbohydrate species in the Gulf of Mexico**. *Mar Chem* 2003, **81**:119–135, https://doi.org/10.1016/s0304-4203(03)00012-4.

13. Lin P, Guo L: **Spatial and vertical variability of dissolved carbohydrate species in the northern Gulf of Mexico following the Deepwater Horizon oil spill, 2010–2011**. *Mar Chem* 2015, **174**:13–25, https://doi.org/10.1016/j.marchem.2015.04.001.

14. McCarthy M, Hedges J, Benner R: **Major biochemical composition of dissolved high molecular weight organic matter in seawater**. *Mar Chem* 1996, **55**:281–297, https://doi.org/10.1016/S0304-4203(96)00041-2.

15. Pakulski JD, Benner R: **An improved method for the hydrolysis and MBTH analysis of dissolved and particulate carbohydrates in seawater**. *Mar Chem* 1992, **40**:143–160, https://doi.org/10.1016/0304-4203(92)90020-B.

16. Pakulski JD, Benner R: **Abundance and distribution of carbohydrates in the ocean**. *Limnol Oceanogr* 1994, **39**:930–940, https://doi.org/10.1016/0304-4203(92)90020-B.

17. * Aluwihare LI, Repeta DJ, Chen RF: **A major biopolymeric component to dissolved organic carbon in surface sea water**. *Nature* 1997, **387**:166–169, https://doi.org/10.1038/387166a0.
Chemical characterisation revealed that the majority of high molecular weight dissolved organic carbon (HMWDOC) at multiple sites across the Atlantic and Pacific is in the form of glycans and likely derives from algae. This study remains one of the key resources on the chemical composition of HMWDOC today.

18. Myklestad SM: **Release of extracellular products by phytoplankton with special emphasis on polysaccharides**. *Sci Total Environ* 1995, **165**:155–164, https://doi.org/10.1016/0048-9697(95)04549-G.

19. Granum E, Kirkvold S, Myklestad SM: **Cellular and extracellular production of carbohydrates and amino acids by the marine diatom Skeletonema costatum: diel variations and effects of N depletion**. *Mar Ecol Prog Ser* 2002, **242**:83–94, https://doi.org/10.3354/meps242083.

20. Azam F, Fenchel T, Field J, Gray JS, Meyer L, Thingstad TF: **The ecological role of water-column microbes in the sea**. *Mar Ecol Prog Ser* 1983, **10**:257–263, https://doi.org/10.3354/meps010257.

21. Alderkamp AC, Buma AGJ, van Rijssel M: **The carbohydrates of Phaeocystis and their degradation in the microbial food web**. *Biogeochemistry* 2007:99–118, https://doi.org/10.1007/s10533-007-9078-2.

22. ** Repeta DJ, Aluwihare LI: **Radiocarbon analysis of neutral sugars in high-molecular-weight dissolved organic carbon: implications for organic carbon cycling**. *Limnol Oceanogr* 2006, **51**:1045–1053, https://doi.org/10.4319/lo.2006.51.2.1045.
The scientists concentrated up to 60,000 L of seawater for monosaccharide-specific radiocarbon analyses. They found that glycans have a shorter residence time in surface waters (<3 years) than expected from bulk radiocarbon measurements. This was the first and still is the landmark study to quantify radiocarbon levels on the monosaccharide level rather than on operationally defined high molecular weight dissolved organic matter fractions.

23. Dittmar T, Lennartz ST, Buck-Wiese H, Hansell DA, Santinelli C, Vanni C, Blasius B, Hehemann JH: **Enigmatic persistence of dissolved organic matter in the ocean**. *Nat Rev Earth Environ* 2021, **2**:570–583, https://doi.org/10.1038/s43017-021-00183-7.

24. Myklestad S: **Production of carbohydrates by marine planktonic diatoms. I. Comparison of nine different species in culture**. *J Exp Mar Biol Ecol* 1974, **15**:261–274, https://doi.org/10.1016/0022-0981(74)90049-5.

25. Boyd PW, Claustre H, Levy M, Siegel DA, Weber T: **Multi-faceted particle pumps drive carbon sequestration in the ocean**. *Nature* 2019, **568**:327–335, https://doi.org/10.1038/s41586-019-1098-2.

