Biochemical Characteristics of the Sea Surface Microlayer in the Central Baltic Sea and Potential Signatures of Cyanobacterial Blooms

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Abstract. The sea surface microlayer (SML) forms the <1 mm thin ocean's boundary with the atmosphere and plays a critical role in mediating air–sea gas exchange and biogeochemical cycling. However, the biological processes shaping its molecular composition remain insufficiently understood. During a research cruise in the central Baltic Sea (Eastern Gotland Basin), we investigated how phytoplankton, including cyanobacteria, influence the biomolecular composition of the SML. Although no major bloom was detected, distinct shifts in phytoplankton composition were observed, leading to pronounced differences in biomolecular characteristics between the SML and underlying water (ULW), and between conditions characterized by high and low cyanobacteria abundance. While SML enrichment patterns and carbohydrate concentrations were comparable to those previously reported for the Western Baltic Sea, concentrations of total amino acids (TAA) and surfactants were substantially higher in this study and under cyanobacteria-dominated phytoplankton conditions~~, suggesting enhanced production by cyanobacteria~~. Distinct molecular signatures were associated with different phytoplankton size classes. During periods of high abundance of ~~small~~ pico- and nanophytoplankton ~~nanpico and nanophytoplankton~~ (P/NP; ~~HPA<20 µm;~~ *Synechococcus*-dominated), the SML was characterized by elevated surfactant and total combined carbohydrate (TCCHO) concentrations. Furthermore, *Synechococcus* sp. co-varied with the non-protein amino acid γ-aminobutyric acid (GABA), particularly under high abundance of P/NP~~pico and nano HPA<20 µm conditions~~. This suggests that the production of surface-active organic matter may be linked to *Synechococcus* sp. In contrast, under high abundance of ~~large~~ microphytoplankton (MP; ~~HPA>20µm;~~ filamentous and colonial cyanobacteria), ~~total amino acids (TAA),~~p particulate amino acids >20 µm (PAA >20 µm)~~,~~ and particulate combined carbohydrates >20 µm (PCCHO >20 µm) were ~~enhanced~~ elevated in the ULW, mirroring particulate organic carbon >20 µm (POC >20 µm) and filamentous/colonial cyanobacterial biomass patterns. The significant correlation between MP~~phytoplankton >20µm~~ biomass and POC >20 µm suggests that the particulate organic carbon pool was largely ~~cyanobacteria~~ derived from filamentous/colonial cyanobacteria, even in the absence of a distinct bloom. Together, our results imply that phytoplankton size structure and taxonomy exert distinct biomolecular imprints on SML chemistry in the Central Baltic Sea. The contrasting roles of filamentous/colonial cyanobacteria (proteinaceous signatures) and *Synechococcus* sp.

(carbohydrate/surface-activity imprint) imply community-dependent modulation of surface activity and, indicate that future changes in biodiversity may potentially impacts air–sea gas exchange in the ocean.

1 Introduction

The sea surface microlayer (SML) forms the ocean's uppermost boundary, directly linking the hydrosphere and atmosphere. The SML covers up to 70% of Earth's surface (Wurl et al., 2017), and plays a pivotal role in global biogeochemical processes (Engel et al., 2017) despite its narrow vertical extent, typically ranging from 50 to 1000 µm (Zhang et al., 2003; Cunliffe et al., 2013). Positioned at the air–sea interface, the SML modulates the exchange of climate-relevant gases such as dimethyl sulphide (DMS), carbon dioxide (CO_2), and methane (CH_4) (Engel et al., 2017), thereby influencing key climate processes (Wurl et al., 2017). These biogeochemical interactions are largely governed by the enrichment of surface-active biomolecules derived from biological production and organic matter cycling (Cunliffe et al., 2013; Thornton, 2014; Engel and Galgani, 2016; Engel et al., 2017; Wurl et al., 2017).

Phytoplankton are the primary source of dissolved organic matter (DOM) in the ocean and contribute substantially to the organic matter enrichment of in the SML. Through exudation, cell breakage, and lysis, phytoplankton release a wide range of organic compounds, including lipids, proteins, amino acids, and carbohydrates, which shape the biochemical composition and dynamics of the SML (Parrish, 1998; Thornton, 2014; Galgani and Engel, 2016; Engel et al., 2018). Transparent exopolymer particles (TEP) and Coomassie stainable particles (CSP) constitute particulate fractions of extracellular polymeric substances (EPS) released by phyto- and bacterioplankton, forming polymeric organic matrices that vary in size, composition, and structure. These particles contribute to the gelatinous and cohesive nature of the SML (Cunliffe and Murrell, 2009; Dreshchinskii and Engel, 2017).

Among the organic compounds accumulating in the SML are surface-active agents (surfactants). The accumulation of surface-active organic matter affects gas transfer velocity (k) by altering its hydrodynamic properties. Surfactants can reduce k by forming viscous films that suppress small scale turbulence and dampen capillary waves (Frew et al., 2004; Jenkinson et al., 2018). A large-scale oceanic study in the Atlantic demonstrated that surfactant enrichment can significantly reduce CO_2 exchange rates, even under moderate to high wind conditions (Sabbaghzadeh et al., 2017). Thus, air–sea gas transfer is highly sensitive to the presence of surfactants at the ocean's surface (Schmidt and Schneider, 2011; Pereira et al., 2018). Surfactant accumulation is particularly pronounced in regions of elevated primary production and has been associated with phytoplankton blooms, grazing, and bacterial degradation (Zutic et al., 1981; Kujawinski et al., 2002; Tsai and Liu, 2003; Satpute et al., 2010), and photochemical degradation (Rickard et al., 2022). A recent meta-analysis revealed that pronounced enrichment of organic matter in the SML is rather uncommon, while nitrogen-containing biomolecules, including amino acids, preferentially accumulate in the SML (Silva et al., 2026). During a diatom culture experiment it has been shown that both, carbohydrate-rich gels (TEP) and proteinaceous gels (CSP) were enriched in the SML, with the latter showing five times higher abundances in

the SML (Galgani and Engel, 2013). -This distinct enrichment of proteinaceous material, which is typically more amphiphilic and surface-active (Cosović & Vojvodić, 1998; Laß et al., 2013; Laß and Friedrichs, 2011, Barthelmeß and Engel, 2022), could contribute disproportionately to physiochemical properties of the SML. Phytoplankton blooms ~~further~~ shape the microbial community inhabiting the SML, the bacterioneuston, through the release of organic substrates that sustain heterotrophic metabolism (Cunliffe et al., 2013; Taylor et al., 2014). During microbial degradation of phytoplankton exudates, high-molecular-weight polymers can be converted into smaller, more amphiphilic molecules. Additionally, bacterioneuston taxa can produce biosurfactants such as glycolipids and lipopeptides that directly lower surface tension (Abraham et al., 1998; Cunliffe et al., 2013; Kurata et al., 2016; Engel et al., 2017).

While mesocosm and incubation experiments have linked phytoplankton blooms to enhanced surfactant concentrations and the accumulation of fresh organic material in the SML (Zutic et al., 1981; Galgani and Engel, 2013, Bibi et al., 2025), field observations remain limited ~~by~~ and are restricted to coarse temporal and spatial resolution (Rolff et al., 2007; Kahru et al., 2025). As a result, the coupling between phytoplankton bloom dynamics and the release of surface-active biomolecules in natural systems is still poorly constrained.

In most studies focusing on phytoplankton bloom dynamics~~s~~, fresh organic matter production is attributed to phytoplankton communities that dominate in terms of biomass and abundance (Mannino & Harvey, 2002; Ploug 2008; Berg et al., 2018)~~,~~. ~~whereas~~ Bibi et al. (2025) explicitly focused on the SML and attributed the release of fresh organic matter and surfactants to blooming phytoplankton taxa, dominating in abundance. Despite the recognized influence of phytoplankton production on organic matter composition in the SML (Wurl et al., 2011; Galgani and Engel, 2013), little is known about how specific phytoplankton species alter the molecular and biogeochemical composition of the SML under natural conditions. Accordingly, we address in our study how dominating, bloom-forming taxa influence the composition of the SML, while acknowledging that less abundant species potentially further contribute.

The semi-enclosed Baltic Sea represents an ideal system to explore the~~se~~ coupled dynamics of phytoplankton blooms, the release of surface-active biomolecules, and the resulting changes in the molecular composition of the SML due to its pronounced spatial and seasonal variability in nutrient inputs, phytoplankton productivity, and community composition (Murray et al., 2019). ~~The Central Baltic Sea harbours a rich reservoir of microbially altered terrestrial material, while also abiotic factors such as solar radiation (Rickard et al., 2022) or anthropogenic pollutants may alter surface activity (Wurl and Obbard, 2004). The Central Baltic Sea~~It is ~~further~~ is particularly susceptible to extensive summer blooms of filamentous cyanobacteria, promoted by warming waters, enhanced stratification, and low nitrogen-to-phosphorus ratios resulting from eutrophication and widespread anoxia (Hajdu et al., 2007; Thornton, 2018). Additionally, filamentous cyanobacteria require an optimal salinity range of 3.8–11.5 PSU (Wasmund 1997), making them a characteristic feature of the Central Baltic Sea in contrast to the more saline Western Baltic Sea (>12 PSU; Lennartz et al., 2014). Climate-driven changes in stratification are expected to further intensify the occurrence and persistence of such blooms (Paerl and Paul, 2012). Filamentous cyanobacteria in the Baltic Sea are diazotrophic, i.e. capable of fixing atmospheric N_2, and dominate the summer phytoplankton biomass when dissolved nitrogen is depleted (Kahru and Elmgren, 2014; Munkes et al., 2021). The bloom-forming taxa, *Nodularia*

spumigena, *Aphanizomenon* sp., and *Dolichospermum* spp., form extensive surface accumulations across the Central Baltic Sea, including the Eastern Gotland Basin, typically peaking between July and August (Wasmund, 1997; Kahru and Elmgren, 2014; Karlson et al., 2015, 2022). Their filamentous morphology is sustained by specific filament-forming proteins (Springstein et al., 2020), and protein-rich EPS, including CSP, have been observed in *Nodularia spumigena* cultures (Endres et al., 2013; Zhi et al., 2023), suggesting a potentially significant contribution to the extracellular amino acid fraction ~~pools~~, which constitutes ~~a component of~~to the broader extracellular organic matter pool. Laboratory and field studies suggest that cyanobacteria produce EPS and glycolipids with pronounced surface activity, facilitating microlayer film formation and altering interfacial properties (De Philippis and Vincenzini, 1998), while experimental evidence highlights further the rapid turnover of phytoplankton bloom-derived organic matter by heterotrophic bacteria. During a filamentous cyanobacterial bloom in the Gulf of Finland (Baltic Sea), heterotrophic bacteria were shown to utilize approximately 25–55% of dissolved organic carbon (DOC) released from the plankton community, with more than half of the accumulated DOC degraded within seven days (Hoikkala et al., 2016). This suggests that a substantial fraction of cyanobacteria-derived compounds entering the SML is short-lived, unless stabilized through transformation or incorporation into particulate or gel-like structures.

On the one hand, the release of such compounds can result in visible surface slicks, which locally modify near-surface physical processes (Wurl et al., 2018, Mustaffa et al., 2020). Under low-wind conditions in the Baltic Sea, the SML rapidly reorganizes into slick-like, polymer- and particle-rich states, consistent with enhanced surface activity during bloom periods (Stolle et al., 2010). During such periods, particulate organic carbon can contribute up to 55% of the surfactant pool (Gašparović and Ćosović, 2003). Seasonal records further indicate that surfactant concentrations in the Western Baltic Sea peak during summer months following the spring bloom (Laß et al., 2013).

~~Biochemical studies in the Baltic Sea~~On the other hand, biochemical studies in the Baltic Sea have shown that the SML is enriched in carbohydrates and amino compounds ~~and carbohydrates~~ relative to the underlying water (Van Pinxteren et al., 2012). Time-series data from the coastal Boknis Eck station in the Western Baltic Sea further demonstrated recurring enrichment of carbohydrates, amino acids, TEP and CSP in the SML during spring (Dreshchinskii and Engel, 2017). ~~In mesocosm experiments, proteinaceous gels (CSP) abundance was five times higher than that of carbohydrate-rich gels in the SML (Galgani and Engel, 2013). Time-series data from the coastal Boknis Eck station in the Western Baltic Sea further demonstrated recurring enrichment of amino acids and CSP in the SML during spring (Dreshchinskii and Engel, 2017).~~ Phytoplankton-derived biopolymers, including amino -acid- and carbohydrate-like components, are thus potential key contributors to surface activity in this region, and are characterized by short turnover times and diel variability typical of fresh phytoplankton exudates (Van Pinxteren et al., 2012; Barthelmeß and Engel, 2022).

~~Laboratory and field studies further suggest that cyanobacteria produce EPS and glycolipids with pronounced surface activity, facilitating microlayer film formation and altering interfacial properties (De Philippis and Vincenzini, 1998). The release of such compounds can result in visible surface slicks, which locally warm the upper sub-millimeter ocean skin and modify near-surface physical processes (Wurl et al., 2018). Under low-wind conditions in the Baltic Sea, the SML rapidly reorganizes into slick-like, polymer- and particle-rich states, consistent with enhanced surface activity during bloom periods (Stolle et al.,~~

~~2010). During such periods, particulate organic carbon can contribute up to 55% of the surfactant pool (Gašparović and Ćosović, 2003). Seasonal records further indicate that surfactant concentrations peak during summer months following the spring bloom and reflecting intensified solar radiation (Laß et al., 2013).~~

Taken together, cyanobacteria can represent major producers of extracellular organic matter, including amino acids, carbohydrates, lipids, and amphiphilic metabolites, that may substantially influence the surfactant pool in the Baltic Sea. This study aims to address the current knowledge gap regarding the role of cyanobacteria in shaping the biomolecular composition of the SML. Using a Neuston catamaran equipped with a net to sample the upper 20 cm (~~s~~Surface) and an additional net to sample the~~n~~ underlying water (ULW-Net, at ~~net~~1m depth), we collected microphytoplankton (MP; cell size >20 µm) ~~and~~ as well as accompanying ~~samples~~ samples to determine the particulate organic matter composition (>20 µm)~~from the uppermost surface and 1 m depth in the central Baltic Sea~~. SML water samples for characterizing ~~the organic matter and~~ pico- and nanophytoplankton abundances (P/NP; cell size ~~<~~≤20 µm) as well as the total organic matter composition, including the dissolved and particulate fraction, were collected by applying specialized samplers, such as the glass plate (Harvey and Burzell, 1972) and the Garrett Screen (Garrett, 1965). Underlying water (~~Underlying water (~~ULW) ~~)~~ samples, used as reference for the SML, were collected at approximately 1 m depth using a manually deployed water sampler. To evaluate the influence of cyanobacteria~~, including filamentous species~~, we assessed the variability of key biomolecular classes in relation to high and low phytoplankton abundance across size fractions i.e. discriminating between ~~pico- and nanophytoplankton~~P/NP (*Synechococcus* sp. dominated) in contrast to ~~microphytoplankton~~MP (filamentous/colonial cyanobacteria dominated). Our overarching goal was to determine how cyanobacteria modulate the biochemical composition of the SML, with implications for gas exchange processes as inferred from surfactant analysis.

2 Methods

2.1 Research area

Samples were collected in July (30.06. – 19.07. 2022) during the cruise EMB295 with the *RV Elisabeth Mann Borgese* in the Central Baltic Sea. The cruise was part of the project “Central Baltic Sea Air Sea Exchange Experiment” (CenBASE). All stations were located in the Eastern Gotland Basin, between 19.1° and 20.2°E and 57.10° and 57.30°N (Fig. 1). Two stations were sampled daily, one in the morning at 6 am and one in the afternoon at 6 pm local time for a total of 15 stations (Table A1). During the cruise, surface waters (3m) had a salinity of 7.26 ± 0.10 PSU and a temperature of 18.86 ± 0.22 °C.

