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Enrichment of saccharides at the air–water interface: a quantitative comparison of sea surface microlayer and foam

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Environmental context. Saccharides contribute substantially to dissolved organic carbon in the ocean and are enriched at the ocean surface. In this study, we demonstrate that saccharides are more enriched in persistent whitecap foam compared to the sea surface. The maturation of bubbles at the air–water interface is thus expected to enhance the enrichment of organic matter at the ocean surface and ultimately in the sea spray aerosol that forms when bubbles burst at the ocean surface.

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ABSTRACT

Rationale. Organic matter accumulates at the ocean surface. Herein, we provide the first quantitative assessment of the enrichment of dissolved saccharides in persistent whitecap foam and compare this enrichment to the sea surface microlayer (SSML) during a 9 day mesocosm experiment involving a phytoplankton bloom generated in a Marine Aerosol Reference Tank (MART). **Methodology.** Free monosaccharides were quantified directly, total saccharides were determined following mild acid hydrolysis and the oligo/polysaccharide component was determined as the difference between total and free monosaccharides. **Results.** Total saccharides contributed a significant fraction of dissolved organic carbon (DOC), accounting for 13% of DOC in seawater, 27% in SSML and 31% in foam. Median enrichment factors (EFs), calculated as the ratio of the concentrations of saccharides relative to sodium in SSML or foam to that of seawater, ranged from 1.7 to 6.4 in SSML and 2.1–12.1 in foam. Based on median EFs, xylitol, mannitol, glucose, galactose, mannose, xylose, fucose, rhamnose and ribose were more enriched in foam than SSML. **Discussion.** The greatest EFs for saccharides coincided with high chlorophyll levels, indicating increasing ocean surface enrichment of saccharides during phytoplankton blooms. Higher enrichments of organic matter in sea foam over the SSML indicate that surface active organic compounds become increasingly enriched on persistent bubble film surfaces. These findings help to explain how marine organic matter becomes highly enriched in sea spray aerosol that is generated by bursting bubbles at the ocean surface.

Keywords: carbohydrates, dissolved organic carbon, enrichment factor, phytoplankton bloom, sea surface microlayer, sugar alcohols, ultrafiltration, whitecap foam.

Introduction

Seawater, in addition to salt, contains complex matrix organic compounds, with saccharides (carbohydrates), proteins and lipids being the predominant compound classes (Larsson *et al.* 1974; Henrichs and Williams 1985; Garabetian *et al.* 1993; Aluwihare *et al.* 1997). Saccharides, in particular, are present in a variety of chemical forms, including sugar alcohols (e.g. arabitol, mannitol), free monosaccharides (e.g. glucose, galactose), oligo/polysaccharides (e.g. glucan, transparent exopolysaccharides or TEP) and saccharides complexed with other molecules such as lipids and protein (e.g. lipopolysaccharides, glycoproteins) (Borch and Kirchman 1997; Verdugo *et al.* 2004; van Pinxteren *et al.* 2012). These saccharides serve as substrates for energy storage and the formation of structural materials (e.g. cell walls) of marine micro-organisms (Haug and Myklestad 1976; Dean Pakulski and Benner 1992; Hung *et al.* 2001; Verdugo *et al.* 2004). They have been estimated to contribute up to 40% of dissolved organic carbon (DOC) in the ocean with levels dependent on biological activity (Dean Pakulski and Benner 1992;

Skoog and Benner 1997; Biersmith and Benner 1998; Engbrodt and Kattner 2005). During a phytoplankton bloom, the molecular composition of saccharides is altered by phytoplankton and bacteria (Ittekkot 1982). Glucose and fructose are the monomers of major energy-related polysaccharides in phytoplankton (e.g. glucan, fructan) and are released in large quantities following the peak of the bloom due to phytoplankton lysis and can also be released under stressed conditions such as low nutrients, elevated temperature and high light exposure (Mopper *et al.* 1980; Ittekkot 1982; Compiano *et al.* 1993; Thornton 2014). Galactose, mannose, xylose, fucose, rhamnose and arabinose comprise less labile, structurally related polysaccharides that are released by bacterial breakdown of phytoplankton cellular materials. Meanwhile, fucose, arabinose and rhamnose-containing polysaccharides are synthesised by stressed phytoplankton under nutrient deficiency, and elevated levels of these carbohydrate monomers are observed during phytoplankton bloom decay (Ittekkot 1982; Ittekkot *et al.* 1982; Compiano *et al.* 1993). In addition, polysaccharides containing rhamnose and arabinose are associated with bacterial secretions and are elevated in areas of the ocean with relatively high bacterial activity (Liebezeit *et al.* 1980; Ittekkot 1982; Mühlenbruch *et al.* 2018; Hasenecz *et al.* 2020). Hence, the changes in the concentrations and molecular distributions of saccharides can provide insights to biochemical processes controlling DOC in the ocean (Ittekkot 1982).