26. * Chin W, Orellana M, Verdugo P: **Spontaneous assembly of marine dissolved organic matter into polymer gels**. *Nature* 1998, **391**:568–572, https://doi.org/10.1038/35345.
The scientists demonstrated that anionic glycans spontaneously aggregate from filtered seawater providing a pathway from dissolved to particulate organic matter bypassing the microbial loop.

27. ** Engel A, Thoms S, Riabesell U, Rochelle-Newall E, Zondervan I: **Polysaccharide aggregation as a potential sink of marine dissolved organic carbon**. *Nature* 2004, **428**:929–932, https://doi.org/10.1038/nature02453.
The authors demonstrated that aggregation of anionic glycans connects the dissolved and particular organic matter pools during mesocosm phytoplankton blooms. This study uncovered a key mechanism contributing to export of organic carbon from the surface ocean.

28. Hedges JI, Baldock JA, Gélinas Y, Lee C, Peterson ML, Wakeham SG: **The biochemical and elemental compositions of marine plankton: a NMR perspective**. *Mar Chem* 2002, **78**: 47–63, https://doi.org/10.1016/S0304-4203(02)00009-9.

29. Lee C, Hedges JI, Baldock JA, Ge Y, Gelinas Y, Peterson M, Wakeham SG: **Evidence for non-selective preservation of organic matter in sinking marine particles**. *Nature* 2001, **409**: 801–804, https://doi.org/10.1038/35057247.

30. Panagiotopoulos C, Sempéré R: **Analytical methods for the determination of sugars in marine samples: a historical perspective and future directions**. *Limnol Oceanogr Methods* 2005, **3**:419–454, https://doi.org/10.4319/lom.2005.3.419.

31. IPCC: **Climate change 2007**. In *Fourth Assessment Report to the Intergovernmental Panel on Climate Change (AR4)*. Cambridge University Press; 2007.

32. Passow U, Carlson CA: **The biological pump in a high CO_2 world**. *Mar Ecol Prog Ser* 2012, **470**:249–272, https://doi.org/10.2307/24876215.

33. Burdige DJ: **Preservation of organic matter in marine sediments: controls, mechanisms, and an imbalance in sediment organic carbon budgets?** *Cheml Rev* 2007, **107**:467–485, https://doi.org/10.1021/cr050347q.

34. S Vidal-Melgosa, et al: bioRxiv https://doi.org/10.1101/2022.03.04.483023.

35. Drula E, Garron ML, Dogan S, Lombard V, Henrissat B, Terrapon N: **The carbohydrate-active enzyme database: functions and literature**. *Nucleic Acids Res* 2022, **50**: D571–D577, https://doi.org/10.1093/nar/gkab1045.

36. The CAZypedia Consortium: **Ten years of CAZypedia: a living encyclopedia of carbohydrate-active enzymes**. *Glycobiology* 2018, **28**:3–8, https://doi.org/10.1093/glycob/cwx089.

37. Avcõ B, Krüger K, Fuchs BM, Teeling H, Amann RI: **Polysaccharide niche partitioning of distinct Polaribacter clades during North Sea spring algal blooms**. *ISME J* 2020, **14**: 1369–1383, https://doi.org/10.1038/s41396-020-0601-y.

38. Kappelmann L, Krüger K, Hehemann JH, Harder J, Markert S, Unfried F, Becher D, Shapiro N, Schweder T, Amann RI, *et al.*: **Polysaccharide utilization loci of North Sea Flavobacteriia as basis for using SusC/D-protein expression for predicting major phytoplankton glycans**. *ISME J* 2019, **13**:76–91, https://doi.org/10.1038/s41396-018-0242-6.

39. Teeling H, Fuchs BM, Bennke CM, Krüger K, Chafee M, Kappelmann L, Reintjes G, Waldmann J, Quast C, Glöckner FO, *et al.*: **Recurring patterns in bacterioplankton dynamics during coastal spring algae blooms**. *Elife* 2016, **5**:1–31, https://doi.org/10.7554/eLife.11888.