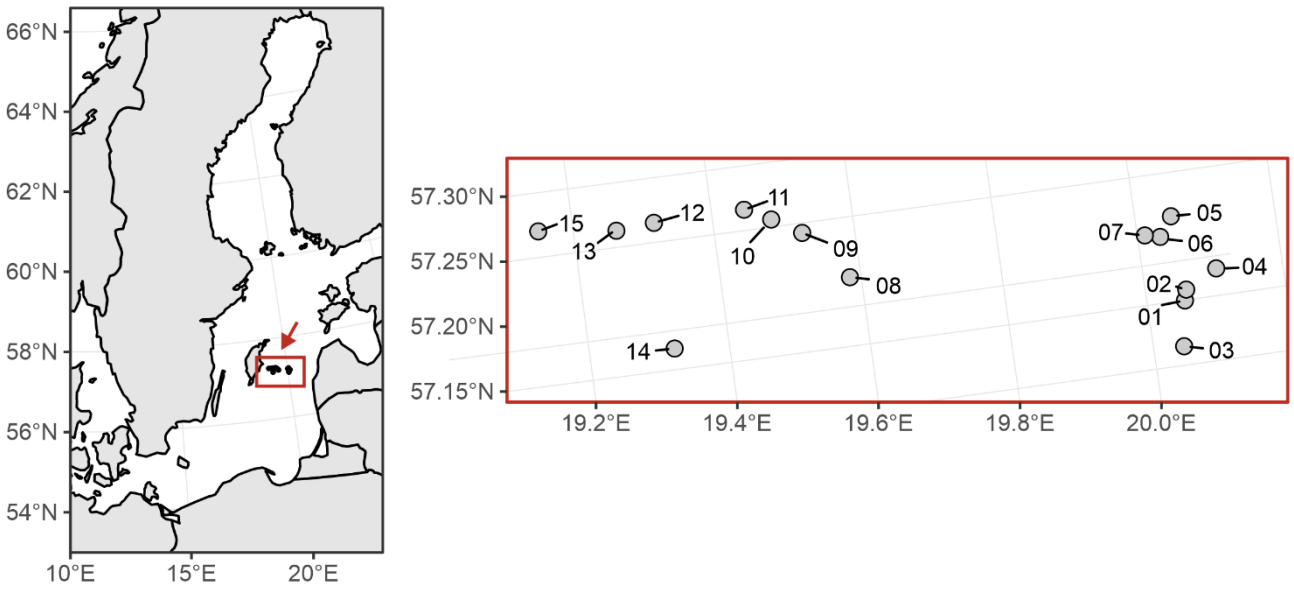

Figure 1: The study area east of Gotland in the Central Baltic Sea is indicated by the red inset (left). The enlarged view of the Eastern Gotland Basin shows the stations, labelled with their station IDs, from the EMB295 cruise (right).

2.2 Sampling

At each station, seawater and organic particles (>20 µm) were sampled. Seawater was sampled from the SML using a glass plate or a Garrett Screen and from the ULW by a manually operated 2L water sampler (Hydrobios, according to Ruttner). Particles >20 µm were collected from the surface using a Neuston catamaran (Fig. S1) and from ~1m depth using a ULW net (Fig. S2).

Seawater sampling was conducted from a working boat positioned ~500 m upwind of the research vessel to minimize contamination and ensure an undisturbed surface. The SML was sampled with the glass plate (Cunliffe & Wurl, 2014; Harvey and Burzell, 1972) and collected into sample-rinsed amber borosilicate glass bottles (250 mL), yielding 7 SML samples. Before sampling, the glass plate and frame were conditioned by sequential rinses with ambient seawater and a small volume of SML sample. Samples were kept shaded in an isolated box and processed within 2 h. For cleaning, the glass plate and bottles were soaked in 10% HCl and thoroughly rinsed with Milli-Q water. The wiper and its frame were flushed with freshwater and then rinsed with Milli-Q. When working boat operations were not possible due to bad weather, the SML was sampled using a Garrett screen (Garrett, 1965) from the bow of the vessel as described in Barthelmeß et al. (2021), yielding 8 SML samples. ULW was collected at 1m using a manually operated water sampler (2 L) and filled into borosilicate bottles (250 mL) (n = 15). The following parameters were derived from seawater sampled with the glass plate or Garrett Screen (SML) and the manually deployed water sampler (ULW): P/NP abundance, total organic carbon (TOC), total combined carbohydrates (TCCHO), total amino acids (TAA), and surfactants (SA). In the following text, the term 'SML' refers to the uppermost

microlayer, from which seawater samples were collected with the glass plate or Garrett screen, and 'ULW' denotes the reference depth sampled with the manually deployed water sampler.

~~Particles >20µm were collected from the surface using a Neuston catamaran (Fig. S1) and from ~1m depth using a ULW net (Fig. S2). Seawater was sampled from the SML using a glass plate or a Garret Screen and from the ULW by a manually operated 2L Niskin bottle.~~

For the particles >20 µm, ~~Thea~~ Neuston catamaran, equipped with a 20 µm mesh-size net attached, was towed at 3 knots on starboard, allowing for the sampling of the upper ~20 cm of the surface. Towing time for the Neuston catamaran was between ~5 min and ~17 min, equivalent to 594 and 15950 L seawater. In order to determine the amount of water that flowed through the net, a flowmeter (Hydro-Bios) was attached below the net opening, which was used to calculate the amount of water based on its rotations as follows:

$$V = N \times 0.3A \times 1000 \quad (1)$$

with V (L) being the sampled water volume, *N* the number of revolutions, and *A* the area of the net opening (m²). The ULW reference depth was sampled with an ULW net with a mesh size of 20 µm and attached to a V-fin and towed with 1.5 knots from starboard at approximately 1 m depth. Towing time was between ~5 min and ~14 min, equivalent to 1636 and 12204 L seawater. The net opening area (A) was 0.0225 m^2 for the Neuston catamaran and 0.045 m^2 for the ULW net. During periods of strong wave action, the flow meter in the Neuston catamaran net opening occasionally emerged above the water surface, interrupting revolutions and yielding low or irregular counts. Consequently, sampled volumes calculated from *N* come with uncertainty. Before hauling in the Neuston catamaran and ULW net, the nets were rinsed with seawater from the outside, so that the entire content of the net was rinsed into the net sock. Once the net was on deck, the samples were rinsed with filtered seawater into a beaker. Due to the high biomass retained in the nets, the samples were diluted with filtered seawater, for which water was collected from 5 m depth and filtered through 3 µm and 0.2 µm pore size. Samples were diluted in different ratios from 2:1 to 1:2 (vol:vol) depending on the thickness of the net catch and gently swirled before subsampling to ensure a homogeneous sample. Consequently, net samples included the particulate fraction >20 µm and the added filtered seawater. Net samples were stored at 4°C between subsampling.~~–~~ Rough weather conditions at station 13 and 14 prevented the deployment of the Neuston catamaran and ULW net, thus no net samples could be taken. Hereafter, ~~In the following,~~ N~~-~~Neuston catamaran and ULW net sample depths are referred to as “Surface” and “ULW-Net”, respectively. Sample sizes were n = 13 for each depth with the following parameters derived: ~~. and related depths will be subsequently addressed as 'S'"M~~MP biomass and abundance, particulate organic carbon >20 µm (POC >20 µm~~?~~), particulate amino acids >20 µm (PAA >20 µm~~?~~), and particulate combined carbohydrates >20 µm (PCCHO >20 µm~~?~~).

~~Seawater sampling was conducted from a working boat positioned ~500 m upwind of the research vessel to minimize contamination and ensure an undisturbed surface. The SML was sampled with the glass plate (Cunliffe & Wurl, 2014; Harvey and Burzell, 1972) and collected into sample rinsed amber borosilicate glass bottles (250 mL) yielding xxx SML samples. Before sampling, the glass plate and frame were conditioned by sequential rinses with ambient seawater and a small volume~~

of SML sample. Samples were kept shaded in an isolated box and processed within ≤2 h. For cleaning, the glass plate and bottles were soaked in 10% HCl and thoroughly rinsed with Milli Q water. The wiper and its frame were flushed with freshwater and then rinsed with Milli Q. When working boat operations were not possible due to bad weather, the SML was sampled using a Garrett screen (Garrett, 1965) from the bow of the vessel as described in Barthelmeß et al. (2021) yielding xxx SML samples. ULW was collected at 1m using a manually operated Niskin bottle (2L) and filled into a borosilicate bottle (250 mL) (n=xxx).seawater sampled with the -or the- and biomass? (abbreviation?) (TOC) (TGCHO) (TAA) (SA)

In the following, Neuston catamaran and ULW net sample depth are referred to as "Surface" and "ULW-Net", respectively. TheIn the following text, the term "'SML" ' refers to the sampled depthuppermost microlayer, from which seawater samples were collected with the glass plate or Garrett screen, and "'ULW" 'denotes the reference depth sampled with the manual Niskin Bottle.

2.3 Microphytoplankton microscopy

Throughout this study, MP refers to phytoplankton with cell sizes >20 µm are referred to as "microphytoplankton" and werewas exclusively sampled from net catches and determined by microscopy. PMicrophytoplankton (>20 µm) were subsampled from net catches. After dilution of the net-tow samples as described above, 200 mL aliquots were transferred to amber glass bottles, preserved with 2 mL acidic Lugol's solution, and stored at 4 °C until processing. For analysis, samples were diluted (1:15 or 1:30) with water of the corresponding salinity, transferred to sedimentation chambers (Hydro-Bios), and left overnight to allow particle settling. Phytoplankton MicrophytoplanktonMP community analysis included taxonomic identification (species composition), microscopic enumeration of abundance (Utermöhl, 1958; DIN EN 15972:2011-11), and biovolume estimation based on measurements of a representative number of cells per taxon (DIN EN 16695:2015-12). Microscopy was performed with a ZEISS Axiovert 25 inverted microscope at 100×, 200×, and 400× magnification. Where possible, organisms were identified to species level, otherwise, they were assigned to genus level or higher taxonomic groups. For microphytoplankton >20µmmicrophytoplanktonMP samples only the 8 most dominant microphytoplanktonMP species were identified: *Aphanizomenon* sp., *Aphanocapsa* sp., *Nodularia spumigena*, *Cylindrotheca closterium*, *Pseudo-nitzschia delicatissima*, *Chaetoceros* sp., *Dinophysis* sp., and *Diplopsalis* (group). For each sample, at least 400 individuals were enumerated, and approximately 20 individuals per taxon were measured for their visible dimensions. For biovolume estimation, each taxon was assigned an appropriate geometric body, and volume was calculated from the measured dimensions. When certain dimensions could not be measured (e.g., due to cell orientation in the chamber), standard correction factors were applied in accordance with DIN EN 16695:2015-12. Abundance was calculated accounting for the dilution factor and reported as cells per sample volume. Biomass was calculated based on biovolume and species-specific carbon content per cell. Throughout this study, microphytoplankton >20µm determined by microscopy are referred to as "Microphytoplankton" "Phytoplankton >20µm".

2.4 Flow cytometry

P/NP refers to phytoplankton ≤20 µm determined by flow cytometry, based on seawater samples collected from the SML and ULW. ~~Seawater samples for flow cytometry were taken from SML and ULW. In the following, phytoplankton ≤20 µm cells determined by flow cytometry are referred to as "Phytoplankton <20µmnano /picophytoplankton".~~ Duplicates of 1.7 mL were preserved with 85 µL glutaraldehyde (GDA), and stored at −80 °C until later analysis. ~~Phytoplankton~~ P/NP cells~~and bacterial cells~~ were quantified using a flow cytometer (Becton, Dickinson and Company FACSCalibur; software - BD Biosciences CellQuest Pro), calibrated with yellow-green latex beads (0.5 and 1 µm in diameter). Autotrophic cells were detected based on their autofluorescence (Marie et al., 1997), classified according to size in picophytoplankton (<2 µm) and nanophytoplankton (2–20 µm), and further differentiated by their characteristic pigments into chlorophyll *a*- and phycoerythrin-rich ~~pico- and nanophytoplankton~~picophytoplankton and -nanophytoplankton after Engel & Galgani (2016) and Zäncker et al. (2017). Picophytoplankton with phycoerythrin were affiliated to the unicellular cyanobacterium *Synechococcus* sp. ~~(Marie et al., 2010).~~ We estimated the biomass of *Synechococcus* sp. based on cell counts. Reported estimates of *Synechococcus* cellular carbon biomass range from approximately 0.1 to 1.5 pg C cell^{-1} (Moisan et al., 2010). Here, we used an average carbon biomass of 0.3 pg C cell^{-1} based on Buitenhuis et al. (2012). ~~In the following, phytoplankton cells determined by flow cytometry are referred to as "Phytoplankton <20µm".~~

2.5 Chlorophyll *a* (Chl *a*)

Chlorophyll *a* (Chl *a*) samples were taken in duplicates from the ~~Niskin bottles~~manually deployed water sampler at 1m depth (ULW). For each sample, 500 mL seawater were filtered onto a GF/F filter (Whatman, 25mm), flash-frozen in liquid nitrogen and stored at –80°C. Analyses were performed within one year of sample collection. Samples were acidified and measured with a fluorometer from Turner Designs (Turner TD 10-AU005) with an excitation at 450 nm and an emission of 670 nm according to the Helcom Combine Manual.~~.~~

2.6 Organic matter analysis

For determination of ~~total organic carbon (~~TOC~~)~~ from SML and ULW, 20 mL seawater were filled into pre-combusted (8 hours at 500°C) glass ampules and acidified by adding 20 µL of 30 % hydrochloric acid (HCl, Suprapure, Sigma-Aldrich). After acidification, the samples were flame-sealed and stored at 4°C until analysed with a TOC analyser (TOC-VCSH, Shimadzu) following Engel and Galgani (2016). TOC analysis was validated daily using deep seawater reference (DSR) material from the Consensus Reference Materials Project of RSMAS (University of Miami), yielding values within the certified range of 42–45 µmol C L^{-1}. Two internal standards with DOC similar to samples were daily prepared using potassium hydrogen phthalate (Merck 109017). TOC concentrations in each sample were determined from 5 to 8 injections, with precision (<4 %) estimated as the standard deviation divided by the mean. Total nitrogen (TN) was determined in parallel with TOC using the TNM-1 detector on the Shimadzu analyser. Nitrogen is combusted and transformed to NOx, which chemi-luminesces

when mixed with ozone and was detected using a photomultiplier (Dickson et al., 2007). The instrument was calibrated every 8–10 days using standard solutions (0, 500, 1000, 1500, 2500, and 5000 µg C L^{-1}) prepared from a potassium hydrogen phthalate standard (Merck 109017). On each measurement day, ultrapure water determined the instrument blank. The detection limit of TOC was 1 µM.

For POC >20 µm, duplicate 20 mL samples of the Ssurface and ULW-Net samples, including the particulate fraction and filtered seawater, were filled into ampules. From each ampoule, two aliquots (0.5–2.0 mL) were filtered onto pre-combusted (8 hours at 500°C) GF/F filters (Whatman, 25 mm) at low constant vacuum (<0.2 mbar), and the filtrate was collected in pre-acid-washed (HCl) Falcon tubes and stored at 4°C. POC filters were stored at –20°C until later analysis for less than a year. For the measurement, filters were wrapped in tin cups and measured using an Euro EA elemental analyser calibrated with an acetanilide standard after Sharp (1974). Filters with ultrapure water were measured as lab blank per run (<10 µg C per filter). During storage in the ampoules, particulate carbon may have dissolved. Therefore, the filtrate was measured in the same way as the TOC samples (see above). After the separated analyses, the carbon concentrations of the filtrate and filters were combined and reported as POC >20 µm. Values were corrected by subtracting the TOC concentration of pre-filtered seawater (ranged between 341.07–457.15 µM) used to rinse the sample out of the net.

On board, samples for ~~total combined carbohydrates >1 kDa (~~TCCHO (>1kDa)~~)~~ and ~~total amino acids (~~TAA~~)~~ were collected from both SML and ULW samples into 20 mL and 4 mL pre-combusted glass vials and stored at –20°C. Particulate fractions of combined carbohydrates (PCCHO >20 µm) and amino acids (PAA >20 µm) were determined from net samples and treated identically as the total fraction, i.e., filled into pre-combusted glass vials of the same respective volumes and stored at −20 °C. TCCHO and PCCHO >20 µm were determined by high-performance anion-exchange chromatography coupled to pulsed amperometric detection (HPAEC-PAD) with a DIONEX ion chromatography system (ICS 6000) (Engel and Händel, 2011). The following neutral sugars were quantified: glucose, mannose and xylose, galactose, arabinose, fucose and rhamnose, the acidic sugars galacturonic acid and glucuronic acid, and the amino sugars galactosamine and glucosamine.

TAA and PAA >20 µm were determined using a high-performance liquid chromatography (HPLC) system following Dittmar et al.~~,~~ (2009) and Lindroth &~~&~~ Mopper~~,~~ (2025). The following thirteen amino acids were quantified: aspartic acid, glutamic acid, serine, glycine, threonine, arginine, alanine, tyrosine, valine, isoleucine, phenylalanine, ~~and~~ leucine, and γ-aminobutyric acid (GABA). Due to hydrolysis, aspartic acid and glutamic acid cannot be distinguished from asparagine and glutamine and are therefore reported as aspartic acid and glutamic acid, respectively.