Breaking waves entrain air in sub-surface seawater. As tiny bubbles rise to the ocean surface, they scavenge surface-active materials in marine DOC (e.g. lipopolysaccharides), leading to their accumulation at the ocean surface (Mopper *et al.* 1995; Zhou *et al.* 1998; Cunliffe *et al.* 2013; Burrows *et al.* 2014). In general, bubbles that reach the surface may either burst instantly (<1 s) or persist for an extended period of time (10–100 s), producing a persistent layer of whitecap foam (Callaghan *et al.* 2012; Modini *et al.* 2013). Elevated levels of either DOC or surface active material in seawater increases bubble lifetime, leading to more persistent bubbles (Callaghan *et al.* 2013; Modini *et al.* 2013; Collins *et al.* 2014). As bubbles age, bubble films decrease in thickness (1 μm–100 nm) as less surface-active materials drain to the base of the bubble creating a highly organic-enriched bubble film (Modini *et al.* 2013; Burrows *et al.* 2014). Surface active materials reside at the interior and exterior surfaces of the bubble film and become enriched (Burrows *et al.* 2014). The drainage creates a thin (20–400 μm), chemically distinct film at the ocean surface referred to as the sea surface microlayer (SSML) (Cunliffe *et al.* 2013; Burrows *et al.* 2014). Bubble films have been predicted to exhibit higher enrichment than the SSML because of their larger surface area to volume ratio and this drainage process (Burrows *et al.* 2014).

The extent of the accumulation of material at the ocean surface is often quantitatively evaluated by enrichment factors (EFs). An EF for species x (saccharides) relative to sodium (Na^+) in phase i (either SSML or foam) over seawater can be calculated by Eqn 1.

$$EF_{x(i)} = \frac{[x]_i / [Na^+]_i}{[x]_{seawater} / [Na^+]_{seawater}} \quad (1)$$

An EF greater than one indicates enrichment of species x relative to sodium in phase i, while an EF less than one indicates depletion. Prior studies have demonstrated enrichment of DOC, organic and inorganic species in the SSML (Compiano *et al.* 1993; Gao *et al.* 2012; van Pinxteren *et al.* 2012). In particular, DOC in the SSML has been reported to be enriched 0.8–1.6 times than in seawater (García-Flor *et al.* 2005; Wurl and Holmes 2008). Furthermore, enrichment of total saccharides has been observed in the SSML with EFs ranging from 0.7 to 12.1 across field and laboratory studies, indicating a selective enrichment of saccharides over bulk DOC (Compiano *et al.* 1993; Gao *et al.* 2012; van Pinxteren *et al.* 2012; Jayarathne *et al.* 2016). It has been proposed that water soluble saccharides may chemically adsorb to organic surfactants that have more affinity towards bubble films and be co-transported to the ocean surface (Burrows *et al.* 2016; Schill *et al.* 2018; Vazquez de Vasquez *et al.* 2022). Such an association may be even stronger with oligo/polysaccharides due to the presence of multiple binding sites (–OH) able to interact with anionic head groups (–COOH) of the surfactant molecules facilitated by multivalent cations (e.g. Mg^{2+}, Ca^{2+}) (Kundu *et al.* 2008; Li and McClements 2014; Vazquez de Vasquez *et al.* 2022). Furthermore, phenolic (Ar–OH), aromatic and other hydroxy (R–OH) functional groups within extracellular polymeric substances (EPS) that are produced by marine micro-organisms can self-assemble by chelation with multivalent cations (Xu *et al.* 2016). These macromolecules form TEP or larger DOC colloids and selectively transfer to the ocean surface via scavenging on rising bubbles and/or by positive buoyancy (Garabetian *et al.* 1993; Dai *et al.* 1998; Verdugo *et al.* 2004). Similarly, aggregation of colloidal dissolved organic matter via multivalent metal ions may provide a conduit from the dissolved to particulate carbon pool, and eventually form marine snow that sinks in the ocean and removes DOC from seawater (Verdugo *et al.* 2004).

Enrichments of saccharides have not been quantitatively evaluated for persistent bubble films. Meanwhile, it has been suggested that extremely high organic enrichment (10^2–10^3) in sea spray aerosol (SSA) may result from organic matter being selectively enriched on bubble film surfaces prior to bursting (Russell *et al.* 2010; Burrows *et al.* 2014). Collins *et al.* (2014) demonstrated a preferential enrichment of organic matter in SSA in the presence of foam compared to free bubble bursting at the ocean surface. Furthermore, fine SSA (with particle diameters <2.5 μm) has been demonstrated to be more enriched in saccharides than coarse SSA (with particle diameters 2.5–10 μm), which is proposed to result from fine SSA generation by the

bursting of bubble films, called film drops, that have the greatest carbohydrate enrichment (Jayarathne *et al.* 2016). Such size-dependent saccharide enrichment in SSA has been demonstrated by several complementary techniques in numerous studies (Russell *et al.* 2010; Quinn *et al.* 2014; Jayarathne *et al.* 2016; Aller *et al.* 2017; Rastelli *et al.* 2017). Furthermore, it was reported that dissolved and particulate saccharides selectively transfer to fine and coarse SSA particles, respectively, which was proposed to result from the inclusion of particulate organic carbon comprised of cell wall materials into coarse particles (Jayarathne *et al.* 2016). On a molecular level, surface activity, chelation of divalent cations and the seawater matrix have been demonstrated to impact saccharide enrichment (Hasenecz *et al.* 2019). In addition, phytoplankton blooms and the enzymatic activity of heterotrophic bacteria are associated with the largest saccharide enrichments in SSA (Hasenecz *et al.* 2020). As the air–water interface is involved in SSA production, it is essential to understand its chemical composition in order to predict the chemical composition of SSA and its potential to influence atmospheric processes and the climate.