40. * Lapébie P, Lombard V, Drula E, Terrapon N, Henrissat B: **Bacteroidetes use thousands of enzyme combinations to break down glycans**. *Nat Commun* 2019, **10**, https://doi.org/10.1038/s41467-019-10068-5.

Genomic data available for Bacteroidetes was analysed to estimate that bacteria within this phylum have evolved a few thousand combinations of enzymes. The scientists consider this number indicates the diversity of actual glycan structures to be much lower than the theoretical limit. The implications of this conclusion are wide-reaching for the entire field of glycobiology and could contribute to estimating the incredible diversity of potential glycan structures synthesised in nature.

41. Martens EC, Koropatkin NM, Smith TJ, Gordon JI: **Complex glycan catabolism by the human gut microbiota: the Bacteroidetes sus-like paradigm**. *J Biol Chem* 2009, **284**: 24673–24677, https://doi.org/10.1074/jbc.R109.022848.

42. Unfried F, Becker S, Robb CS, Hehemann JH, Markert S, Heiden SE, Hinzke T, Becher D, Reintjes G, Krüger K, *et al.*: **Adaptive mechanisms that provide competitive advantages to marine Bacteroidetes during microalgal blooms**. *ISME J* 2018, **12**:2894–2906, https://doi.org/10.1038/s41396-018-0243-5.

43. * Pluvinage B, Grondin JM, Amundsen C, Klassen L, Moote PE, Xiao Y, Thomas D, Pudlo NA, Anele A, Martens EC, *et al.*: **Molecular basis of an agarose metabolic pathway acquired by a human intestinal symbiont**. *Nat Commun* 2018, **9**, https://doi.org/10.1038/s41467-018-03366-x.

The scientists describe the function and structure of the enzymes used by the human gut bacterium *Bacteroides uniformis* NP1 for complete depolymerisation of agarose, a galactan cell wall glycan produced by red algae. The study advances knowledge of the complex and specific mechanisms employed by microorganisms to access energy stored in complex algal glycans.

44. Neumann AM, Balmonte JP, Berger M, Giebel HA, Arnosti C, Voget S, Simon M, Brinkhoff T, Wietz M: **Different utilization of alginate and other algal polysaccharides by marine *Alteromonas macleodii* ecotypes**. *Environ Microbiol* 2015, **17**: 3857–3868, https://doi.org/10.1111/1462-2920.12862.

45. Hobbs JK, Lee SM, Robb M, Hof F, Barr C, Abe KT, Hehemann JH, McLean R, Abbott DW, Boraston AB: **KdgF, the missing link in the microbial metabolism of uronate sugars from pectin and alginate**. *Proc Natl Acad Sci U S A* 2016, **113**: 6188–6193, https://doi.org/10.1073/pnas.1524214113.

46. Reisky L, Préchoux A, Zühlke MK, Bäumgen M, Robb CS, Gerlach N, Roret T, Stanetty C, Larocque R, Michel G, *et al.*: **A marine bacterial enzymatic cascade degrades the algal polysaccharide ulvan**. *Nat Chem Biol* 2019, **15**:803–812, https://doi.org/10.1038/s41589-019-0311-9.

47. Ficko-Blean E, Préchoux A, Thomas F, Rochat T, Larocque R, Zhu Y, Stam M, Génicot S, Jam M, Calteau A, *et al.*: **Carrageenan catabolism is encoded by a complex regulon in marine heterotrophic bacteria**. *Nat Commun* 2017, **8**, https://doi.org/10.1038/s41467-017-01832-6.

48. * Robb CS, Hobbs JK, Pluvinage B, Reintjes G, Klassen L, Monteith S, Giljan G, Amundsen C, Vickers C, Hettle AG, *et al.*: **Metabolism of a hybrid algal galactan by members of the human gut microbiome**. *Nat Chem Biol* 2022, https://doi.org/10.1038/s41589-022-00983-y.

Using a combination of genomics, biochemical assays and structural biology, the scientists determined the biochemical pathway for porphyran depolymerisation in two human gut bacteria, one of which is porphyranolytic and the other agarolytic. The study provides insight into algal glycan deconstruction and the competitive and/or syntrophic relationship of members of the human gut microbiome.