The detection limit for combined carbohydrates and amino acids was 5−10 nM and ~1 nM, respectively (Dittmar et al., 2009~~.~~; Engel & Händel, 2011). Amino acid and carbohydrate concentrations are expressed in µM and their corresponding carbon-equivalent in µM C.~~, and the corresponding concentrations in µM.~~

2.7 Surfactants

For ~~surface activity~~SA analysis, ~~triplicates of 18 mL~~ an 18 mL aliquot of SML and ULW ~~samples~~ derived seawater was~~ere~~ transferred by a syringe into pre–acid-washed (HCl) and pre-combusted (8 hours at~~,~~ 500°C) 20 mL glass vials, and immediately stored at −20 °C. ~~One of three replicate samples was analysed.~~ Samples were measured within 12 months after collection using phase-sensitive alternating current voltammetry (797 VA Computrace polarograph Metrohm, Switzerland), following the method initially introduced by Cosović & Vojvodić (1982). This technique is based on the discharge of an electrochemical double layer formed at the polar–non-polar interface of a hanging mercury drop electrode (Scholz, 2015), which interacts with surfactants present in the sample. The resulting changes in capacitive current, relative to a pure electrolyte blank, were used to quantify environmental surfactants. Prior to measurement, the sample's ionic strength was standardized by adding an appropriate volume of a 3 M sodium chloride (NaCl) solution. Samples were measured in glass vials at room temperature. Measurements were conducted with a 60 s deposition time and a voltage sweep ranging from −0.6 V to −1 V. To prevent contamination, all measuring vials were pre-cleaned with 10 % HCl, rinsed with Milli-Q water, and combusted at 500°C overnight. Calibration was performed using the artificial, non-ionic surfactant Triton X-100 (TX-100, Sigma-Aldrich, Germany, molecular weight: 625 g mol^{-1}).

2.8 Data handling

Statistical analysis was executed in RStudio (Version 2025.05.0). Data analysis comprised the calculation of mean (M) and standard deviation (SD), and all reported values follow the format M ± SD unless indicated otherwise. The median was used as a threshold to divide the dataset into ~~-~~phytoplankton abundance groups (see Section 3.1)~~two groups~~, ensuring an equal number of samples in each group and allowing for balanced statistical comparison. For characterizing the SML, enrichment factors (EFs) were calculated by dividing the concentration in the SML by the corresponding concentration in the ULW:

$$\mathbf{EF} = \frac{[\boldsymbol{C}_{\mathbf{SML}}]}{[\boldsymbol{C}_{\mathbf{ULW}}]} \quad (2)$$

For statistical comparison of the ~~biomass,~~ MP and P/NP abundance conditions (see Section 3.1), and depth categories~~pairs~~ (SML vs. ULW; Surface vs. ULW-Net), normality was tested for each group using the ~~if both groups had n ≥ 3 and passed a~~ Shapiro–Wilk normality test. If both groups passed the normality test ($p > 0.05$ in each group), a two-sample Welch's t-test was applied~~used,~~; otherwise, a Wilcoxon rank-sum test was used. We considered that null hypotheses testing and correlations were significant at $p < 0.05$.

For correlations, relative abundances were used. Parameters with only two data points (*Diplopsalis* and *Dinophysis sp.*) were excluded from the correlation. Correlations between taxon-specific phytoplankton biomass and mol percent (mol %)~~relative concentrations~~ of TAA, TCCHO, PAA >20 µm, and PCCHO >20 µm ~~PCCHO, TCCHO, PAA and TAA~~ were tested using Spearman's rank correlation (ρ). Analyses were conducted separately for the SML/ULW ~~surface~~ and Surface~~ULW~~/ULW-Net by subsetting the dataset by depth. To facilitate structure-revealing visualization, carbohydrates and amino acids were ordered

by their similarity of correlation patterns with biomass ~~in the SML and ULW~~. Significances were encoded in the correlation matrices as *, **, and *** for p <~~-~~0.05, p <~~-~~0.01, and p <~~-~~0.001, respectively.

3. Results

3.1 Phytoplankton distribution and composition

To examine whether ~~filamentous~~ and which phytoplankton groups~~, including filamentous cyanobacteria,~~ influence the biomolecular composition of seawater ~~in the SML, and ULW, Surface and ULW Net~~, we compared stations with varying ~~phytoplankton~~P/NP and MP abundances~~, and differentiated between >20µm and <20µm size classes~~. We used the median abundance to group ~~microphytoplankton and~~ P/NP and MP ~~nanophytoplankton~~ into high and low abundance conditions by referring to the samples of the reference depth (ULW and ULW-Net ~~and ULW~~, respectively). A summary of this classification scheme is provided in Table A2 and will be explained in more detail with the help of Fig.~~.~~ 2. Figure 2 provides an overview of Chl a concentration, ~~microphytoplankton, and~~ P/NP, and MP~~nanophytoplankton~~ abundances encountered across stations in a chronological order. Overall, the spatial patterns of phytoplankton abundance and Chl *a* reflected pronounced variability across the stations (Fig. 2). Chl *a* concentration in the ULW ranged from 1.60 to 3.05 µg L^{-1} (2.06 ± 0.34 µg L^{-1}), showing a gradual increase towards station 15, except for station 05, 11, and 12 (Fig. 2a). ~~Microphytoplankton. At station 13 and 14, weather conditions were too rough to deploy the Neuston catamaran and ULW net, thus no net samples could be taken.~~ P/NP~~Nano /picophytoplankton~~ abundances were ~~rather~~ similar between the SML and ULW, with mean values ~~concentrations~~ of 69 ± 50 × 10^3 cells mL^{-1} and 68 ± 39 × 10^3 cells mL^{-1}, respectively, and with an overall mean of 69 ± 45 × 10^3 cells mL^{-1} (Fig. 2b). Across stations, abundance~~s~~ of P/NP ~~nano /picophytoplankton (Fig. 2c)~~ increased from station 01 to 12, followed by a pronounced steep increase towards station 15, where the maximum value (205 × 10^3 cells mL^{-1}) was recorded. MP abundance ranged between 13 and 1658 cells mL^{-1} with an overall mean of 287 ± 320 cells mL^{-1} ~~with one high value~~and reaching a maximum at station 02 (1658 cells mL^{-1}) (Fig. 2c). In the Surface, mean MP abundance was 202 ± 200 cells mL^{-1}, compared to 371 ± 388 cells mL^{-1} in the ULW-Net. At station 13 and 14, weather conditions were too rough to deploy the Neuston catamaran and ULW net, thus no net samples could be taken.

~~shows the station specific abundances of microphytoplankton >20µm and nano /picophytoplankton<20µm for sampled depths, estimated by microscopy and flow cytometry, respectively.~~ The dashed lines in Fig.~~.~~ 2b and 2c represent the median values~~, calculated from ULW-Net and ULW samples~~which were taken to group stations into high and low phytoplankton abundance ~~regimes~~conditions.~~,~~ ~~i.e.~~For P/NP (incl. Chl *a*- and phycoerythrin-rich picophytoplankton and ~~-~~nanophytoplankton), the median abundance was 53 × 10^3 cells mL^{-1} and for ~~microphytoplankton~~MP, the median abundance was 300 ~~x 10^3~~ cells mL^{-1} ~~for microphytoplankton >20µm~~ (incl. *Aphanizomenon sp.*, *Aphanocapsa sp.*, *Nodularia spumigena*~~, Aphanizomenon sp.~~, *Cylindrotheca closterium*, *Pseudo-nitzschia delicatissima*, *Chaetoceros* sp., *Dinophysis* sp., and *Diplopsalis* (group) ~~(group))~~ ~~and for phytoplankton <20µm (incl. Chl *a*- and phycoerythrin-rich pico- and nanoplankton) the median was 53 × 10^3 cells mL^{-1}, respectively~~. ~~Stations~~ Accordingly, stations ~~with ULW/ULW-Net concentrations~~ above the respective medians were

classified as a condition characterized by high~~"H~~high,", while those below were classified as a condition characterized by ~~a regime characterized by "L~~low.~~"~~low abundances. Subsequently, stations with ~~Accordingly, m~~Hhigh ~~m~~phytoplanktonP/NP ~~>20µm~~ abundance ~~w~~regimes ~~are~~ere ~~subsequently a~~addressed as~~ddressed as~~ '~~was grouped into high (HPA>20µm~~High P/NP' conditions~~)~~, while stations with ~~and~~ low ~~microphytoplankton~~P/NP abundance were addressed as~~regimes (as~~ '~~LPA<20µm~~Low P/NP' conditions~~) categories~~ (Fig. 2b). The same ~~categories~~categories were implemented to ~~describe~~classify conditions based on MP abundances~~,phytoplankton <20µm regimes~~, either referring to high ('High MP') or low ('Low MP') abundance ~~conditions~~ (Fig. 2c). ~~Summarized~~In summary, the following four conditions were introduced and will be used throughout the text: ~~'High MP' vs. 'Low MP' and~~ 'High P/NP' vs. 'Low P/NP' and 'High MP' vs. 'Low MP'~~which are used throughout this work~~. It is important to highlight that in 10 out of 13 common stations, the abundances of P/NP~~microphytoplankton~~ corresponded inversely to those of the MP~~nano-/picophytoplankton~~, i.e. stations characterized by elevated abundances of ~~microphytoplankton~~P/NP (~~H-Micro~~High P/NP) generally showed reduced abundances of MP ~~nano-/picophytoplankton (L-Nano~~Low MP), and vice versa. At two stations, no net samples were derived and thus no ~~microphytoplankon~~MP ~~regime~~condition could be assigned.

~~A summary of this classification is provided in Table A2. Overall, the spatial patterns of phytoplankton abundance and Chl *a* reflected pronounced variability across the stations (Fig. 2).~~

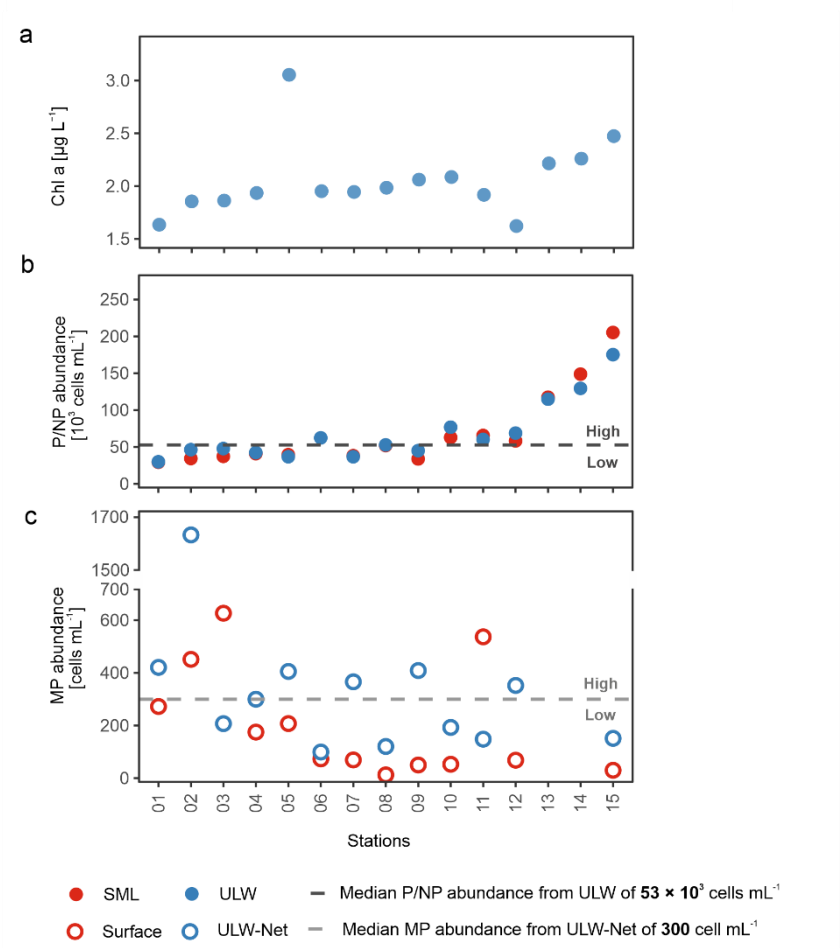

Figure 22: Chlorophyll *a* (Chl *a*) concentrations (a) in the underlying water (ULW), ~~(b) phytoplankton abundance >20µm in surface net samples and ULW-Net samples and~~ (bc) pico- and nanophytoplankton (P/NP) ~~<20µm~~ abundance ~~for~~ in the sea surface microlayer (SML) and ULW, and (c) microphytoplankton (MP) abundance in Surface and ULW from net (ULW-Net) samples across stations ~~sampled~~ during EMB-295. The dashed horizontal ~~light- and dark grey~~ lines mark the median abundance of ~~MP (light grey) and~~ P/NP (dark grey) and MP (light grey) ~~abundance~~in the ULW and ULW-Net, respectively~~s according to the size classes~~. ~~Samples~~ Stations were ~~grouped~~ classified into the condition characterized by ~~low phytoplankton >20µm abundance (LPA>20µm) or~~ low P/NP (L~~l~~ow P/NP~~phytoplankton <20µm abundance (LPA<20µm))~~ ~~or~~and low MP (Low MP) abundances, if below the respective ~~if below the~~ median values ~~in the ULW~~. Samples were classified ~~and~~into the condition characterized by high P/NP (High ~~high phytoplankton >20µm abundance (HPA>20µm~~P/NP)~~)~~ ~~or~~ and high MP (High MP) abundances~~high phytoplankton <20µm abundance (HPA<20µm~~, if above the respective ~~) if above~~median values. ~~Station~~ The station order corresponds to temporal sequence of sampling conducted during the cruise.

~~Chl *a* concentrations in the ULW ranged from 1.60 to 3.05 µg L^{-1} (2.06 ± 0.35 µg L^{-1}), showing a gradual increase towards stations 22_07, except for station 12_24 and stations 18_02, and 21_02 (Fig. 2a). Phytoplankton >20µm abundance ranged between 12.7 and 1658 cells mL^{-1} with an overall mean of 287 ± 327 cells mL^{-1} with one high value at station 12_07 (1658 cells mL^{-1}) (Fig. 2b). At station 22_02 and 22_04, weather conditions were too rough to deploy the Neuston catamaran and ULW net, thus no net samples could be taken. Abundances of phytoplankton <20µm (Fig. 2c) increased in both the SML and~~

~~ULW from station 12_03 to 21_02, followed by a pronounced step increase towards station 22_07, where the maximum value (205 x 10^3 cells mL^{-1}) was recorded. In 10 out of 13 common stations, the abundances of phytoplankton >20µm were inversely related to those of the <20µm fraction, indicating that stations characterized by elevated abundances of >20µm phytoplankton generally showed reduced abundances of phytoplankton <20µm, and vice versa.~~

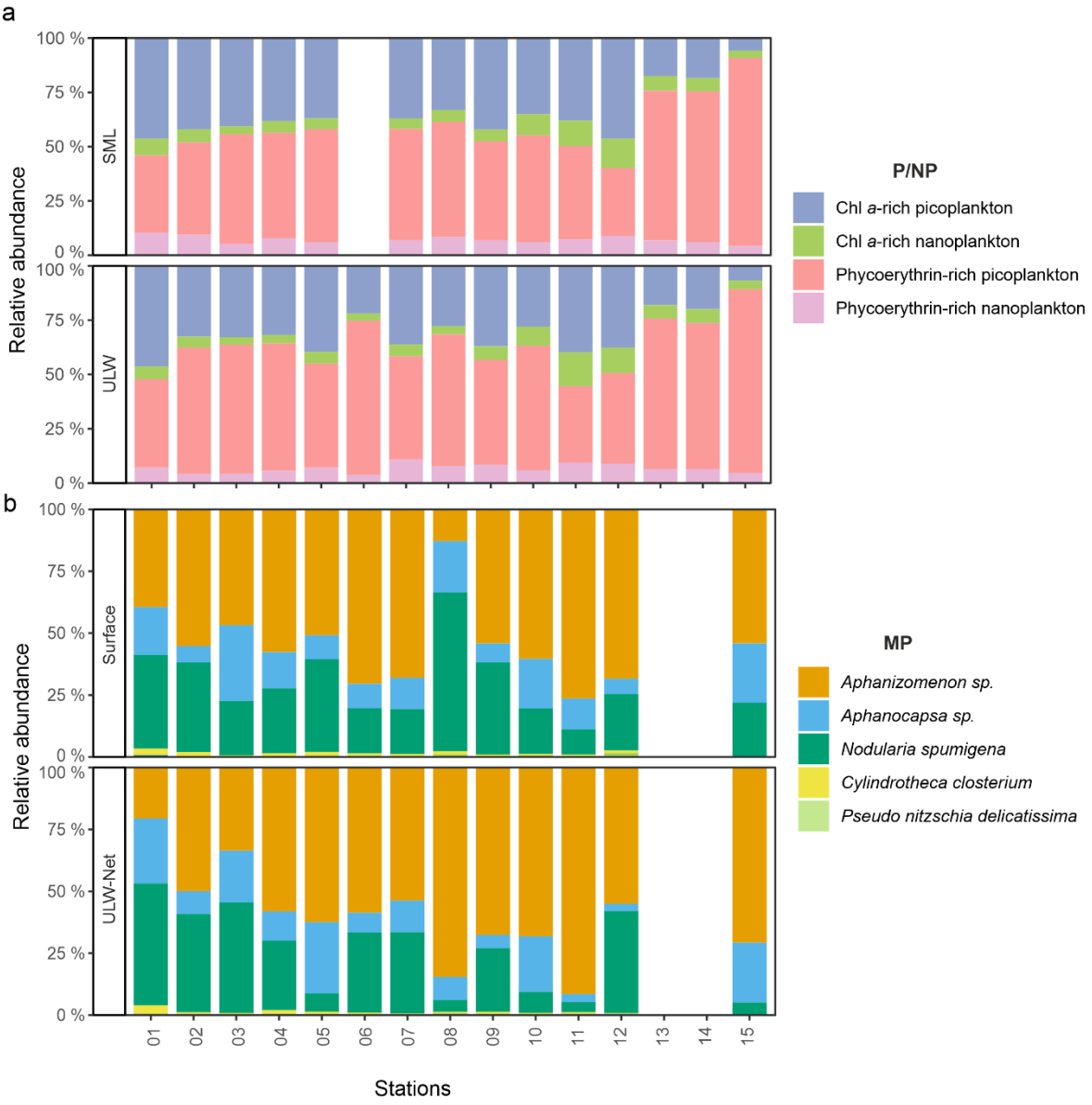

Figure 3: Stacked bar plot of the relative abundance for (a) the relative abundance of the four pico- and nanophytoplankton (P/NP) groups in sea surface microlayer (SML) and underlying water (ULW) samples ~~dominant phytoplankton species (>20 µm) in surface and ULW-Net samples~~, and (b) dominant microphytoplankton (MP) species in Surface and ULW from net (ULW-Net) samples~~the~~