The central objective of this study is the quantitative assessment of saccharide enrichment in SSML and sea foam over a full phytoplankton bloom cycle. A Marine Aerosol Reference Tank (MART) was used for foam production providing an accurate mimic for wave breaking, air entrainment and bubble generation that occurs in the marine environment (Stokes *et al.* 2013). This study provides insight to the enrichment of saccharides in sea foam compared to SSML that is relevant to the formation of SSA at the air–water interface.

Experimental

Sample collection and preparation

A mesocosm was created in a MART following the method described by Lee *et al.* (2015) during the Investigation into Marine Particle Chemistry and Transfer Science (IMPACTS) laboratory study. The experiment was conducted under natural sun light using natural sea water collected at the end of Scripps Pier (La Jolla, CA; 32°52′00″N, 117°15′21″W; 275 m offshore). Guillard's f medium diluted by a factor of two ($f/2$) including Na_2SiO_3 was used as nutrients to stimulate the growth of phytoplankton. A full list of nutrient components, their concentrations and microorganisms present in a parallel MART experiment are described in detail by Lee *et al.* (2015). The phytoplankton biomass of the MART was monitored immediately before the sample collection by chlorophyll-*a* (chl-*a*) levels using a Wetlabs ECO BBFL2 sensor and Turner AquaFluor handheld unit, with further details and calibration procedures provided by Wang *et al.* (2015).

Seawater samples were collected from 15 to 20 cm below the air–water interface of the MART using a disposable plastic pipette and SSML samples were collected from the upper 35–42 μm of the air–water interface following the membrane filter method for nine consecutive days (Cunliffe *et al.* 2013). Foam samples were collected from day 3 to 9 using an auto-pipette by rastering the pipette tip over the foam layer (Supplementary Fig. S1). The foam was generated by plunging the MART acheived by impacting a water sheet on the water surface to mimic the plunging jet of water from a breaking wave crest (Stokes *et al.* 2013; Collins *et al.* 2014). The MART was plunged for 5 min and accumulated foam was immediately collected. Several plunging cycles (10–15 cycles) were carried out to collect sufficient volume of foam for the chemical analysis. All samples were stored in polypropylene bottles in the dark and frozen (−20°C). Prior to chemical analysis, samples were filtered (450 nm PTFE filters, Whatman) to isolate DOC, operationally defined as solutes and colloids smaller than 450 nm. A subset of seawater, SSML and foam samples (corresponding to days 1–3, 5, 7 and 9) were subjected to ultrafiltration for fractionation of material <3 kDa and <100 kDa using Amicon centrifugal ultracel membrane filters (Sigma-Aldrich). These cutoff diameters are referenced to globular proteins and in general ~1 kDa refers to a globular protein of ~1 nm in diameter (Ogura 1974; McCarthy *et al.* 1996; Erickson 2009). Based on that approximation DOC smaller than 450 nm corresponds to solutes and colloids smaller than ~450 kDa.

Saccharide and DOC analysis

Instrumental analysis of saccharides was performed by high performance anion exchange chromatography (HPAEC) (Dionex-ICS 5000) with pulsed amperometric detection (PAD) following the conditions described by Jayarathne *et al.* (2016). Samples were analysed in four ways: (1) direct analysis to quantify free monosaccharides, (2) hydrolysis using trifluoroacetic acid (0.1 M) at 100°C for 12 h for total saccharides, (3) 3 kDa ultrafiltration and then hydrolysis and (4) 100 kDa ultrafiltration and then hydrolysis. This allowed for saccharides to be quantified in four size bins: free monosaccharides, low molecular weight (LMW) oligo- and polysaccharides less than 3 kDa, high molecular weight (HMW) polysaccharides ranging from 3 to 100 kDa and colloidal polysaccharides ranging from 100 kDa to 450 nm. Analytical uncertainties were propagated from the method detection limits and 10% of the saccharide concentration based on spike recovery samples.

DOC was analysed using a Sievers 5310C Laboratory Total Organic Carbon Analyzer (GE Instruments) and inorganic ion concentrations were analysed by ion-exchange chromatography coupled with conductivity detection as described in detail elsewhere (Jayarathne *et al.* 2014). The enrichment of saccharide relative to Na^+ in SSML and foam with respect to seawater was calculated using Eqn 1. Equal volumes of day 1–4 and day 5–9 seawater, SSML and foam samples were composited together to represent time periods of high chl-*a* and bacteria, respectively.