49. Krüger K, Chafee M, Francis TB, Glavina del Rio T, Becher D, Schweder T, Amann RI, Teeling H: **In marine Bacteroidetes the bulk of glycan degradation during algae blooms is mediated by few clades using a restricted set of genes**. *ISME J* 2019, **13**: 2800–2816, https://doi.org/10.1038/s41396-019-0476-y.

50. ** Sichert A, Corzett CH, Schechter MS, Unfried F, Markert S, Becher D, Fernandez-Guerra A, Liebeke M, Schweder T, Polz MF, *et al.*: **Verrucomicrobia use hundreds of enzymes to digest the algal polysaccharide fucoidan**. *Nat Microbiol* 2020, **5**:1026–1039, https://doi.org/10.1038/s41564-020-0720-2.

A species of Verrucomicrobia, *Lentimonas* sp. CC4, was isolated that specialises in fucoidan degradation. Degradation was shown to involve hundreds of enzymes and a specialised biocompartment, the genes for most of which are encoded on a mega-plasmid, and are induced with specific substrates. The study highlights the complexity of algal glycan degradation and the metabolic cost for bacteria.

51. Becker S, Scheffel A, Polz MF, Hehemann JH: **Accurate quantification of laminarin in marine organic matter with enzymes from marine microbes**. *Appl Environ Microbiol* 2017, **83**:1–14, https://doi.org/10.1128/AEM.03389-16.

52. N Steinke N et al., bioRxiv doi: 10.1101/2021.11.10.468175.

53. Larsbrink J, Rogers TE, Hemsworth GR, McKee LS, Tauzin AS, Spadiut O, Klinter S, Pudlo NA, Urs K, Koropatkin NM, *et al.*: **A discrete genetic locus confers xyloglucan metabolism in select human gut Bacteroidetes**. *Nature* 2014, **506**:498–502, https://doi.org/10.1038/nature12907.

54. Hehemann JH, Kelly AG, Pudlo NA, Martens EC, Boraston AB: **Bacteria of the human gut microbiome catabolize red seaweed glycans with carbohydrate-active enzyme updates from extrinsic microbes**. *Proc Natl Acad Sci U S A* 2012, **109**: 19786–19791, https://doi.org/10.1073/pnas.1211002109.

55. ** Ndeh D, Rogowski A, Cartmell A, Luis AS, Baslé A, Gray J, Venditto I, Briggs J, Zhang X, Labourel A, *et al.*: **Complex pectin metabolism by gut bacteria reveals novel catalytic functions**. *Nature* 2017, **544**:65–70, https://doi.org/10.1038/nature21725.

The scientists characterised 21 enzymes of a Bacteroidetal human gut bacterium that deconstructs rhamnogalacturonan II, one of the most complex extracellular matrix glycan known in plants. Equally impressive to the extensive enzymology presented is the fact that the authors were able to solve the previously unknown structure of RGII by enzymatically dissecting it with their newly discovered set of enzymes. This study set the bar incredibly high regarding what can be achieved in PUL characterisation.

56. * Luis AS, Jin C, Pereira GV, Glowacki RWP, Gugel SR, Singh S, Byrne DP, Pudlo NA, London JA, Baslé A, *et al.*: **A single sulfatase is required to access colonic mucin by a gut bacterium**. *Nature* 2021, **598**:332–337, https://doi.org/10.1038/s41586-021-03967-5.

The scientists characterised twelve different sulfatase enzymes of the human gut bacterium *Bacteroides thetaiotaomicron* that are collectively active on all known sulphate linkages in O-glycans and found that one sulfatase is essential for O-glycan utilisation. This study provides insight into the mechanisms dictating substrate specificity and demonstrates for the first time that certain steps exist in the complex

cascades for glycan degradation may be disproportionately important, adding another layer of complexity.

57. Hehemann JH, Correc G, Thomas F, Bernard T, Barbeyron T, Jam M, Helbert W, Michel G, Czjzek M: **Biochemical and structural characterization of the complex agarolytic enzyme system from the marine bacterium *Zobellia galactanivorans***. *J Biol Chem* 2012, **287**:30571–30584, https://doi.org/10.1074/jbc.M112.377184.