~~relative abundance of the four phytoplankton groups (<20µm) in SML and ULW samples~~**. Colors for** MP~~phytoplankton >20µm~~ **denote five of the eight identified phytoplankton taxa. Abundance of *Chaetoceros* sp., *Dinophysis* sp., and *Diplopsalis* (group) were <1 % and are not shown.**

~~Across the stations, the >20µm phytoplankton community was strongly cyanobacteria dominated by filamentous cyanobacteria in both surface and ULW Net samples (Fig. 3a). *Aphanizomenon sp*. was the dominant species at almost all stations and in both layers and accounted for a mean abundance of 158 ± 169 cells mL^{-1}. Secondary contributions came from *Nodularia spumigena* (84 ± 130 cells mL^{-1}), followed by *Aphanocapsa sp*. (41 ± 49 cells mL^{-1}), which were consistently present but more variable among stations. Diatoms were a minor component of the >20µm phytoplankton community. *Cylindrotheca closterium* (3.3 ± 4.5 cells mL^{-1}) and *Pseudo-nitzschia delicatissima* (1.1 ± 0.8 cells mL^{-1}) were typically present at low percentages (<2%). Overall, variability in relative species abundance among stations was moderate, and the dominance of filamentous cyanobacteria persisted across the section and depths. Relative abundances for *Chaetoceros sp*., *Dinophysis sp*. and *Diplopsalis* (group) were <2% and are thus not visible in Fig. 3. Higher resolution of the relative abundance <4% can be found in the supplementary material (Fig. S3).~~

Within the P/NP community, ~~P~~picophytoplankton containing the pigment phycoerythrin (affiliated to the unicellular cyanobacterium *Synechococcus* sp.) were most abundant (42 ± 41 ~~×~~ 10^3 cells mL^{-1}), representing ~~at almost all stations~~ more than 50 % of the total community by number~~ at almost all stations, i.e. SML phytoplankton <20µm: 69 ± 52 x 10^3 cells mL^{-1} and ULW phytoplankton <20µm: 68 ± 41 x 10^3 cells mL^{-1}~~, at almost all stations, followed by picophytoplankton containing Chl *a* (18 ± 4.9 × 10^3 cells mL^{-1}) (Fig. 3~~a~~b). During stations 13~~22–02~~, 14~~22–04~~, and 15~~22–07~~, phycoerythrin-rich picophytoplankton abundance increased in the SML and ULW up to 178 ~~×~~ 10^3 cells mL^{-1} and 148 ~~×~~ 10^3 cells mL^{-1}, respectively, and made up more than 80% of the P/NP ~~phytoplankton <20µm~~ community by number~~. Nanophytoplankton varied little between stations and depth~~. Chl *a*-rich nanoplankton showed mean values about 4.3–4.5 ± 2.9 × 10^3 cells mL^{-1} in the SML and ULW and~~.~~ p~~P~~hycoerythrin-rich nanoplankton varied about 4.5 ± 2.3 ~~×~~ 10^3 cells mL^{-1} in the SML and 4.4 ± 2.2 ~~×~~ 10^3 cells mL^{-1} in the ULW. Both varied little between stations and depth. P/NP abundance in the SML was not available for station 06.~~Overall, *Aphanizomenon* sp. exhibited the highest phytoplankton >20µm abundance, followed by *Nodularia spumigena* and *Aphanocapsa* sp..~~

Across the stations, the MP community was dominated by filamentous cyanobacteria in both Surface and ULW-Net samples (Fig. 3a). *Aphanizomenon* sp. was the dominant species at almost all stations and in both layers and accounted for a mean abundance of 158 ± 166 cells mL^{-1}. Secondary contributions came from *Nodularia spumigena* (84 ± 128 cells mL^{-1}), followed by *Aphanocapsa* sp. (41 ± 48 cells mL^{-1}), which were consistently present but more variable among stations. Diatoms were a minor component of the MP community. *Cylindrotheca closterium* (3.3 ± 4.4 cells mL^{-1}) and *Pseudo-nitzschia delicatissima* (1.1 ± 0.8 cells mL^{-1}) were typically present at low percentages (<2 %). Overall, variability in relative species abundance among stations was moderate across the stations and depths. Relative abundances for *Chaetoceros* sp., *Dinophysis* sp. and *Diplopsalis* (group) were <2 % and are thus not visible in Fig. 3. ~~H~~A figure displaying a higher resolution of the relative

abundance <4 % can be found in the supplementary material (Fig. S3). ~~P~~MP~~hytoplankton <20µm~~ abundances were approximately three orders of magnitude ~~higher~~ lower than those of P/NP~~phytoplankton >20µm~~.

~~Microscopic~~ Apart from abundances, microscopic analysis further enabled biomass estimation of MP~~phytoplankton >20µm~~. Pronounced differences in the biomass of dominant ~~>20µm~~ MP~~phytoplankton~~ taxa between S~~s~~urface and ULW-Net samples were observed during both ~~LPA>20µm~~Low MP and ~~HPA>20µm~~High MP ~~periods~~conditions (~~, as shown in~~ Fig~~.ure~~ 4). In addition, calculated *Synechococcus* sp. (phycoerythrin-rich picophytoplankton) biomass (see section 2.4) was included for the same conditions to enable a comparison with the ~~>20µm~~ MP~~phytoplankton~~ fraction.

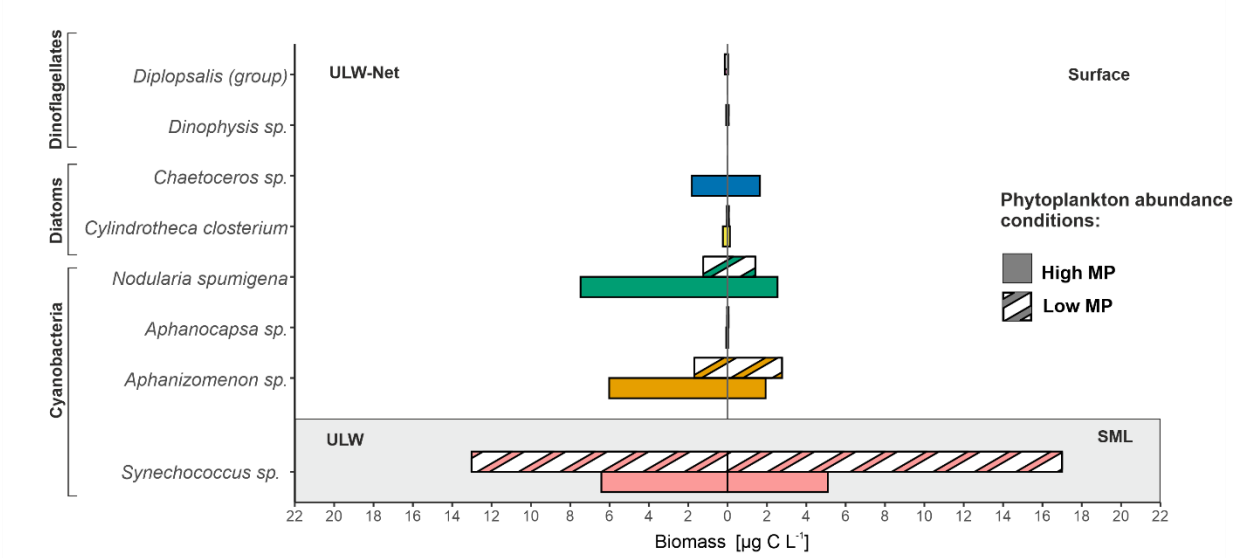

Figure 4: Mean biomass (µg C L^{-1}) of dominant micro~~phytoplankton (MP) >20µm~~ taxa ~~and *Synechococcus* sp. (<20 µm)~~ in S~~s~~urface and net-derived underlying water ~~from net~~ (ULW-Net) samples, as well as of *Synechococcus* sp. in sea surface microlayer (SML) and underlying water (ULW) samples ~~for *Synechococcus* sp~~. Data are differentiated by ~~phytoplankton~~ MP abundance~~abundance level~~ conditions, ~~(~~solid bars ~~=~~ represent ~~HPA>20µm, h~~High MP~~Phytoplankton >20 µm~~ a~~A~~bundance (High MP~~);~~),~ hatched bars ~~=~~ represent low MP abundance (~~LPA>20µm~~Low MP~~), Low Phytoplankton >20µm Abundance~~). ~~Bars represent biomass for each taxon, with c~~Colors ~~indicating~~ differ in accordance with annotated taxa~~species identity~~. *Pseudo-nitzschia delicatissima* was excluded from the figure due to its negligible biomass contribution (<0.01 µg C L^{-1}).

In general, MP~~phytoplankton~~ biomass ~~>20µm~~ was higher in the ULW-Net with an overall mean of 8.98 ± 10.50 µg C L^{-1} compared to the ~~surface~~ biomass of 4.59 ± 4.15 µg C L^{-1} in the Surface. The highest biomass contributions within MP~~phytoplankton~~ species ~~>20µm~~ were from *Aphanizomenon* sp. and *Nodularia spumigena* ranging from 0.05 to 16.04 µg C L^{-1} and 0.16 to 26.55 µg C L^{-1}, respectively. *Nodularia spumigena* showed the highest biomass in the ULW-Net during~~at HPA>20µm~~High MP conditions (7.48 ± 8.07 µg C L^{-1}) and was also present in the Surface at lower biomass. *Aphanizomenon* sp. occurred in both layers with generally greater values in the ULW-Net during~~at HPA>20µm~~High MP conditions (6.02 ± 4.39 µg C L^{-1}). *Cylindrotheca closterium* and *Chaetoceros* sp. occurred under~~at HPA>20µm~~High MP conditions only with <

0.20 µg C L^{-1}~~)~~. Other taxa, including *Aphanocapsa* sp., *Dinophysis* sp., and *Diplopsalis* (group), made up less than 0.10 µg C L^{-1}.

Synechococcus sp. exhibited higher biomass values than the ~~>20µm~~MP ~~phytoplankton~~ taxa, with a mean ~~value~~ of 12.63 ± 12.18 µg C L^{-1}, showing no significant difference between SML and ULW samples. Under ~~HPA>20µm~~High MP conditions~~(which corresponds mostly with LPA<20µm conditions)~~, *Synechococcus* sp. biomass was considerably lower (5.76 ± 1.52 µg C L^{-1}) compared to ~~LPA>20µm~~Low MP conditions~~s (which corresponds to HPA<20µm conditions)~~, during which it increased to 16.41 ± 15.59 µg C L^{-1}. In summary, the phytoplankton community was characterized either by a dominance of filamentous cyanobacteria (*Aphanizomenon* sp. and *Nodularia spumigena*) or the unicellular cyanobacterium *Synechococcus* sp.~~.~~

3.2 Biomolecular concentrations are shaped by phytoplankton

The enrichment and concentrations of the biochemical parameters were grouped ~~into HPA/LPA >20µm and HPA/LPA<20µm, in order to elucidate potential influences of the different phytoplankton classes~~with respect to depths and phytoplankton ~~regimes~~abundance conditions. The supplement provides ~~A~~an overview of all parameters ~~is provided in the Supplement~~ (Fig. S5 ~~&~~ and S6) as well as EFs for TOC, TAA, surfactants, and TCCHO at each station (Fig. S7). In the following, we ~~focus on those~~present parameters derived from SML and ULW seawater samples under P/NP conditions (Fig. 5), as well as parameters

derived from net sampling in Surface and ULW-Net under MP conditions ~~that based on under which phytoplankton regime they exhibit the most pronounced differences~~ (Fig. 6) ~~(Fig. 5 and Fig. 6)~~.

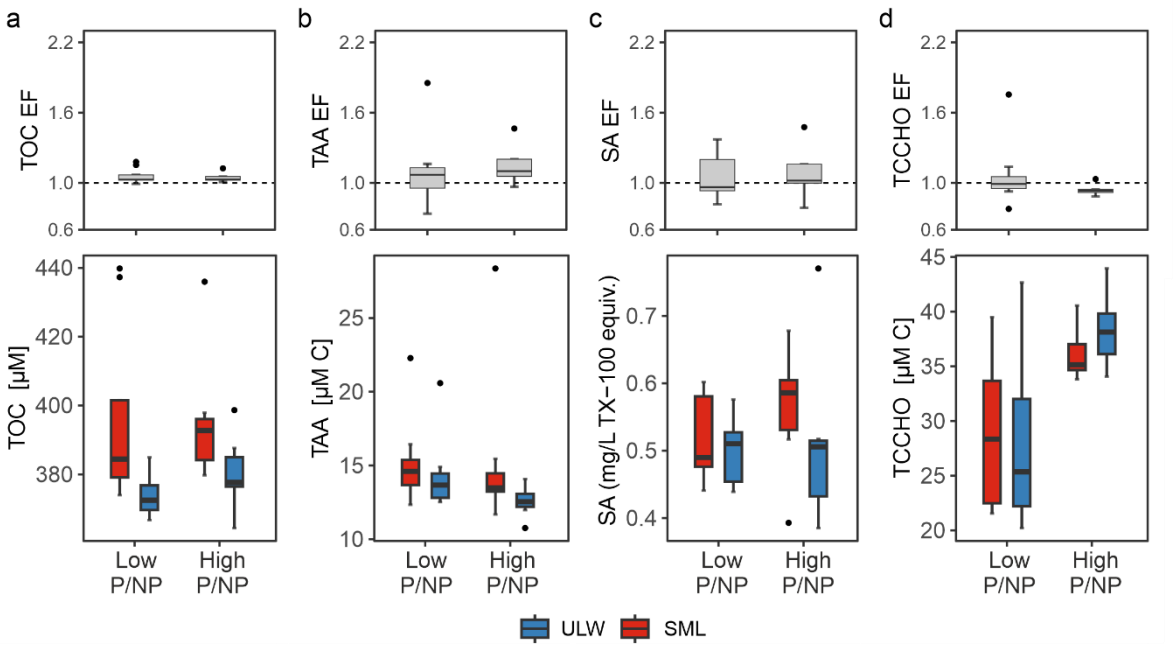

Figure 5: Concentration differences during low pico- and nanophytoplankton~~phytoplankton >20µm~~ abundance ~~abundance (LPA>20µm~~Low P/NP) and high pico- and nanophytoplankton ~~phytoplankton >20µm~~ abundance (~~HPA>20µm~~High P/NP) conditions ~~for~~in the sea surface microlayer (SML) and underlying water (ULW) for (a) total organic carbon (TOC), ~~and~~ (b) total amino acids (TAA), (c) ~~,~~ surfactant (SA) concentrations, and (d) total combined carbohydrates (TCCHO) are presented~~surfactants (c) and total combined carbohydrates (TCCHO) (d) were differentiated for high and low phytoplankton <20µm abundance (HPA<20µm and LPA<20µm)~~. Enrichment factors (EFs) for each parameter are shown for the respective condition~~abundance groups~~.

~~This section first~~First, this section addresses variations in relation to P/NP conditions and parameters ~~directly~~ measured in seawater (Fig. 5~~a and 5b~~) ~~conditions (), as shown in Figure 5a and b~~. TOC concentrations during ~~(Fig. 5a) showed a clear slight~~ enrichment in the SML ~~SML during LPA>20µm~~Low P/NP conditionss were~~, with~~ significantly higher ~~values~~ in the SML (39~~68~~ ± 2~~53~~ µM) compared to the ~~underlying water layer~~ULW (~~ULW;~~ 37~~45~~ ± 6 µM, p = 0.04~~406~~). ~~,~~ Fig. 5a). Despite the ~~increase~~significant difference, TOC EFs were close to 1 across stations (1.1 ± 0.1)~~)~~, which resulted from the overall elevated and unusually high TOC concentrations encountered in the Baltic Sea~~,~~. ~~As a result~~Consequently, overall ~~which~~~~O~~~~o~~high TOC concentrations reduced the relative SML enrichment, while absolute differences between the SML and ULW ~~still~~ remain statistically significant. Under ~~HPA>20µm~~High P/NP conditions~~s~~, TOC concentrations did not differ significantly between the SML (396 ± 10 µM) and ULW~~two depths~~ (381 ± 10 µM).