Results and discussion

Biological activity of the seawater

The initial chl-*a* concentration of the seawater was 3.1 μg L^{-1} (day 0) indicating a mild phytoplankton bloom was occurring in the coastal ocean (Quinn *et al.* 2014; Lee *et al.* 2015). Addition of nutrients and exposure to natural sunlight triggered the growth of phytoplankton, increasing to a maximum chl-*a* level of 45.4 μg L^{-1} on day 2 (Fig. 1). Natural levels of chl-*a* in the open and coastal ocean have been observed in the range of 0.03–40 μg L^{-1} (Cloern 1996; Quinn *et al.* 2014). Chl-*a* levels rapidly declined to a minimum of 0.24 μg L^{-1} on day 5. Potential reasons for this decline include nutrient deficiency, growth of heterotrophic bacteria and viruses and mechanical breakdown of phytoplankton due to plunging of the MART (Azam and Malfatti 2007; Lee *et al.* 2015). After day 5, chl-*a* levels steadily increased up to 3.1 μg L^{-1} by the end of experiment on day 9. The growth of phytoplankton after day 5 was likely promoted by nutrients released to the seawater by the crash of the previous phytoplankton bloom, a process that is commonly observed in the ocean (Ittekkot 1982; Norrman *et al.* 1995; Azam and Malfatti 2007).

The ratio of the sum of fucose and rhamnose concentrations to the sum of arabinose and xylose concentrations in seawater was used as an indicator for the bacterial activity in the tank (Fig. 1). Typically, ratios <1 indicate the presence of less-labile organic matter which is indicative of higher bacterial concentration (Frimmel 1998; Engbrodt and Kattner 2005; Jiao *et al.* 2010). In this experiment, this ratio decreased below one (0.69) on day 4, with a consistent decrease to 0.50 on day 9 indicating the growth of marine bacteria after the phytoplankton bloom (Frimmel 1998; Engbrodt and Kattner 2005).

Contribution of saccharides to DOC

The total quantified saccharide concentration (<450 nm) in seawater ranged from 0.9 to 5.1 μM and averaged 3 ± 1 μM. These concentration levels agree well with previously reported saccharide concentrations in seawater (Amon and Benner 2003; Engbrodt and Kattner 2005). The total saccharide concentration in SSML ranged from 1.4 to 51 μM, averaging 18 ± 15 μM. In foam, saccharide concentrations ranged from 11 to 32 μM and averaged 22 ± 7 μM. Total measured saccharides comprised a considerable fraction of DOC in seawater (13%), SSML (27%) and foam (31%).

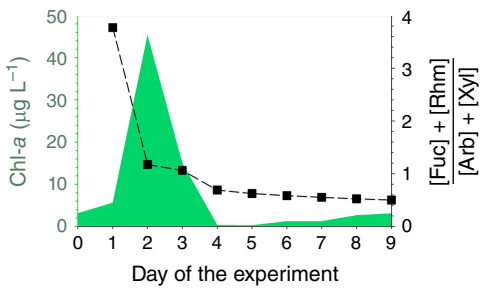

Fig. 1. Chlorophyll-*a* concentration and ratio of fucose and rhamnose to arabinose and xylose concentrations in seawater. Chlorophyll-*a* concentration peaked on day 2 and came to a minimum on day 5. Saccharide ratio decreased to below one from day 4 indicating higher bacterial activity from day 4 to 9.

Sugar alcohols

Concentrations of three sugar alcohols – xylitol, arabitol and mannitol – varied from below method detection limits to 674 ± 67 nM for mannitol on day 9 in the SSML (Supplementary Table S1). Sugar alcohol contributions to quantified total saccharides were small, contributing an average of 2.1 ± 0.8% in seawater, 2.5 ± 1.9% in SSML and 2.4 ± 0.5% in foam with a maximum contribution of 5.8% on day 9 in SSML. From this, we conclude that xylitol, arabitol and mannitol have minor contributions to the total saccharide pool in the ocean. The sugar alcohol concentration significantly increased at the latter part of the mesocosm suggesting a probable bacterial origin (Fig. 2*a–c*) (Pramanik *et al.* 2011; Dai *et al.* 2015). Sugar alcohols were primarily ($>43\%$) in the form of free monosaccharides (Fig. 3*a*), likely due to direct release of free alditols by bacteria from lignocellulosic material breakdown (Pérez-Bibbins *et al.* 2016). Furthermore, a systematic distribution of sugar alcohols in different size fractions was not observed (Fig. 3), suggesting that the transfer of sugar alcohols to the ocean surface was relatively independent of particle size.

Energy-related saccharides

Concentrations of energy-related saccharides were elevated during the phytoplankton bloom, declined with bloom crashing and consistently increased thereafter (Fig. 2*d*, *e*). The high concentrations of energy-related saccharides as the phytoplankton bloom progressed were likely due to the synthesis of energy storage products (e.g. glucans, fructans) and their release to surrounding water upon cell lysis (Ittekkot 1982; Compiano *et al.* 1993; Mopper *et al.* 1995). Bacteria rapidly utilise these labile polysaccharides as energy substrates, leading to their sharp decline in concentration after the bloom crashed (Handa and Yanagi 1969). In this process, either *in situ* enzymatic hydrolysis or extra-cellular hydrolysis by bacterial enzymes could release free monosaccharides, producing free glucose and fructose (Mopper *et al.* 1980), which was observed on day 3 following the peak of the phytoplankton bloom. The steady increase of total saccharide from day 4 was likely related to breakdown of more stable structural saccharides (e.g. cellulose, hemicellulose) by bacterial hydrolysis (Hecky *et al.* 1973; Haug and Myklestad 1976). The dominant form of energy-related saccharides was the LMW fraction that accounted for 34–65% by mass (Fig. 3*b*). The colloidal fraction considerably increased in SSML and foam (27–36%) relative to seawater, likely due to enrichment of cellular materials at the air–water interface.