58. Correc G, Hehemann JH, Czjzek M, Helbert W: **Structural analysis of the degradation products of porphyran digested by *Zobellia galactanivorans* β-porphyranase A**. *Carbohydr Polym* 2011, **83**:277–283, https://doi.org/10.1016/j.carbpol.2010.07.060.

59. Reisky L, Büchsenschütz HC, Engel J, Song T, Schweder T, Hehemann J-H, Bornscheuer UT: **Oxidative demethylation of algal carbohydrates by cytochrome P450 monooxygenases**. *Nat Chem Biol* 2018, **14**:342–344, https://doi.org/10.1038/s41589-018-0005-8.

60. Panagiotopoulos C, Repeta DJ, Mathieu L, Rontani JF, Sempéré R: **Molecular level characterization of methyl sugars in marine high molecular weight dissolved organic matter**. *Mar Chem* 2013, **154**:34–45, https://doi.org/10.1016/j.marchem.2013.04.003.

61. Humphrey W, Dalke A, Schulten K: *VMD: Visual Molecular Dynamics*. 1996.

62. Hehemann JH, Arevalo P, Datta MS, Yu X, Corzett CH, Henschel A, Preheim SP, Timberlake S, Alm EJ, Polz MF: **Adaptive radiation by waves of gene transfer leads to fine-scale resource partitioning in marine microbes**. *Nat Commun* 2016, **7**, https://doi.org/10.1038/ncomms12860.

63. Gore J, Youk H, van Oudenaarden A: **Snowdrift game dynamics and facultative cheating in yeast**. *Nature* 2009, **459**:253–256, https://doi.org/10.1038/nature07921.

64. Thomas F, Barbeyron T, Tonon T, Génicot S, Czjzek M, Michel G: **Characterization of the first alginolytic operons in a marine bacterium: from their emergence in marine *Flavobacteriia* to their independent transfers to marine *Proteobacteria* and human gut *Bacteroides***. *Environ Microbiol* 2012, **14**:2379–2394, https://doi.org/10.1111/j.1462-2920.2012.02751.x.

65. Arnosti C, Wietz M, Brinkhoff T, Hehemann JH, Probandt D, Zeugner L, Amann R: **The biogeochemistry of marine polysaccharides: sources, inventories, and bacterial drivers of the carbohydrate cycle**. *Ann Rev Mar Sci* 2021, **13**:81–108, https://doi.org/10.1146/annurev-marine-032020-012810.

66. Fletcher HR, Biller P, Ross AB, Adams JMM: **The seasonal variation of fucoidan within three species of brown macroalgae**. *Algal Res* 2017, **22**:79–86, https://doi.org/10.1016/j.algal.2016.10.015.

67. Pluvinage B, Ficko-Blean E, Noach I, Stuart C, Thompson N, Mcclure H, Buenbrazo N, Wakarchuk W, Boraston AB: **Architecturally complex O-glycopeptidases are customized for mucin recognition and hydrolysis**. *Proc Natl Acad Sci U S A* 2021:118, https://doi.org/10.1073/pnas.2019220118.

68. Marcus SE, Verhertbruggen Y, Hervé C, Ordaz-Ortiz JJ, Farkas V, Pedersen HL, Willats WG, Knox JP: **Pectic homogalacturonan masks abundant sets of xyloglucan epitopes in plant cell walls**. *BMC Plant Biol* 2008, **8**, https://doi.org/10.1186/1471-2229-8-60.

69. Lucaci AR, Bulgariu D, Bulgariu L: **In situ functionalization of iron oxide particles with alginate: a promising biosorbent for retention of metal ions**. *Polymers* 2021, **13**, https://doi.org/10.3390/polym13203554.

70. Moore CM, Mills MM, Arrigo KR, Berman-Frank I, Bopp L, Boyd PW, Galbraith ED, Geider RJ, Guieu C, Jaccard SL, *et al.*: **Processes and patterns of oceanic nutrient limitation**. *Nat Geosci* 2013, **6**:701–710, https://doi.org/10.1038/ngeo1765.