~~For~~ TAA~~,~~ concentrations ~~(Fig. 5b)~~ were ~~increased~~ slightly higher ~~from~~ in the SML (15.32~~4.29~~ ± 2.86~~3.14~~ µM C ~~(~~≙ 3.59~~30~~ ± 0.72 µM) than in the ULW ~~to~~ (14.41~~16.20~~ ± 2.47~~5.99~~ µM C ~~(~~≙ 3.33~~85~~ ± 0.57~~1.52~~ µM) ~~in the SML~~ under ~~LPA>20µm~~Low P/NP conditions~~s~~, however, this difference was not statistically significant (Fig. 5b). Similarly, under High P/NP conditions,

TAA concentrations did not differ significantly, despite elevated concentrations in the SML ~~In the SML, TAA showed a higher median concentration during HPA>20µm~~ (15.56 ± 5.33 µM C ≙ 3.72 ± 1.35 µM ~~14.8 µM C~~) compared to the ULW ~~than during LPA>20µm~~ (12.56 ± 0.97 µM C ≙ 2.92 ± 0.20 µM ~~13.59 µM C)), although mean values did not differ~~. ~~This tendency was more pronounced~~ The minor concentration differences between the SML and ULW resulted in similar EFs under both Low P/NP (1.1 ± 0.3; median = 1.1) and High P/NP (1.2 ± 0.4; median = 1.1) conditions. ~~in the <20µm size fraction (Fig. S6a), where TAA concentrations were slightly higher under LPA<20µm conditions (14.86 ± 2.80 µM C ≙ 3.46 ± 0.69 µM) than under HPA<20µm conditions (14.06 ± 4.27 µM C ≙ 3.32 ± 1.08 µM). When samples were pooled across categories (i.e., not distinguished by HPA/LPA), TAA concentrations differed significantly between depths (SML: 15.43 ± 4.34 µM C ≙ 3.65 ± 1.10 µM; ULW: 13.55 ± 2.21 µM C ≙ 3.14 ± 0.50 µM; p = 0.076), resulting in an average EF of 1.2 ± 0.4 (median = 1.1). During HPA<20µm conditions, surfactant concentrations (Fig. 5c) were elevated in the SML~~

Surfactant concentrations were comparable between SML (0.52 ± 0.06 mg L^{-1} TX-100 equiv.) and ULW (0.50 ± 0.05 mg L^{-1} TX-100 equiv.) under Low P/NP conditions, with an EF of 1.1 ± 0.2 (median = 1.0), as shown in Fig. 5c. Under High P/NP conditions, ~~addressed~~surfactant concentrations were elevated in the SML (0.56 ± 0.08 mg L^{-1} TX-100 equiv.) compared to the ULW (0.52 ± 0.12 mg L^{-1} TX-100 equiv.), however, the difference was ~~-~~not significant. This ~~(0.56 ± 0.09 mg L^{-1} TX-100 equiv.) relative to the ULW (0.52 ± 0.14 mg L^{-1} TX-100 equiv.),~~ correspon~~ded~~ding to an EF of 1.1 ± 0.2 (median = 1.1), which is similar to the EFs observed during Low P/NP conditions. ~~In contrast, surfactant EFs were lower under LPA<20µm conditions (1.1 ± 0.2; median = 1.0). This pattern is further supported by the >20µm size fraction (Fig. S5c), where during LPA>20µm higher surfactant concentrations were detected in the SML (0.56 ± 0.11 mg L^{-1} TX-100 equiv.) compared to the ULW (0.45 ± 0.06 mg L^{-1} TX-100 equiv.) and average EF of 1.2 ± 0.2 (median: 1.3).~~ Depth-related differences in TCCHO concentrations were not significant under either Low or High P/NP conditions (Fig. 5d). However, when samples were considered irrespective of depth, TCCHO concentrations were significantly higher under High P/NP conditions~~TCCHO concentrations (Fig. 5d) were significantly elevated during HPA<20 µm conditions~~ (37.21 ± 2.88~~3.0~~ µM C ≙ 6.38 ± 0.49~~50~~ µM) compared to Low P/NP conditions ~~LPA<20 µm~~ (28.3~~76~~ ± 6.96~~7.18~~ µM C ≙ 4.85 ± 1.19~~23~~ µM, p = 0.007). EFs were comparable between Low P/NP (1.1 ± 0.3; median = 1.0) and High P/NP (0.9 ± 0; median = 0.9) conditions.~~Depth-related differences in TCCHO remained insignificant. Station-specific enrichment factors are presented in the Supplement (Fig. S7).~~

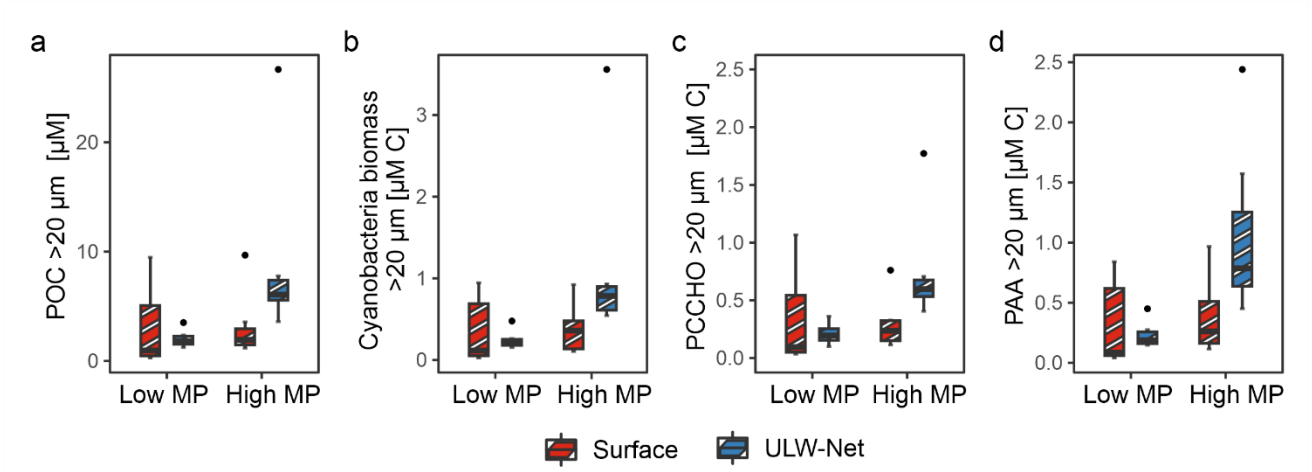

Figure 6: Concentration differences during low microphytoplankton ~~>20µm~~ (~~LPA>20µM~~Low MP) and high microphytoplankton ~~>20µm~~ abundance (~~HPA>20µM~~High MP) conditions in Surface (red, striped) and ULW-Net (blue, striped) ~~-~~ for (a) particulate organic carbon (POC) >20 µm, (b) cyanobacteria biomass >20 µm, (c) particulate combined carbohydrates (PCCHO) >20 µm ~~(PCCHO>20µm)~~, and (d) particulate amino acids (PAA) >20 µm ~~(PAA>20µm)~~ are presented~~for surface (red, striped) and ULW-Net (blue, striped) samples~~.

Second, ~~In Fig. 6,~~ the particulate organic matter composition of net-derived samples is presented and accordingly grouped into ~~microphytoplankton~~MP ~~regimes~~conditions (Fig. 6). During ~~HPA>20µm~~High MP ~~-~~conditions~~s~~, POC >20 µm concentrations differed significantly between depths (Fig. 6a), with markedly higher values in the ULW-Net (8.89 ± 7.36~~95~~ µM) compared to the S~~s~~urface (3.09 ± 2.79~~3.02~~ µM; p = 0.02). In contrast, depth-related differences were not evident under ~~LPA>20µm~~Low MP conditions~~s~~, where concentrations were lower in both S~~-the s~~urface (3.07 ± 3.67~~92~~ µM) and ULW-Net (2.04 ± 0.72~~82~~ µM) compared to ~~HPA>20µm~~High MP conditions. Cell-based estimates of cyanobacterial biomass >20 µm ~~Within the POC>20µm pool, related MPphytoplankton microphytoplankton biomass contributed~~accounted on average for 12.6 ± 4.7 % ~~12.7 ± 4.6% of~~to the ~~total~~ POC >20 µm (Fig. 6b).~~, with the cyanobacteria dominating the assemblage (Fig. 6b).~~ Their biomass reached 1.13 ± 1.0~~8~~ µM C in the ULW-Net and was significantly reduced at the S~~s~~urface (0.37 ± 0.2~~9~~ µM C; p = 0.01).

PCCHO >20 µm and PAA >20 µm showed a S~~s~~imilar pattern between depth under High MP conditions~~s were reflected in PCCHO>20µm~~(Fig. 6c and 6d) ~~(Fig. 6c)~~. PCCHO >20 µm concentrations were elevated i~~, which showed elevated concentrations i~~n the ULW-Net ~~-~~(0.74 ± 0.4~~6~~3 µM C ≙ 0.12 ± 0.0~~7~~8 µM) compared to the ~~s~~Surface (0.29 ± 0.2~~1~~~~2~~ µM C ≙ 0.05 ± 0.0~~3~~~~4~~ µM; p = 0.02). PCCHO >20 µm ~~These compounds represented~~accounted for 10.3 ± 2.3 % of the POC >20 µm pool and 1.3 ± 1.2 % of TCCHO.~~,~~ Contributions of PCCHO to ~~the~~ TCCHO ~~pool~~ differed between abundance conditions, with ~~contributing~~ 1.7 ± 1.3 % ~~and 0.9 ± 0.9%~~ under ~~HPA>20µm~~High MP conditions and 0.9 ± 0.9 % under ~~and~~ ~~LPA>20µm~~Low MP conditions~~s, respectively~~. ~~A comparable trend was observed for PAA>20µm (Fig. 6d), which~~ PAA >20 µm increased from 0.38 ± 0.32 µM C (≙ 0.08 ± 0.07 µM) in~~at~~ the S~~s~~urface to 1.07 ± 0.71 µM C (≙ 0.23 ± 0.16 µM) in the ULW-Net (p = 0.05) (Fig. 6d). PAA >20 µm contributed 12.8~~9~~ ± 6.4 % to the POC >20 µm pool and 0.3–18.6 % (3.8 ± 4.1 %) to TAA. PAA

contributions to TAA were~~, with relatively higher contributions~~higher during ~~HPA>20µm~~High MP conditions (5.4 ± 4.8 %) than during ~~LPA>20µm~~Low MP conditions (1.9 ± 1.9 %)~~ conditions~~.

In summary~~Overall~~, the biochemical parameter revealed differences between depth and phytoplankton abundance conditions. ~~surfactants, and~~ TOC ~~tended to~~ exhibited ~~higher~~ elevated concentrations ~~SML concentrations~~ in the SML during Low P/NP conditions, whereas TAA concentrations were only marginally higher in the SML ~~during LPA>20µmLow P/NP conditions~~. During High P/NP conditions, TCCHO concentrations were higher and ~~. TAA concentrations, however, were marginally higher during HPA>20µm conditions.~~surfactant concentrations were elevated in the SML compared to Low P/NP conditions, although this difference was not significant. ~~Pa~~~~Conversely, pa~~rticulate fractions (PAA >20 µm and PCCHO >20 µm) reflected the expected enrichment of cyanobacterial biomass >20 µm and POC >20 µm in the ULW-Net under ~~HPA>20µm~~High MP condition~~s~~s. Further, we found that MP~~phytoplankton >20µm~~ biomass was significantly related to POC >20 µm (R^2 =-0.94; p <-0.001) (Fig. S4), and accounted for 5.67~~4~~ – 38.32~~ 28.5~~ % (~~mean: 1~~3.5 ± 6.2~~2.7~~ %) of the POC >20 µm pool, primarily driven by the contributions of *Nodularia spumigena* and *Aphanizomenon* sp.~~.~~

3.3 Biomolecular composition of amino acids and carbohydrates

To highlight distinct differences in compound composition~~ between the size classes~~, the relative molecular composition of ~~amino acids and~~ combined carbohydrates and amino acids for the total and particulate (>20µm) fractions were compared (Fig. 7).

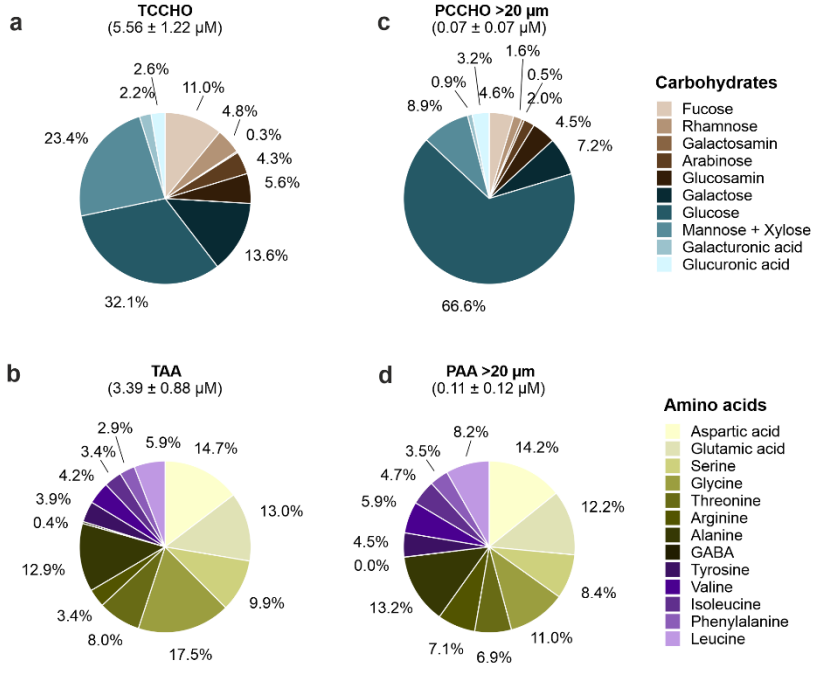

Figure 7: Composition of combined carbohydrates and amino acids in total and particulate pools. The pie charts summarize the relative contributions of individual compounds (a) to total combined carbohydrates (TCCHO), (b) total amino acids (TAA), (c~~b~~)

particulate combined carbohydrates (PCCHO) >20 µm ~~(PCCHO)~~, ~~(c) total amino acids (TAA),~~ and (d) particulate amino acids (PAA) >20 µm ~~(PAA)~~. Slice labels give each mol% of the pool. Chart titles report the M ± SD concentration (µM) of the molecular concentrations of the corresponding pool across all samples.

A few key compounds strongly dominated carbohydrate composition, while several constituents contributed only marginally. In contrast, ~~.A~~amino acid compositions showed a more even distribution among individual compounds ~~was characterized by a more diverse contribution of individual compounds.~~ Differences are first described for the total fraction (Fig. 7a, b), followed by the particulate fraction (Fig. 7c, d).

~~Amino acid composition was characterized by a more diverse contribution of individual compounds.~~ TCCHO (5.6 ± 1.2 µM) was characterized by a predominance of glucose (32.1 mol %) and mannose & xylose (23.4 mol %), followed by galactose (13.6 mol %) and glucosamine (11.0 mol %) (Fig. 7a). ~~-~~The TAA pool (3.4 ± 0.8 µM) was mainly composed of glycine (17.5 mol %), aspartic acid (14.7 mol %), glutamic acid (13.0 mol %), and alanine (12.9 mol %) (Fig 7c). Within the ~~In the~~ PCCHO~~particulate~~ >20µm pool ~~(>20 µm)~~ (0.06 ± 0.07 µM), glucose dominance became even more pronounced, accounting for 66.6 mol %, while the contributions of mannose & xylose (8.9 mol %), galactose (7.2 mol %), and glucosamine (4.5 mol %) were comparatively smaller (Fig. 7b). An elevated fraction of glucuronic acid and galactosamine was also characteristic of the PCCHO >20 µm pool in comparison to the TCCHO pool. ~~The total amino acid pool (TAA: 3.4 ± 0.8 µM) was mainly composed of glycine (17.5 mol%), aspartic acid (14.7 mol%), glutamic acid (13.0 mol%), and alanine (12.9 mol%).~~ The ~~particulate fraction~~pool of PAA >20 µm (~~PAA>20 µm;~~ 0.11 ± 0.12 µM) exhibited a comparable composition as the TAA, dominated by particulate aspartic acid (14.2 mol %), glutamic acid (12.2 mol %), alanine (13.2 mol %), and glycine (11.0 mol %) (Fig. 7d). Shifts in relative proportions suggest subtle differences in the source of amino acids between fractions. Relative shifts in the contributions of γ-aminobutyric acid (GABA), arginine, leucine, phenylalanine, valine, and tyrosine were observed. While GABA was elevated in the TAA pool, the latter amino acids were enriched within PAA~~the particulate~~ >20 µm pool (Fig. 7d, mainly purple).