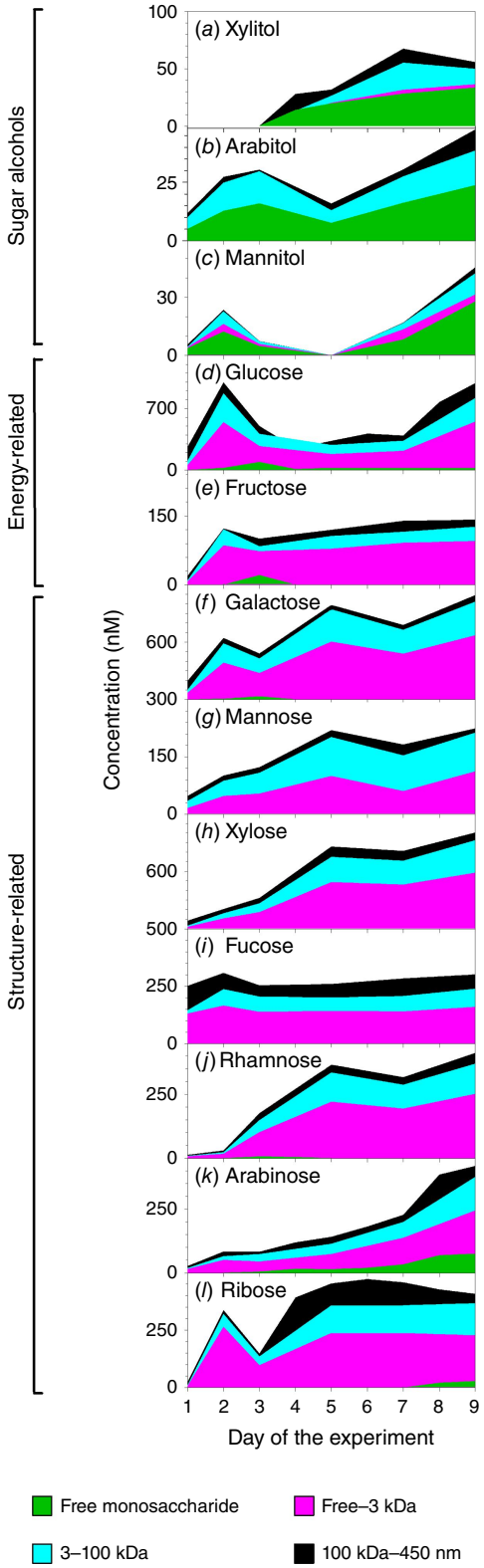

Fig. 2. Variation of sugar alcohol (*a*–*c*), energy-related saccharide (*d*, *e*) and structure-related saccharide (*f*–*l*) concentrations in the seawater during the mesocosm experiment.

Structure-related saccharides

Concentrations of structural saccharides differed from the previously discussed energy-related saccharides in that they were not elevated during the phytoplankton bloom and instead steadily increased throughout the experiment (Fig. 2*f*–*k*). This is likely due to gradual bacterial degradation of more stable cellular materials, such as marine particulate organic carbon (POC) or high molecular weight DOC (Coombs and Volcani 1968; Handa and Yanagi 1969; Haug and Myklestad 1976; Liebezeit *et al.* 1980; Mopper *et al.* 1980). The saccharide composition in the ocean was observed to shift towards structural polysaccharides at the end of a mesocosm as a result of preferential bacterial uptake of LMW algal exopolymers during the initial stage, followed by feeding on less labile structural components (Chrost and Faust 1983; Gershey 1983). In this process bacteria reduce detrital organic matter to soluble foams and convert algal exopolysaccharides into bacterial polysaccharides as evident by elevated levels of structural and bacterial-related saccharides at the end of the experiment (Mopper *et al.* 1995). Galactose has some characteristics of energy-related saccharides such as elevated concentrations during the phytoplankton bloom and release of free galactose monosaccharide after bloom crashing. This trend is probably due to galactan, the polysaccharide form of galactose that is used as an energy storage material by some phytoplankton species (Ittekkot *et al.* 1982; Biersmith and Benner 1998). Ribose also showed a distinct variation pattern over the experiment (Fig. 2*i*) relative to other structure-related saccharides. The lysis of phytoplankton nucleotides during the phytoplankton bloom and the lysis of bacterial nucleotides at the latter part of the bloom is likely the source of ribose oligo/polysaccharides (Cowie and Hedges 1984; McCarthy *et al.* 1996). Unlike sugar alcohols and energy-related saccharides, structure-related saccharides showed a distinct distribution pattern in different compartments. The LMW saccharide (free–3 kDa) fraction dominated (44–59%) the seawater saccharide pool while the HMW saccharide (3–100 kDa) fraction dominated the SSML and foam (45–88%) saccharide pool (Fig. 3*c*). This is attributed to selective transfer of higher molecular weight oligo/polysaccharides towards ocean surface likely due to scavenging on rising bubbles due their high surface activity. Furthermore, smaller surface active oligo/polysaccharides can coagulate to form HMW polysaccharides and these could rise to the ocean surface due to positive buoyancy (Ogura 1977; McCarthy *et al.* 1996).