71. Kopplin G, Rokstad AM, Mélida H, Bulone V, Skjåk-Bræk G, Aachmann FL: **Structural characterization of fucoidan from *Laminaria hyperborea*: assessment of coagulation and inflammatory properties and their structure-function relationship**. *ACS Appl Bio Mater* 2018, **1**:1880–1892, https://doi.org/10.1021/acsabm.8b00436.

72. Luthuli S, Wu S, Cheng Y, Zheng X, Wu M, Tong H: **Therapeutic effects of fucoidan: a review on recent studies**. *Mar Drugs* 2019, **17**:487, https://doi.org/10.3390/md17090487.

73. Gärdes A, Iversen MH, Grossart HP, Passow U, Ullrich MS: **Diatom-associated bacteria are required for aggregation of *Thalassiosira weissflogii***. *ISME J* 2011, **5**:436–445, https://doi.org/10.1038/ismej.2010.145.

74. Wang BX, Wu CM, Ribbeck K: **Home, sweet home: how mucus accommodates our microbiota**. *FEBS J* 2021, **288**:1789–1799, https://doi.org/10.1111/febs.15504.

75. Laine R: **A calculation of all possible oligosaccharide isomers both branched and linear yields 1.05 × 10^{12} structures for a reducing hexasaccharide: the Isomer Barrier to development of single-method saccharide sequencing or synthesis systems**. *Glycobiology* 1994, **4**:759–767.

76. * Srivastava J, Sunthar P, Balaji P v: **The glycan alphabet is not universal: a hypothesis**. *Microb Genom* 2020, **6**:1–14, https://doi.org/10.1099/mgen.0.000452.
The scientists use a curated set of bacterial and archaeal proteins involved in monosaccharide biosynthesis to argue that the glycan 'alphabet' (i.e., monosaccharides) is not universal, and varies even on the strain level. This hypothesis reframes our understanding of the evolution of glycans.

77. ** Vieira PS, Bonfim IM, Araujo EA, Melo RR, Lima AR, Fessel MR, Paixão DAA, Persinoti GF, Rocco SA, Lima TB, *et al.*: **Xyloglucan processing machinery in Xanthomonas pathogens and its role in the transcriptional activation of virulence factors**. *Nat Commun* 2021, **12**, https://doi.org/10.1038/s41467-021-24277-4.
The scientists characterised the molecular strategy employed by a pathogenic *Xanthomonas* bacterium to degrade xyloglucans, defensive cell wall glycans of plants. They discovered that this system differs from that employed by commensal bacteria, and that xyloglucan breakdown products upregulate expression of virulence factors. This finding sheds light on the complex glycan-mediated interactions between eukaryotes and bacteria.

78. ** Brunet M, le Duff N, Barbeyron T, Thomas F: **Consuming fresh macroalgae induces specific catabolic pathways, stress reactions and Type IX secretion in marine flavobacterial pioneer degraders**. *ISME J* 2022, https://doi.org/10.1038/s41396-022-01251-6.
Zobellia galactanivorans is shown to attack macroalgae tissue with secreted enzymes. This invokes defence in the algae and an active stress response of *Z. galactanivorans*. This study shows degradation of glycans in a more natural context than the test tube is stressful for both bacteria and the algae.

79. Pudlo NA, Pereira GV, Parnami J, Cid M, Markert S, Tingley JP, Unfried F, Ali A, Varghese NJ, Kim KS, *et al.*: **Diverse events have transferred genes for edible seaweed digestion from marine to human gut bacteria**. *Cell Host Microbe* 2022, **30**:314–328.e11, https://doi.org/10.1016/j.chom.2022.02.001.

80. ** Werlang CA, Chen WG, Aoki K, Wheeler KM, Tymm C, Mileti CJ, Burgos AC, Kim K, Tiemeyer M, Ribbeck K: **Mucin O-glycans suppress quorum-sensing pathways and genetic transformation in *Streptococcus mutans***. *Nat Microbiol* 2021, **6**:574–583, https://doi.org/10.1038/s41564-021-00876-1.
The glycans of a specific salivary mucin, MUC5, were demonstrated to suppress quorum sensing pathways and genetic transformation in *Streptococcus mutans*. The findings of this study imply that glycans can interact with protein machineries involved in the flow of genetic information between bacteria, and could by unknown mechanisms inhibit acquisition of genes encoding enzymes targeting them for degradation.