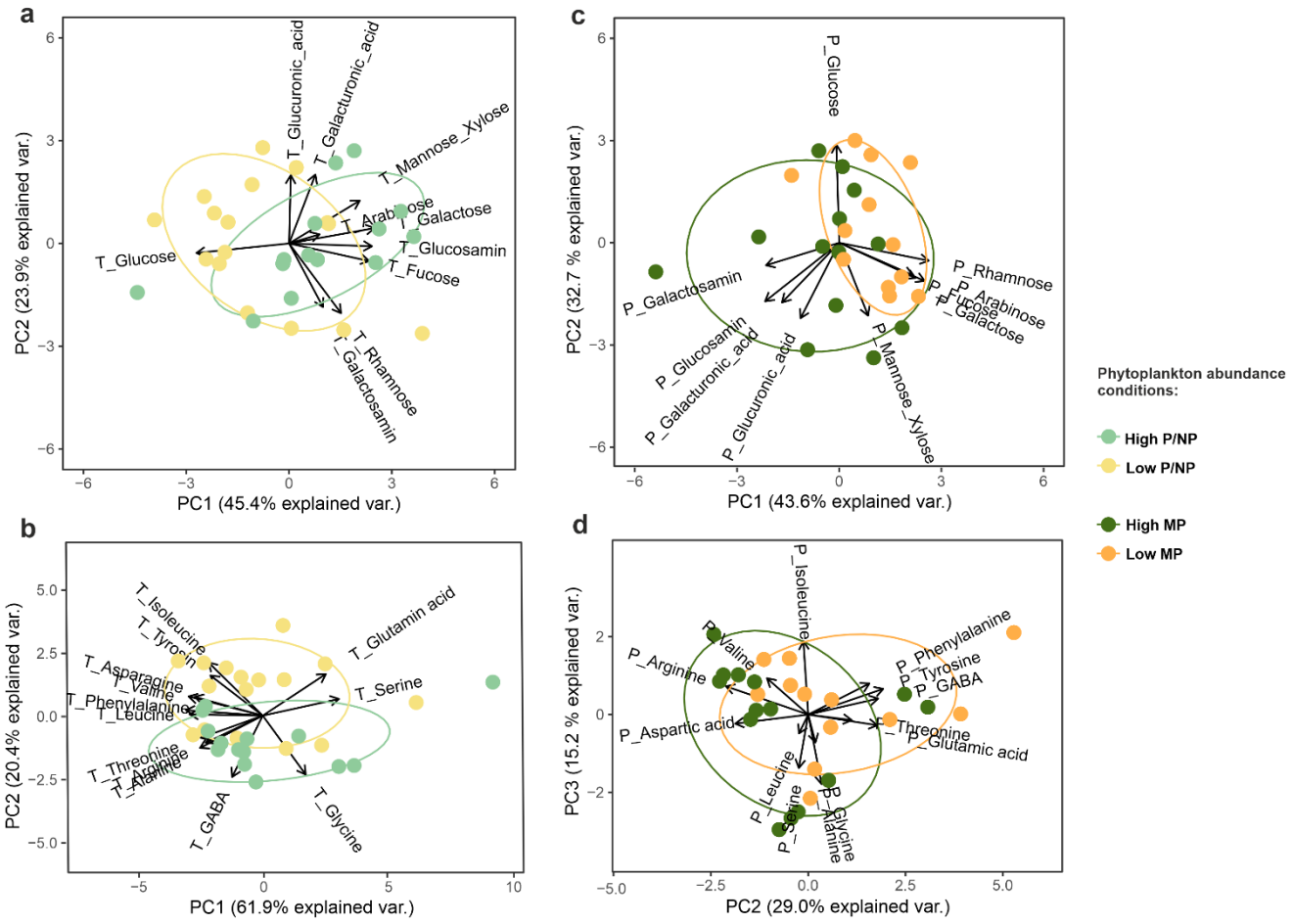

Figure 8: Principal component analysesis (PCA) wereas conducted to detect compositional differences between for both microphytoplankton (MP) and pico- and nanophytoplankton (P/NP) abundance conditionssize classes. Biplots show (a) total combined carbohydrates (TCCHO), (b) total amino acids (TAA) particulate combined carbohydrates (PCCHO), (c) particulate combined carbohydrates (PCCHO) >20 µm,total amino acids (TAA), (d) and particulate amino acids (PAA) (PAA >20 µm). Scores are colored based onby HPA<20µmHigh P/NP (light green), LPA<20µmLow P/NP (light yellow), HPA>20µmHigh MP (dark green) and LPA>20µmLow MP (dark yellow) conditions. Arrows show variable loadings; axes are scaled to unit variance and annotated with percent variance explained. SStations for which no P/NPphytoplankton <20µm abundance data were available are annotated as 'na', preventing assignment to a specific abundance level.

Principal component analysis (PCA) revealed systematic compositional differences between low (LPA<20µmLow P/NP) and high (HPA<20µmHigh P/NP) conditions phytoplankton abundance (Fig. 8a, b). For total combined carbohydratesTCCHO (Fig. 8a), conditions separated along both, the PC1 and PC2 axis, explained explaining 45.4 % and 23.3 % of the variance, respectively, and together accounted for 68.7 % of variation in the data (Fig. 8a). LPA<20µmLow P/NP conditions wasas mainly characterized by the high contribution of total total glucose, while under HPA<20µmHigh P/NP conditions, showed higher contributions of total galactose, glucosamine, fucose and mannose & xylose were observed. For total amino acidsTAA (Fig. 8c), the PC1 explained 61.9 % of the variance (PC2: 20.4%), while categories separated mainly along PC2 (20.4 %

explained variance) (Fig. 8b). Positive PC2 loadings were driven by total glutamic acid, isoleucine and tyrosine, whereas negative PC2 loadings were associated with e.g. total GABA and total glycine. The PC1 axis, explaining most of the variance, was loosely related to a separation between ULW (negative values, e.g., total phenylalanine, leucine, arginine, -tyrosine) and the SML (positive values for total glutamic acid, serine, glycine) (Fig. S8).

The compound-specific analysis of PCCHO >20 µm and PAA >-20 µm ~~(Fig. 8b, d)~~ revealed distinct compositional differences between High MP and Low MP conditions~~HPA > 20µm and LPA > 20µm~~, primarily separating along PC1 (explained variance: 43.6 %; Fig. 8c) and PC2 (explained variance: 29.0 %; Fig. 8d), respectively~~, respectively~~. ~~-~~During ~~HPA>20µm~~High MP conditions, -PCCHO >20 µm was characterized by elevated contributions of particulate galactosamine, along with notable proportions of particulate glucosamine, galacturonic acid, and glucuronic acid (Fig. 8c~~b~~). In contrast, ~~the LPA>20µm~~Low MP condition~~s~~ was associated with higher relative ~~abundances~~ contribution of particulate rhamnose, fucose, arabinose, and galactose. The PCA of PAA >20 µm further indicated that particulate GABA, tyrosine, phenylalanine, and glutamic acid were associated with~~the main contributors under~~ ~~LPA>20µm~~Low MP condition~~s~~~~s~~, whereas the enrichment of arginine and aspartic acid characterized most samples associated with ~~HPA>20µm~~High MP -condition~~s~~~~s~~ (Fig. 8d).

3.4 Species-specific correlations

To investigate potential links between phytoplankton species and major biomolecules, we conducted a correlation analysis between species-associated biomass and the biomolecular composition of carbohydrates and amino acids within the total and particulate >20 µm ~~(>20µm)~~ ~~and total~~ fraction~~s and~~ ~~for~~ of the ~~surface/~~SML/Surface as well as the ULW/ULW-Net~~/ULW~~. *Dinophysis acuminata*, *Dinophysis* (group) and *Chaetoceros* sp. were excluded from the correlation matrix due to their low ~~and~~ abundance.

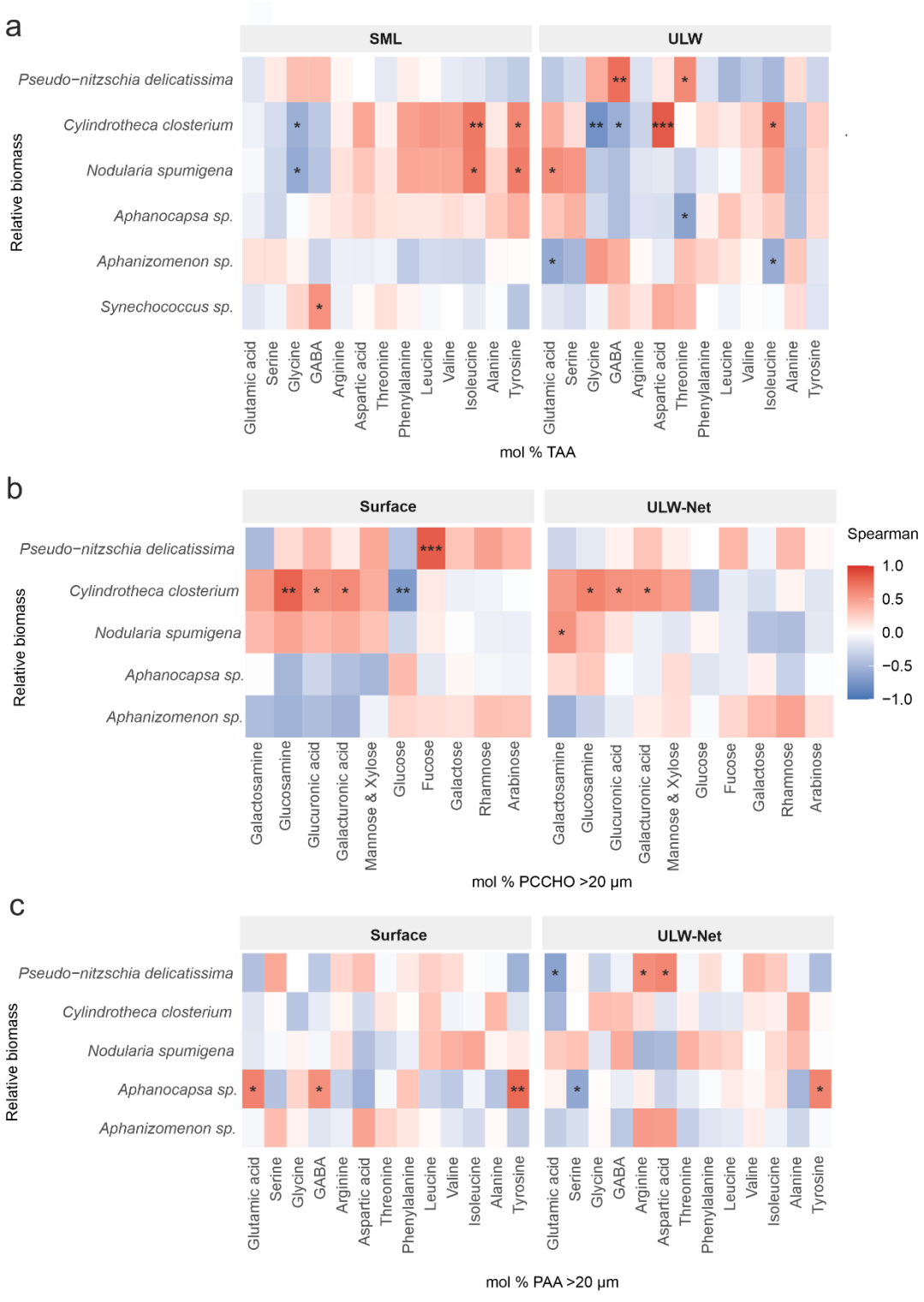
a
SML
ULW
Pseudo−nitzschia delicatissima
Cylindrotheca closterium
Nodularia spumigena
Aphanocapsa sp.
Aphanizomenon sp.
Synechococcus sp.
Relative biomass
Glutamic acid
Serine
Glycine
GABA
Arginine
Aspartic acid
Threonine
Phenylalanine
Leucine
Valine
Isoleucine
Alanine
Tyrosine
mol % TAA
b
Surface
ULW-Net
Spearman
1.0
0.5
0.0
−0.5
−1.0
Galactosamine
Glucosamine
Glucuronic acid
Galacturonic acid
Mannose & Xylose
Glucose
Fucose
Galactose
Rhamnose
Arabinose
mol % PCCHO >20 µm
c
mol % PAA >20 µm

Figure 9: Heatmaps of Spearman rank-order correlations (ρ) between relative phytoplankton biomass and mol % of (a) total amino acids (TAA)~~particulate combined carbohydrates (PCCHO>20µm)~~, (b) particulate combined carbohydrates (PCCHO) >20 µm ~~total amino acids (TAA)~~, and (c) particulate amino acids (PAA) >20 µm ~~(PAA>20µm)~~ in the ~~surface~~/SML/Surface (left) and ULW/ULW-Net~~t~~/~~ULW~~ (right). Carbohydrates and amino acids have been reordered by hierarchical clustering to group positively- and negatively-associated carbohydrates and amino acids. Tile colors range from blue (ρ = –1) through white (ρ = 0) to red (ρ = +1), and significant correlations are marked with asterisks (* p <0.05; ** p <0.01; *** p <0.001). Correlations with biomass of *Synechococcus* sp. were only performed for TAA.

For TCCHO, no positive correlations with phytoplankton species were found, thus, results are only presented within the supplementary information (Fig. S9). The relative biomass of the diatom *Cylindrotheca closterium* (biomass) correlated significantly negatively with total glucosamine (ρ = -0.60, p = 0.03), fucose (ρ = -0.60, p = 0.03) and rhamnose (ρ = -0.55, p = 0.05) in the SML and in the ULW with total fucose (ρ = -0.66, p = 0.01).

Among TAA (Fig. 9a), positive correlations for *Nodularia spumigena* and *Cylindrotheca closterium* were observed in the SML with total isoleucine (ρ =0.68, p = 0.01; ρ =0.62, p = 0.024), and tyrosine (ρ =0.66, p = 0.013; ρ =0.62, p = 0.024) and a negative correlation with total glycine. *Aphanizomenon* sp. correlated negatively with total glutamic acid (ρ = -0.60, p = 0.029) and total isoleucine (ρ = -0.58, p = 0.039). *Synechococcus* sp. biomass showed the only positive correlation in the SML with total GABA (ρ =0.57, p = 0.041). In the ULW, *Nodularia spumigena* biomass showed positive association with total glutamic acid (ρ =0.59, p = 0.035), ~~different from~~ in contrast to the SML. *Cylindrotheca closterium* biomass correlated highly positively with total aspartic acid (ρ =0.84, p = 0.00038) and less strongly with isoleucine (ρ =0.69, p = 0.0087), but negatively with total glycine (ρ = -0.78, p = 0.0017) and GABA (ρ = -0.57, p = 0.044). *Pseudo-nitzschia delicatissima* biomass showed positive correlation with total GABA (ρ = 0.74, p = 0.0038) and total threonine (ρ = 0.61, p = 0.028), while a negative correlation with total threonine (ρ = -0.65, p = 0.017) was observed for *Aphanocapsa* sp. biomass.

For PCCHO >20 µm, several significant positive correlations with ~~individual~~ phytoplankton species were observed (Fig. 9b). In the ~~s~~Surface, the biomass of *Cylindrotheca closterium* showed the strongest positive correlation with particulate glucosamine (ρ = 0.79, p = 0.0013), followed by positive correlations with particulate glucuronic acid (ρ = 0.57, p = 0.044) and galacturonic (ρ = 0.60, p = 0.031) acid (Fig. 9a). Furthermore, in the S~~s~~urface, *Pseudo-nitzschia delicatissima* biomass was significantly correlated with particulate fucose (ρ =0.82, p = 0.0006). *Cylindrotheca closterium* biomass was negatively correlated with particulate glucose (ρ = -0.71, p = 0.0067). Other phytoplankton groups exhibited weaker or non-significant correlations in the S~~s~~urface. In the ULW-Net, *Cylindrotheca closterium* retains its positive, although weaker, correlation to particulate glucosamine (ρ = 0.64, p = 0.018), glucuronic acid (ρ =0.57, p = 0.044), and galacturonic acid (ρ =0.55, p = 0.049).