Enrichment of saccharides in foam and SSML over seawater

Total saccharides (< 450 nm) were significantly enriched ($P < 0.05$) in SSML and foam with individual median EFs ranging from 1.7–6.4 to 2.1–12, respectively (Fig. 4).

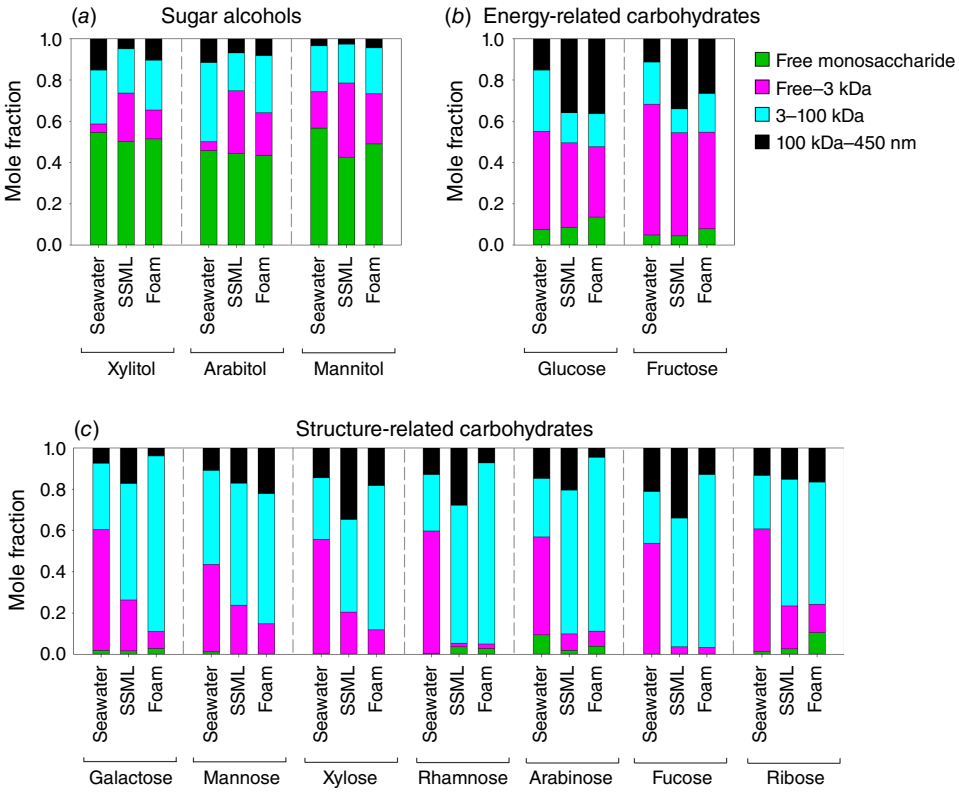

Fig. 3. Relative composition of sugar alcohols (*a*), energy-related saccharides (*b*) and structure-related saccharides (*c*) in different size fractions.

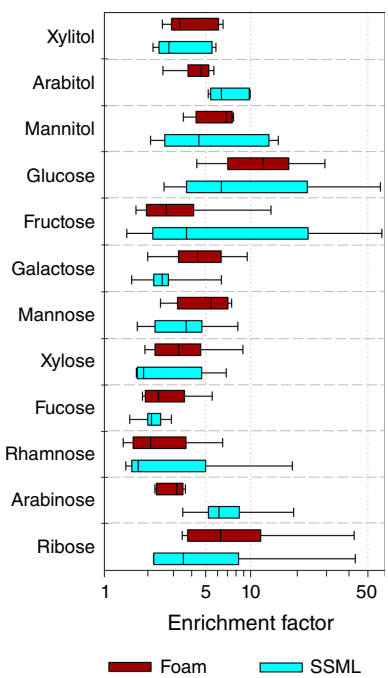

Fig. 4. Boxplot graphs showing EFs of total saccharides (<450 nm) in SSML ($n = 9$) and foam ($n = 7$). (The two end caps indicate the data range, boxes indicate the first quartile, median and third quartile, respectively.) All the carbohydrates were significantly enriched in SSML and foam.

This enrichment provides evidence for scavenging of the saccharides on bubble surfaces and their accumulation at the ocean surface where SSA is generated. Median EFs for xylitol, mannitol, glucose, galactose, mannose, xylose, fucose, rhamnose and ribose demonstrated greater enrichment in foam compared to SSML. The relatively higher EFs in the foam layer provide the first quantitative evidence of further enrichment of saccharides on bubble films compared to SSML. This is attributed to thinning the bubble film by draining the seawater constituents keeping the surface active materials on the bubble film (Mopper *et al.* 1995; Zhou *et al.* 1998; Modini *et al.* 2013; Collins *et al.* 2014). This phenomenon could lead to further enrichment on the bubble film with bubble ageing and could result in an extremely enriched bubble film at the time of bursting to generate SSA that is highly enriched in organic matter and saccharides.

The enrichment process was dynamic with the greatest EFs occurring on days 2–4 with peak chl-*a* levels (Supplementary Fig. S2) indicating higher accumulation of saccharides in SSML and foam during the active bloom period. This observation demonstrates that the saccharide enrichment at the ocean surface is influenced by the biological activity of the seawater.