81. ** Wheeler KM, Cárcamo-Oyarce G, Turner BS, Dellos-Nolan S, Co JY, Lehoux S, Cummings RD, Wozniak DJ, Ribbeck K: **Mucin glycans attenuate the virulence of Pseudomonas**. *Nat Microbiol* 2020, **4**:2146–2154, https://doi.org/10.1038/s41564-019-0581-8.
The scientists demonstrate that glycans associated with mucin secreted in the human gut cause a switch to a less virulent phenotype in the opportunistic pathogen *Pseudomonas aeruginosa*, including downregulation of virulence genes involved in quorum sensing, siderophore biosynthesis and toxin secretion. This finding expands our

understanding of the defensive mechanism of mucin in particular, and by extension extracellular matrix glycans, from merely physical to also biochemical.

82. Moran MA, Kujawinski EB, Schroer WF, Amin SA, Bates NR, Bertrand EM, Braakman R, Brown CT, Covert MW, Doney SC, *et al.*: **Microbial metabolites in the marine carbon cycle**. *Nat Microbiol* 2022, **7**:508–523, https://doi.org/10.1038/s41564-022-01090-3.

83. Repeta DJ: **Chemical characterization and cycling of dissolved organic matter**. In *Biogeochemistry of Marine Dissolved Organic Matter*. Edited by Hansell DA, Carlson CA, Academic Press; 2015:21–63, https://doi.org/10.1016/B978-0-12-405940-5.00002-9.

84. * Amicucci MJ, Nandita E, Galermo AG, Castillo JJ, Chen S, Park D, Smilowitz JT, German JB, Mills DA, Lebrilla CB: **A nonenzymatic method for cleaving polysaccharides to yield oligosaccharides for structural analysis**. *Nat Commun* 2020, **11**:1–12, https://doi.org/10.1038/s41467-020-17778-1.

A novel method for non-enzymatic degradation of glycans to reproducibly yield unique fingerprints of oligosaccharides diagnostic of the parent glycans is reported by the scientists. This method could be highly valuable for future studies of algal glycans as it provides an alternative to the commonly used acid hydrolysis which destroys higher order information about glycan structures.

85. Moosburner MA, Gholami P, McCarthy JK, Tan M, Bielinski VA, Allen AE: **Multiplexed knockouts in the model diatom Phaeodactylum by episomal delivery of a selectable Cas9**. *Front Microbiol* 2020, **11**, https://doi.org/10.3389/fmicb.2020.00005.

86. Ren W, Pengelly R, Farren-Dai M, Shamsi Kazem Abadi S, Oehler V, Akintola O, Draper J, Meanwell M, Chakladar S, Świderek K, Moliner V, Britton R, Gloster TM, Bennet AJ: **Revealing the mechanism for covalent inhibition of glycoside hydrolases by carbasugars at an atomic level**. *Nat Commun* 2018, **9**, https://doi.org/10.1038/s41467-018-05702-7.

87. Reintjes G, Fuchs BM, Scharfe M, Wiltshire KH, Amann R, Arnosti C: **Short-term changes in polysaccharide utilization mechanisms of marine bacterioplankton during a spring phytoplankton bloom**. *Environ Microbiol* 2020, **22**:1884–1900, https://doi.org/10.1111/1462-2920.14971.

88. Crawford CJ, Wear MP, Smith DFQ, d'Errico C, McConnell SA, Casadevall A, Oscarson S: **A glycan FRET assay for detection and characterization of catalytic antibodies to the *Cryptococcus neoformans* capsule**. *Proc Natl Acad Sci U S A* 2021, **118**, e2016198118, https://doi.org/10.1073/pnas.2016198118.

89. Tyrikos-Ergas T, Sletten ET, Huang JY, Seeberger PH, Delbianco M: **On resin synthesis of sulfated oligosaccharides**. *Chem Sci* 2022, **13**:2115–2120, https://doi.org/10.1039/d1sc06063e.