Within the PAA >20 µm pool, only ~~Among TAA (Fig. 9b), *Nodularia spumigena* and *Cylindrotheca closterium* revealed similar correlation. For both, positive correlations were observed in the SML with total isoleucine (ρ =0.68, p = 0.01; ρ =0.62, p = 0.024), and tyrosine (ρ =0.66, p = 0.013; ρ =0.62, p = 0.024) and a negative correlation with total glycine. *Aphanizomenon sp.* correlated negatively with total glutamic acid (ρ = 0.60, p = 0.029) and total isoleucine (ρ = 0.58, p = 0.039). *Synechococcus sp.* biomass showed the only positive correlation in the SML with GABA (ρ =0.57, p = 0.041). In the ULW, *Nodularia spumigena* biomass showed positive association with total glutamic acid (ρ =0.59, p = 0.035), different from the~~

~~SML. *Cylindrotheca closterium* biomass correlated highly positively with total aspartic acid (ρ =0.84, p = 0.00038) and less strongly with isoleucine (ρ =0.69, p = 0.0087), but negatively with total glycine (ρ = -0.78, p = 0.0017) and GABA (ρ = -0.57, p = 0.044). *Pseudo-nitzschia delicatissima* biomass showed positive correlation with total GABA (ρ = 0.74, p = 0.0038) and total threonine (ρ = 0.61, p = 0.028), while a negative correlation with total threonine (ρ = -0.65, p = 0.017) was observed for *Aphanocapsa sp.* biomass.~~

~~Further,~~ *Aphanocapsa* sp. showed ~~the only~~ statistically significant positive ~~associations~~ correlations in the Ssurface ~~with PAA>20µm~~ (Fig. 9c). Its biomass correlated positively with particulate glutamic acid (ρ = 0.65, p = 0.017), GABA (ρ = 0.58, p = 0.039) and strongest with tyrosine (ρ = 0.76, p = 0.0024) (Fig. 9c). ~~No other phytoplankton taxa exhibited significant correlations with any PAA>20µm in the surface.~~ In the ULW-Net, two taxa displayed weak but significant positive links. *Pseudo-nitzschia delicatissima* biomass correlated with arginine (ρ = 0.58, p = 0.036) and aspartic acid (ρ = 0.63, p = 0.021), while *Aphanocapsa* sp. biomass correlated positively with tyrosine (ρ = 0.64, p = 0.019). Negative correlations were observed ~~appeared~~ between *Pseudo-nitzschia delicatissima* biomass and total glutamic acid (ρ = -0.65, p = 0.016) and *Aphanocapsa* sp. biomass and total serine (ρ = -0.62, p = 0.025).

4. Discussion

4.1 Phytoplankton composition in the Central Baltic Sea

The overarching goal of this study was to determine whether phytoplankton dynamics are reflected in SML composition, with a specific focus on cyanobacteria. To contextualize biomolecular dynamics, changes in the dominant phytoplankton members throughout the cruise will be discussed first. About 96 % of the MP biomass (6.78 ± 8.28 µg C L^{-1}) ~~>20µm~~ was contributed by cyanobacteria, with an estimated mean ~~cyanobacteria~~ biomass ~~>20µm~~ of 6.52~~78~~ ± 8.12~~45~~ µg C L^{-1}. *Aphanizomenon* sp., *Nodularia spumigena*, and *Aphanocapsa* sp. represented the dominant ~~genera~~taxa, with the first two typically occurring in filamentous life stages (Wasmund, 1997) and the latter forming non-filamentous colonies (Komárek, 2003). *Nodularia* and *Aphanizomenon* were also shown to generally represent the dominant genera during the Baltic Sea summer in the Eastern Gotland Basin (Ploug, 2008; Zettler et al., 2024; HELCOM, 2025). During our cruise, *Aphanizomenon* sp. showed a mean biomass of 3.17 ± 3.37~~43~~ µg C L^{-1} and *Nodularia spumigena* of 3.31 ± 5.15~~25~~ µg C L^{-1} (Fig. 4). This is lower than the estimate by Karlson et al. (2022), who reported a mean summer biomass of 15 µg C L^{-1} for both genera from the period 2000 – 2020. Wasmund (1997) suggested that, based on data collected from 1979–1993 in the Baltic proper and addressing *Aphanizomenon* sp. as the dominant genus, a biomass of up to 22 µg C L^{-1} (200 µg L^{-1} wet weight) can still be considered as a background concentration, while everything above should be defined as a bloom. According to the HELCOM report (2025), the recent mean of cyanobacterial biomass from June to August (2000 – 2023) was slightly below the long-term mean of 220 µg L^{-1} (wet weight), which corresponds to the bloom threshold set by Wasmund (1997) for *Aphanizomenon* sp.~~.~~ Overall, in comparison to previous published values, our ~~species~~taxa-specific biomass estimates for *Aphanizomenon* sp. and *Nodularia spumigena* are in the same order of magnitude and, following the interpretation of Wasmund (1997), do not align with bloom conditions.

C~~C~~yanobacterial biomass >20 µm sampled here made up 5.2~~4~~ to 28.7~~5~~% (mean: 12.7 %) of ~~the~~ POC >20 µm, which was on average 4.4~~0~~ ± 5.2~~33~~ µM (Fig. 6b). Nausch et al. (2002) reported a mean surface POC concentration of 26.8 µM for the Baltic Sea, however, including all particles >0.7 µm. ~~-~~Likely, our cruise was slightly too early in the year to catch the summer blooms and we witnessed only the beginning accumulation of cyanobacterial biomass. In general, the spatial pattern of cyanobacteria accumulations on the surface is extremely patchy, as documented from remote-sensing and field studies (Kahru et al., 1994; Kutser, 2004; Seppälä et al., 2007; Karlson et al., 2022). A recent paper from Kahru et al. (2025) showed the frequency of the occurrence of cyanobacteria blooms from June to August during 2000–2024. For the area where our cruise was conducted, they found that roughly every fifth year no major accumulation of cyanobacterial biomass occurred. Additionally, they suggested that instead of sea surface temperature, surface irradiance causes the initiation of such blooms, implying that temporal seasonal offsets in the accumulation of biomass might occur in dependence on weather dynamics.

The Chl *a* concentration detected in this study (2.06 ± 0.3~~45~~ µg L^{-1}) was lower than later in the same year (3.23 µg L^{-1}, August 2022), and close to our research area during a subsequent EMB298 cruise (Zettler et al., 2024). However, Bunse et al. (2019) noted Chl *a* concentrations similar to ours, and ranging from 1.68 to 2.41 µg L^{-1} during the summer months (June-September) in 2011 to 2014 west of Gotland. Our data showed that Chl *a* concentration increased over the course of the cruise ~~time~~ from 1.63 ± 0.015 µg L^{-1} at the first station to 2.47 ± 0.1 µg L^{-1} at the last station (Fig. 2a). In parallel, also P/NP ~~smaller phytoplankton <20µm~~ cells increased during our cruise (Fig. 2b). Other studies reported that picophytoplankton can significantly contribute to Chl *a* (Sondergaard, 1991; Stal et al., 1999; Ohlendieck et al., 2000; Stal, 2003; Tamm et al., 2018). We found an overall P/NP ~~phytoplankton <20µm~~ cell abundance of 6~~986~~ ± 45~~8~~ ~~×x~~ 10^3 cells mL^{-1} based on flow cytometry for the Central Baltic Sea. This is comparable to other studies, which found picocyanobacteria abundances of 150 to 550 ~~×x~~ 10^3 cells mL^{-1} during summer (Albertano et al., 1997; Mazur-Marzec et al., 2013). In June 2015, a study in the Gotland Basin observed phytoplankton (including phycoerythrin- and Chl *a*-rich pico- and nanoplankton) abundances of ~ 96 ~~×x~~ 10^3 cells mL^{-1} at 1m depth (Cisternas-Novoa et al., 2019), which are in line with our cell counts of the ULW (68 ± 41 ~~x~~× 10^3 cells mL^{-1}). Zufia et al. (2021) established that the abundance of phycoerythrin-rich picophytoplankton peaked during summer, which was consistent with other Baltic Sea studies (Mazur-Marzec et al., 2013; Larsson et al., 2014; Tamm et al., 2018). Overall, Chl *a* concentration and P/NP~~phytoplankton <20 µm~~ abundances fell within the expected range for Baltic Sea summer conditions.

To compare the biomass of *Synechococcus* sp. with other studies, we estimated their biomass based on cell counts. Reported estimates of *Synechococcus* cellular carbon content range from 0.1 to 1.5 pg C $cell^{-1}$ (Moisan et al., 2010). Here, we used an average carbon content of 0.3 pg C $cell^{-1}$ based on Buitenhuis et al. (2012) and also applied by Hepach et al. (2020) for the Baltic Sea. We calculated an overall average *Synechococcus* sp. biomass of 12.63 ± 12.18 µg C L^{-1}, which did not differ between SML and ULW. The elevated *Synechococcus* sp. biomass during ~~HPA<20µm~~High P/NP conditions is comparable to other biomass values found for picophytoplankton during summer (Paczkowska et al., 2017). Additionally, Paczkowska et al. (2017) investigated that during summer (August), picocyanobacteria were the dominant size group, forming 40-90% of the total biomass in all basins of the Baltic Sea. This aligns with our findings, which show that~~, especially during HPA<20µm~~, *Synechococcus* sp. biomass was ~~significantly~~ higher than that of filamentous cyanobacteria-dominated, even under High MP

conditions (Fig. 4) ~~HPA>20µm~~. Other studies also align with these findings (Andersson et al., 1996; Hajdu et al., 2007), and report a *Synechococcus* contribution of 65% to phytoplankton biomass in the Baltic Proper with nitrogen-fixing cyanobacteria (*Aphanizomenon* spp. and *Nodularia* spp.) being the second dominant group (Stal et al., 1999).

4.2 General SML dynamics in dependence of phytoplankton composition

Although the associated MP~~phytoplankton >20µm~~ biomass reported here does not indicate the presence of a typical cyanobacteria bloom, phytoplankton members and biomass dynamically changed throughout the cruise. Dominant phytoplankton members were represented by filamentous (*Aphanizomenon* sp. and *Nodularia spumigena*), colonial (*Aphanocapsa* sp.) and unicellular (*Synechococcus* sp.) cyanobacteria. These bloom-forming taxa typically dominate phytoplankton abundance and biomass (see Section 4.1) and are therefore likely the primary contributors to organic matter production. Nevertheless, less abundant species (with relatively ~~high~~large ~~in~~ cell sizes or high per-cell biomass) may also further contribute to SML biomolecular composition via EPS production, or the release of surface-active compounds. However, these minor contributions are not the focus of this study~~, but should be considered~~.

The phytoplankton community during this study potentially influenced the organic matter pool as ~~clear~~ differences in biomolecular concentrations were revealed between depths (SML vs. ULW, Surface vs. ULW-Net) and abundance conditions (~~HPA>20µm~~High MP vs. ~~LPA>20µm~~Low MP, High P/NP vs. Low P/NP). The highest average EF was detected for TAA (1.2 ± 0.4), while TCCHO and TOC exhibited EFs of approximately 1, independent of phytoplankton abundance. Previously reported EFs in the summerly W~~w~~estern Baltic Sea averaged around 1.1 for dissolved and particulate amino acids (Barthelmeß and Engel, 2022). At the W~~w~~estern Baltic Sea time series station Boknis Eck, an earlier study reported great seasonal variability ~~of~~ in TAA and TCCHO concentrations and SML enrichment during two consecutive years, ~~however,~~ with EFs ranging between 0.8 and 1.2 (Dreshchinskii and Engel, 2017). TAA concentrations in the SML peaked in autumn with a maximum EF of 2.4 (Dreshchinskii and Engel, 2017), which is comparable to the highest TAA EF of 2.3 (Fig. S7; station 06) reported in this study. TCCHO concentrations in the SML peaked in autumn (~5 µM) and were comparable to those observed in this study (SML: 5.53 ±, 1.06 µM), although the maximum reported EF (1.4) was slightly lower than the highest value found here (1.8; Fig. S7, station 07).

~~. A recent meta-analysis revealed that pronounced enrichment of organic matter in the SML is rather uncommon, while nitrogen-containing biomolecules, including amino acids, preferentially accumulate in the SML (Silva et al., 2025, under review).~~ The enrichments of TAA and TCCHO in the SML of the Central Baltic Sea found in this study are thus in line with previous reports and further emphasize that SML enrichment patterns are compound-specific. At the time series station Boknis Eck, only one SML sample showed TAA concentration >3.0 µM during two consecutive years (Dreshchinskii and Engel, 2017). Hence, TAA concentrations observed during this study~~in the Central Baltic Sea,~~ (e.g. with a mean of 3.72 ± 1.35 µM ~~3.85 ± 1.52 µM~~ in the SML during ~~HPA>20µm~~High MP condition) were thus substantially higher than concentrations previously ~~observed~~ recorded in the Western Baltic Sea.

The enrichment of surfactants in the SML was similar across phytoplankton abundance conditions, with comparable EF values observed for High P/NP (1.1 ± 0.2; median = 1.1) and Low P/NP (1.1 ± 0.2; median = 1.0). Although the median EF was slightly higher ~~by 0.1~~ during High P/NP conditions, the overall differences were small and not statistically significant ~~differed in dependence of phytoplankton abundance, as the EF during HPA<20µm (1.1 ± 0.2; median = 1.1) exceeded the EF during LPA<20µm (1.1 ± 0.2; median = 1.0)~~. During ~~HPA<20µm~~High P/NP, we further measured the highest surfactant concentrations (0.56 ± 0.08 ~~0.56 ± 0.09~~ mg L^{-1} TX-100 equiv.) in the SML (Fig. 5c). In line with our results, averaged EFs of surfactants ranged between 0.9 and 1.4 in coastal regimes of the North Sea and Baltic Sea (Stolle et al., 2020; Barthelmeß and Engel, 2022). EFs of surfactants are generally lower in eutrophic regimes (Wurl et al., 2011), such as the Baltic Sea. However, exceptionally high surfactant concentrations may occur in coastal regions or under specific oceanic conditions at low wind regimes and tend to condense into visible surface slicks, exceeding a concentration of 0.65 mg/ L equiv. TX-100 (Wurl et al., 2016; Sabbaghzadeh et al., 2017; Mustaffa et al., 2020). Depending on the region and season, previously reported surfactant concentrations in coastal seas differ considerably. For the SML in a coastal transect off North East England, the authors reported a seasonal minimum and maximum of 0.08 and 0.38 mg/ L equiv. TX-100, respectively (Pereira et al., 2016). During spring, diel variability of SML surfactant concentrations ranged between 0.17 and 0.26 mg/ L equiv. TX-100 at a coastal station of the North Sea (Stolle et al., 2020). In the Western Baltic Sea, SML surfactant concentrations varied between 0.28 and 0.49 mg/ L equiv. TX-100 during two consecutive seasons (Barthelmeß and Engel, 2022). Estuarian and riverine surfactant concentrations, in contrast, frequently exceeded 1.00 mg/ L equiv. TX-100 (Rickard et al., 2022). In summary, surfactant concentrations reported here were rather high in comparison to other coastal stations including the Western Baltic Sea (Barthelmeß and Engel, 2022).

Although~~,~~ TOC enrichment was close to 1, concentrations varied significantly with depth during ~~HPA<20µm~~High P/NP (Fig. S6d). The average TOC concentrations in the SML presented here was 39~~6~~8 ± 2~~2~~2~~3~~ µM. TOC and DOC concentrations in the Baltic Sea are comparable, as POC constitutes only a minor fraction of TOC (Stråat et al., 2016). In the Baltic Proper, it is estimated that 74 to 77 % of DOC in spring and autumn, respectively, can be attributed to riverine input (Seidel et al., 2017). DOC concentrations steadily decline towards the Western Baltic Sea due to mixing with inflowing North Sea water, also reducing the contribution of terrestrial DOC (Seidel et al., 2017). Within the Western Gotland Sea, DOC concentration exhibited a seasonal range of 327 to 472 µM (mean 361 µM), while peaking during the summer months, reflected by an increase of ~50 µM (Bunse et al., 2019). This summer increase is potentially associated with autochthonous production (Seidel et al., 2017). Depending on the season and region, TOC concentrations in the Baltic Sea are exceptionally high in comparison to other coastal seas, and due to the high terrestrial DOC load. In summary, the general SML enrichment pattern as well as carbohydrate concentrations aligned with previous results reported from the Western Baltic Sea or elsewhere. TAA and surfactant concentrations, however, were notably elevated in the Central Baltic Sea in comparison to the Western Baltic Sea. The observed summer~~Summerly~~ TOC variability can likely be attributed to phytoplankton production.

4.3 Specific biomolecular pattern associated with distinct phytoplankton members

In line with categorizing MPphytoplankton into high and low abundance (and corresponding to high and low cyanobacteria biomass), POC, cyanobacterial biomass >20 µm, PAA and PCCHO >20 µm concentration were highest in the ULW-Net during HPA>20µmHigh MP. PAA and PCCHO >20 µm contributed on average 12.9 ± 6.4 % and 10.1 ± 2.3 % to POC >20 µm, respectively. This corresponds roughly to the proportion of amino acids and carbohydrates reported for particulate organic matter in the surface ocean (~30 %, pore size ~0.4µm, Kaiser and Benner, 2009). Cell-based MPphytoplankton biomass estimates and measured POC >20 µm concentrations diverged considerably, as the biomass contributed only 13.5 ± 6.21 % to POC >20 µm concentrations. Satellite and in-situ observations corroborate that phytoplankton biomass in temperate and more productive regimes substitutes between 10 to 30 % of POC only (Arteaga et al., 2016). The residual POC, which was not explained by the apparent biomass, may be attributed to the associated extracellular material constituting the filamentous and colonial lifestyle of cyanobacteria, with contributions of detached gel-like particles, inhabiting heterotrophic bacteria as well as detrital materialcan be attributed to heterotrophic plankton, and detritus, including extracellular material constituting the filamentous and colonial lifestyle of cyanobacteria, and gel-like particles (Mari and Kiørboe, 1996; Engel et al., 2004; Pannard et al., 2016, Cisternas-Novoa et al. 2019). The Indeed, the observed correlation between POC >20 µm and cellular MP biomass (Fig. S4) >20µm indicates that particulate organic matter was largely associated with filamentous and colonial cyanobacteria, including detrital and extracellular components. During this study, POC >20 µm concentration contributed in average 1.2 ±1.4 % to TOC and varied with conditions (HHigh MP: 1.6 ±1.7 % of TOC; LLow MP: 0.7 ±0.7 % of TOC)POC>20µm concentration was related to cyanobacterial cellular biomass >20µm (relative contribution of cyanobacterial biomass to POC>20µm: HPA >20 µm: 1.6 ± 1.7%; LPA >20 µm: 0.7 ± 0.7%) (HPA>20µm: 1.6 ± 1.7; LPA>20µm: 0.7 ± 0.7%). Our results , confirming the assumption that filamentous or colonial cyanobacteria can influence the particulate total organic matter pool of the Central Baltic Sea, even in spite the absence of a bloom. PAA accounted for a significantly larger proportion of TAA under HPA>20µmHigh MP conditions (5.4 ± 4.8 %) than under LPA>20µmLow MP conditions (1.9 ± 1.9 %). In contrast, the overall contribution of PCCHO >20 µm to TCCHO (1.3 ± 1.2%) and the difference between conditions were considerably smaller.