The size of the saccharide played a significant role in the enrichment process. LMW oligo/polysaccharides (free–3 kDa) were the major enriched species for sugar alcohols (Fig. 5*a*, *b*) and showed 2–15 times greater EFs than those for total dissolved (< 450 nm) saccharides. The enrichment of

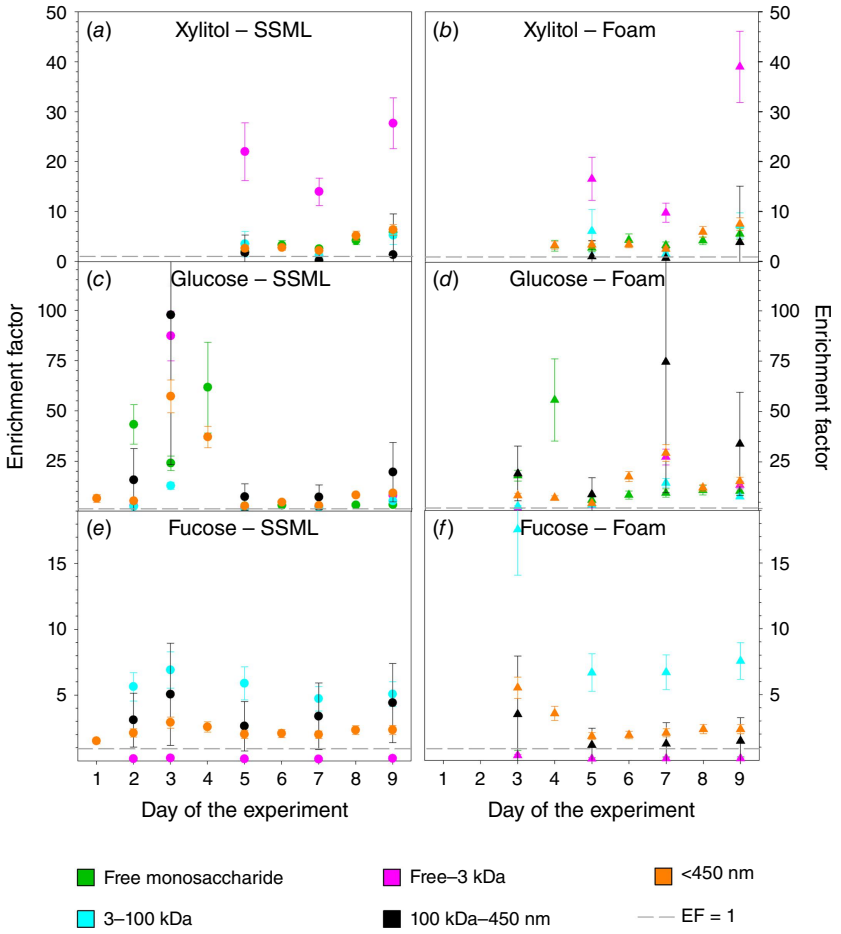

Fig. 5. Enrichment of different saccharide fractions of (*a*, *b*) xylitol, (*c*, *d*) glucose and (e, *f*) fucose in SSML and foam.

energy-related saccharides was dominated by colloidal (100 kDa–450 nm) polysaccharides (Fig. 5*c*, *d*). This is likely due to bulky glucan and fructan polysaccharides and TEP which are found to be effectively transported to the ocean surface by scavenging on bubble surfaces due to their larger radius and/or positive buoyancy (Marty *et al.* 1988; Verdugo *et al.* 2004; Kuznetsova *et al.* 2005; Burrows *et al.* 2014; Dai *et al.* 2015). Furthermore, these bulky colloids could drain back to the SSML during the bubble ageing, thus resulting in higher EFs in SSML than foam (Supplementary Fig. S2*d*, *e*). HMW (3–100 kDa) saccharides dominated the enrichment of structure-related saccharides (Fig. 5*e*, *f*) showing a 2–4 times higher enrichment than total dissolved (<450 nm) saccharides. This enrichment was more prominent in foam than SSML. This is likely due to a higher surface activity of these saccharides than other saccharide types, and coating of interior and exterior surfaces of the bubble film by these highly surface-active saccharides (Burrows *et al.* 2014). In addition this could be due to the co-adsorption of HMW saccharides into organic surfactants such as fatty acids and effective transfer of them into the SSML and greater enrichment in foam (Vazquez de Vasquez *et al.* 2022). Interestingly, LMW structure-related oligo/polysaccharides were depleted in both SSML and foam. According to the competitive Langmuir adsorption model, there is a competition within molecules for surface area at the air–water interface, therefore the most surface-active compounds are retained at the air–water interface, while less surface-active molecules tend to be in the bulk sea water. The depletion of LMW polysaccharides in both SSML and foam could result from their low surface activity compared to HMW saccharides and colloidal polysaccharides, which show higher EFs in SSML (Burrows *et al.* 2014).

Interestingly, free monosaccharide fractions of glucose, galactose, fructose, xylitol, arabitol and mannitol were significantly enriched in SSML and foam with EFs ranging from 3 to 18 despite their complete solubility in water. This suggests a preferential movement of these water-soluble saccharides towards the ocean surface and provides experimental evidence to support the theoretical concept of the OCEANFILM-2 model that describes co-adsorption of water soluble saccharides on organic surfactants and their enrichment at the air–water interface (Burrows *et al.* 2016). Furthermore, these EFs of monosaccharides at the SSML is also supported by the work of Vazquez de Vasquez *et al.* (2022) which showed co-adsorption interactions of glucuronate which is the representative monomer of alginate at a proxy SSML (Vazquez de Vasquez *et al.* 2022). In addition, the enrichment of free monosaccharides at the ocean surface may also

Table 1. Glucose EFs measured in SSML, foam and sea spray aerosol in the present and prior studies.

Study location (campaign name) – sample	Measurement	SSML EF	Foam EF	SSA diameter (μm)	SSA EF	Reference
Coastal California, USA (IMPACTS) – MART	Free glucose	2.5–61.8	6.0–55.9	–	–	This study
	Free–3 kDa	2.1–7.8	3.6–25.3			
	3–100 kDa	1.4–12.8	2.9–14.6			
	100 kDa–450 nm	7.0–97.6	8.8–74.6			
	Total glucose	2.6–57.1	4.3–29.4			
Coastal California, USA (IMPACTS) – wave flume	Total glucose	1.1–3.7	–[A]	<2.5	53–340	Jayarathne *et al.* (2016)
				2.5–10	17–138	
Coastal California, USA (BEAST) – control	Total glucose	–	–	<1	700–20 000	Hasenecz *et al.* (2020)
				>1	93–780	
Coastal California, USA (BEAST) – addition of heterotrophic bacteria	Total glucose	–	–	<1	8300–420 000	Hasenecz *et al.* (2020)
				>1	280–940	
Baltic Sea, Germany	Free glucose	0.6–1.2	–	–	–	van Pinxteren *et al.* (2012)
Laboratory studies of model systems	Free glucose	1.0	–	<2.5	<1	Hasenecz *et al.* (2019)

[A]Dashes indicate that data is not available.

result from faster enzymatic hydrolysis rates at the air–water interface due to favourable conditions (e.g. higher temperature and dissolved oxygen), even though there are other conditions (e.g. high UV radiation) that could decrease rates of enzymatic hydrolysis (Whatley *et al.* 1951; Levinson 1968; Mopper *et al.* 1980; Compiano *et al.* 1993).

The EF of glucose measured in this study is compared to prior studies of its EF in SSML and SSA to gain a better understanding of the enrichment process (Table 1). The EFs of free glucose in SSML in the field study by van Pinxteren *et al.* (2012) and the laboratory model study by Hasenecz *et al.* (2019) indicate a slight depletion or no enrichment. The EF for free glucose in the SSML indicates enrichment, which could be influenced by the observed high biological activity within the active bloom period compared to these prior studies. Total glucose demonstrates enrichment in the SSML in this study and that of Jayarathne *et al.* (2016), with different ranges of EF likely a result of different biological systems. These increased EFs for total glucose relative to free glucose reflect the selective transfer of oligomers or polysaccharides into the SSML. In the aerosol phase, the EF further increased. Jayarathne *et al.* (2016) showed that the EFs of total glucose in SSA particles were greater than those in the SSML, by factors of 50–90 for $PM_{2.5}$ and 15–40 for PM_{10}. The EFs can be further magnified in smaller SSA particles, such as PM_1, because of size-dependent enrichment and the presence of heterotrophic bacteria as shown in Hasenecz *et al.* (2020).

The comparison of EFs across all seawater, SSML, foam and SSA implies a connection between the enrichment of organic matter in foam and the larger EFs in SSA. With EFs for saccharides in foam exceeding those of SSML, it indicates that the maturation of bubble films at the ocean surface leads to greater organic enrichment. The process of this enrichment is likely due to the drainage of less surface-active molecules at the air–water interface, which leads to greater enrichment of highly surface-active molecules on the thin bubble film. Hence, ultimately those molecules on the thin bubble film are those that are transferred into the SSA.

Conclusions

Here we provide the first quantitative enrichment of saccharides on bubble film surfaces where SSA is generated. We observed higher saccharide enrichment in persistent foam compared to SSML, which suggests that maturation of bubbles at the air–water interface contributes to enrichment of organic matter at the ocean surface and ultimately in SSA. Structure-related saccharides, particularly those with HMW, are selectively enriched at the ocean surface. Because of the size of HMW structure-related saccharides, they are unlikely to be transferred to sub-micrometre sized particles, and are more likely to be in super-micron SSA. The quantitative results obtained from this study support the theoretical concept of free monosaccharide enrichment at the ocean surface (Burrows *et al.* 2014, 2016) and field observations of saccharide enrichment in SSA.

Supplementary material

The supplementary material includes a table of saccharide and sodium ion concentrations in bulk sea water, sea surface microlayer and foam (Supplementary Table S1), a picture of the marine aerosol reference tank (MART) before and after

plunging (Supplementary Fig. S1), a figure of the daily variation of total saccharide (< 450 nm) enrichment factors (Supplementary Fig. S2) and the daily variation of DOC (< 450 nm) enrichment factors (Supplementary Fig. S3). Supplementary material is available online.

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Data availability. The data that support this study are available in University of California San Diego (UCSD) Library Digital Collections (Jayarathne *et al.* 2022).

Conflicts of interests. The authors declare no conflicts of interest

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