PAA >20 µm showed high fractions of the particulate amino acid arginine in comparison to TAA (Fig. 7d vs. 7b). Arginine defined a specific cluster of the HPA>20µmHigh MP conditions community (PCA Fig. 8d), which was most likely associated with co-occurring *Pseudo-nitzschia delicatissima* and *Aphanizomenon* sp. (Fig. 9c), of which the later constituted a considerably higher biomassand was associated with *Pseudo-nitzschia delicatissima*. The fraction of arginine in the PAA pool (>20 µm) of the Central Baltic Sea was particularly higher than in the Western Baltic Sea (Barthelmeß & Engel, 2022), where filamentous cyanobacteria are mostly absent. Moreover, PCCHO >20 µm was composed of elevated fractions of glucose and glucuronic acid in comparison to the total fraction (Fig. 7a, cb). While particulate glucose defined filamentous and colonial cyanobacteria (>20µm) during HPA>20µmHigh MP and LPA>20µmLow MP conditionss equally (Fig. 8cb), elevated ratios of glucuronic acid, glucosamine, galacturonic acid, and galactosamine aligned with HPA>20µmHigh MP conditionss (Fig.

8b) and further correlated with *Cylindrotheca closterium* and *Nodularia spumigena* (Fig. 9a), of which the later constituted the higher biomass. The higher percentage of particulate glucose is characteristic for productive regimes, as reported in previous studies (Engel et al., 2012; Barthelmeß and Engel, 2022). ~~HPA<20µmdominated by *Synechococcus* sp. , on the other hand, aligned with galactose (Fig. 8a, c) and elevated ratios of the non-proteinogenic amino acid GABA (Fig. 9b), which is often associated with advanced heterotrophic degradation (Dauwe et al., 1999; Davis et al., 2009; Barthelmeß and Engel, 2022).~~

As outlined above, the contributions of ~~large~~ MP~~(>20µm)~~ and P/NP~~small (<20µm) phytoplankton~~ members were notably reciprocal (High MP conditions correspond to Low P/NP conditions and vice versa). The co-occurrence of specific phytoplankton taxa is not random but potentially relates to trophic or allelopathic interactions, such as the transfer of newly fixed nitrogen from filamentous cyanobacteria to diatoms (Chen et al., 2011) or species-specific selection via the release of allelochemicals. *Nodularia spumigena* may cause a decline in growth and physical cell damage to specific diatoms by the release of toxins (Śliwińska-Wilczewska et al., 2019), or be adversely affected by diatoms (Lage et al., 2022). In the later study, co-culturing resulted in an upregulated release of specific peptides by *Nodularia*. *spumigena*. Allelopathic interaction between Baltic strains of cyanobacteria has been also observed, such as a multifactorial growth suppression of *Nodularia spumigena* by *Synechococcus* sp. (Barreiro Felpeto et al., 2018). Allelopathic effects may thus explain why reciprocal patterns were found for the ~~categorization~~ conditions of MP~~phytoplankton~~ and P/NP abundance ~~into larger and smaller cells (20µm)~~ i.e. elevated contributions of *Synechococcus* sp. ~~co~~occurred with decreased cyanobacterial biomass >20 µm in 10 out of 13 sample sets (Table A2). To summarize, specific biomolecular patterns of the SML could be associated with the particulate fraction and the occurrence of filamentous and colonial cyanobacteria, as well as with the total fraction and the predominant occurrence of picophytoplankton (*Synechococcus* sp.), respectively.

4.4 The influence of cyanobacteria on the ambient organic matter pool

The reciprocal pattern of the occurrence of MP and P/NP ~~small and large cyanobacteria~~ further allows to determine whether filamentous and colonial or unicellular cyanobacteria potentially exhibit a biomolecular imprint on the total organic matter pool. In F~~f~~igure 8a, galactose and glucose defined the main variance along PC1 (TCCHO). While the former represented ~~HPA<20µm~~High P/NP conditions, the latter aligned with ~~HPA>20µm~~High MP condition~~s~~. The variance along PC2 was associated with glucuronic acid and further influenced samples related to ~~HPA>20µm~~High MP condition~~s~~. As previously noted, glucose and glucuronic acid defined major differences between the PCCHO (>20 µm) and TCCHO pool (Fig. 7a, b). The described pattern can therewith be interpreted as a subtle biomolecular imprint of ~~large~~ filamentous and colonial cyanobacteria on the ambient TCCHO pool. In Figure 8b~~9b~~, the main variance along PC1 was defined by a bundle of amino acids (incl. total arginine, leucine, phenylalanine), which are often associated with fresher material from the surface ocean, and were opposed by total glutamic acid, serine and glycine of which the latter two define degraded rather than freshly produced organic matter (Dauwe et al., 1999; Kaiser and Benner, 2009). Amino acids characteristic of fresher material were thus associated with the ULW (Fig. S8). Consistently, the PCA reveals a more pronounced separation of TAA composition between SML and ULW samples (Fig. S8; PC1)~~,~~ than between the High P/NP and Low P/NP condition (Fig. 8b; PC2). This pattern

suggests that depth-related differences exert a stronger influence on TAA variability than the distinction between P/NP-associated conditions. However, ~~Data separated only into the defined categories of HPA H Nano and LPA<20µm along PC2, which explained considerably less variance of the TAA data. While *Synechococcus* sp. occurred in similar abundances in both the SML and ULW,~~ filamentous and colonial cyanobacteria dominated in the ULW during ~~HPA>20µm~~High MP conditions (Fig. 4), while *Synechococcus* sp. occurred in similar abundances in both the SML and ULW. Tentatively, a biomolecular imprint of filamentous and colonial ~~large~~ cyanobacteria defined by predominantly particulate arginine ~~and~~ but also leucine (PAA, Fig. 8d) can thus be detected along the negative ~~PC2~~PC1 (TAA, Fig. 8b). This aligns as well with the subtle recognized differences between the average mean composition of PAA (>20 µm) and TAA (Fig. 7c, d).

Heterocystous cyanobacteria, such as *Nodularia* sp. and *Aphanizomenon* sp. are a monophyletic group (Komárek & Komárková, 2006; Tomitani et al., 2006 ~~(Tomitani et al., 2006)~~). Filamentous and colonial cyanobacteria with the ability to fixate atmospheric nitrogen accumulate cyanophycin within their heterocysts. Cyanophycin is a polymer composed of arginine and aspartate (Flores et al., 2019). Specific anabolic pathways using the four nitrogen atoms of arginine therewith establish cyanophycin as a liable nitrogen reservoir in heterocystous cyanobacteria during unbalanced growth conditions (Flores et al., 2019) and may explain the particularly high fraction of arginine in the PAA >20 µm pool as well as its subtle influence on the composition of the ULW (TAA). While cyanobacteria accumulate cyanophycin within their heterocysts (Flores et al., 2019), these specialized cells rely on the supply of carbohydrates from adjacent vegetative cells (Nürnberg et al., 2015; Stuart et al., 2016). Interestingly, glucose dominates this intercellular trophic exchange and further constitutes the associated extracellular material (Nürnberg et al., 2015; Stuart et al., 2016). Within cyanobacterial mats, glucose polymers are made available by the release of extracellular enzymes (Stuart et al., 2016). In accordance, an increased fraction of uronic acids and amino sugars has been attributed to aid EPS aggregation as summarized by Engel et al. (2020). Glucose, amino sugars and uronic acids were elevated in PCCHO >20 µm (Fig. 7b) and associated to ~~HPA>20µm~~High MP conditions (Fig. 8b) and thus characterized in particular the extracellular material of the filamentous and colonial cyanobacteria, which is further inhabited by a rich heterotrophic community. Heterotrophic bacteria profit from the extracellular and aggregated resources, likewise replenishing the pool of extracellular proteins further (Stuart et al., 2016). To conclude, we found that both MP~~phytoplankton~~ and P/NP ~~size fractions~~ influenced the ambient total organic matter pool, as evident from specific biomolecular contributions, which can likely be explained by trophic and allelopathic interactions.

4.5 How surfactants relate to biomolecular dynamics

In general, elevated surface activity has been associated with both the particulate and dissolved fraction as well as with fresh and degraded organic matter profiles (Zutic et al., 1981; Engel et al., 2018b; Barthelmeß and Engel, 2022). As summarized by Barthelmeß and Engel (2022), amino acids accumulating in the SML are usually characterized by a higher polarity and are represented by arginine, glutamic acid, and serine. This is again supported by the data presented here, as ~~the amino acids total~~total -serine and glutamic acid seemed to be relatively more abundant in the SML (Fig S8).

~~Heterotrophic bacteria release surfactants to enhance substrate availability and uptake (Satpute et al., 2010)~~Explicitly arginine has been suggested as a potent candidate to enhance surface activity (Engel et al., 2018b). ~~and explicitly arginine has been suggested as a potent candidate to enhance surface activity (Engel et al., 2018b).~~ While relatively higher fractions of arginine accompanied the predominant occurrence of ~~large~~ filamentous and colonial cyanobacteria ~~(Fig. 8d)~~ in the ULW (Fig. 8c, d)~~. Net~~, surfactant concentrations were higher by trend within the SML under the prevalence of the unicellular ~~small~~ c~~c~~yanobacteriu~~m~~a *Synechococcus* sp. (~~HPA<20µm~~High P/NP). ~~. Higher surfactant enrichment has been shown to occur in alignment with advanced organic matter degradation (Wurl et al., 2011; Barthelmeß and Engel, 2022). GABA characterized the organic matter pool during HPA<20µmHigh P/NP and has been associated with, first, advanced bacterial processing (Davis et al., 2009) and, second, the accumulation of surfactants at the air-sea interface (Engel et al., 2018b). Here~~On the one hand, we found ~~also~~ elevated fractions of galactose ~~and concentrations of *Synechococcus* sp. biomass (20.59 ± 15.17 µg C L^{-1})~~ as well as Chl *a* during ~~HPA<20µm~~High P/NP characterized by elevated *Synechococcus* sp. biomass (20.59 ± 15.17 µg C L^{-1}). ~~This indicates in contrast that a~~Elevated Chl a concentration and galactose fractions indicate that a system is typically dominated by phytoplankton production rather than bacterial degradation (Barthelmeß et al., 2021; Engel et al., 2012). ~~Morover, *Synechococcus* sp. has been shown to form CSP rich aggregates (Cisternas-Novoa et al., 2015). Given the proteinaceous nature of CSP, amino acids and other surface active organic compounds likely act as precursors for their formation, with hydrophobic amino acid side chains facilitating aggregation at in the SML (Wurl & Holmes, 2008; Cunliffe et al., 2013; Thornton et al., 2016, 2018). In conclusion, we suggest that the surfactant pools during our study were dominated by elevated phytoplankton production in contrast to heterotrophic microbial processing, respectively.~~ On the other hand, heterotrophic bacteria release surfactants to enhance substrate availability and uptake (Satpute et al., 2010). Higher surfactant enrichment has been shown to occur in alignment with advanced organic matter degradation (Wurl et al., 2011; Barthelmeß and Engel, 2022). GABA characterized the organic matter pool during High P/NP and has been associated with, first, advanced bacterial processing (Davis et al., 2009) and, second, the accumulation of surfactants at the air-sea interface (Engel et al., 2018b).

Direct attribution of individual biomolecules to cyanobacterial production versus heterotrophic processing remains limited, because most available studies rely on correlations with community composition or gene expression rather than direct compound-specific source tracing (Berg et al., 2018; Barthelmeß and Engel, 2022). Thus, the SML surfactant pool, explicitly during High P/NP conditions, should be understood as the outcome of an interplay between cyanobacterial inputs and subsequent microbial reworking, rather than as a signal attributable to one group alone. In conclusion, we suggest that the surfactant pools during our study were dominated by condition-dependent, elevated phytoplankton production with ~~condition-dependent~~ potential contributions from heterotrophic microbial processing. Notably, while ~~T~~the Central Baltic Sea harbours a rich reservoir of microbially altered terrestrial material, ~~while~~ also abiotic factors such as solar radiation (Rickard et al., 2022) or anthropogenic pollutants may alter surface activity (Wurl and Obbard, 2004).

In ~~general~~general,~~comparison to the Western Baltic Sea,~~ elevated TAA~~amino acid~~ concentrations in the Central Baltic Sea likely reflect the high biomass of filamentous and colonial cyanobacteria. Surfactant concentrations reported here were also

rather high in comparison to other coastal stations. ~~, whereas enhanced surfactant levels may be attributed to the small cyanobacteria *Synechococcus sp.* contributing to the surface active organic matter pool.~~ This is in line with Mustaffa et al. (2020), who encountered an extensive *Trichodesmium* sp. bloom in the open ocean Pacific, which provoked a slick-covered surface. ~~Surfactant concentrations reported here were rather high in comparison to other coastal stations,~~ High surfactant concentrations ~~suggest~~suggest~~ing~~ a pronounced suppression of air-sea gas fluxes (Pereira et al., 2016; Mustaffa et al., 2020) and exceeding the effect size of the surfactant pool, which is present in the Western Baltic Sea (Barthelmeß and Engel, 2022).

5. Conclusion

This study examined whether phytoplankton dynamics are reflected in the composition of the ~~sea surface microlayer (~~SML~~)~~, focusing on ~~filamentous~~ cyanobacteria. Although no typical bloom occurred, the phytoplankton community varied dynamically throughout the cruise, resulting in clear differences in biomolecular composition between depths (SML vs. ULW; Surface vs. ULW-Net) and between phytoplankton defined conditions (High P/NP vs. Low P/NP; High MP vs. Low MP).~~and high versus low cyanobacteria dominated phytoplankton >20µm abundance (HPA>20µm vs. LPA>20µm).~~ SML enrichment patterns and carbohydrate concentrations generally aligned with previous observations from the Western Baltic Sea, while ~~total amino acid (~~TAA~~)~~ and surfactant concentrations were notably higher in the Central Baltic Sea. This likely reflects enhanced phytoplankton production under a favourable salinity range (3.8–11.5 PSU~~6–9 PSU~~), supporting filamentous and colonial diazotroph ~~filamentous~~ cyanobacteria, and unlike the more saline Western Baltic Sea (>12 PSU). Distinct biomolecular signatures indicated contributions from both MP and P/NP~~large and small phytoplankton~~. Elevated ~~total combined carbohydrate (~~TCCHO~~)~~ concentrations during ~~HPA<20µm~~High P/NP conditions suggest that P/NP~~smaller phytoplankton~~, dominated by~~such as~~ *Synechococcus* sp., drove carbohydrate and surfactant production, whereas the tendency to higher TAA and PAA concentrations during ~~HPA>20µm~~High MP conditions, dominated by *Aphanizomenon* sp. *Nodularia spumigena* and *Aphanocapsa* sp, point to a stronger influence of filamentous/colonial cyanobacteria on proteinaceous material. Compared to the Western Baltic Sea, elevated surfactant and ~~total amino acid~~TAA concentrations, along with the observed biomolecular imprints, indicate that cyanobacteria have a strong influence on the organic matter and surfactant pool in the Central Baltic Sea.

Appendix A

Table A 1: Overview of stations sampled during EMB295 cruise. A cross for each station was set when sampling of particulate matter >20 µm with the Neuston catamaran (cat) and ULW net. It is indicated when SML sampling took place with glass plate or Garrett Screen and ULW sampling with a~~the~~ manually ~~conducted~~ deployed water sampler~~Niskin bottle~~. Morning and afternoon sampling took place at each station, except for the first and last station.

StationStation ID	Date	Time [local timeDaytime]	Neuston cCatamaran	ULW net	Glas Plate	Garrett Screen	Manuael water samplerNiskin Bottle
0112-03	06.07.2022	pm16:17:00	x	x		x	x
0212-07	07.07.2022	am04:00:00	x	x		x	x
0312-11	07.07.2022	pm16:12:00	x	x		x	x
0412-16	08.07.2022	am04:26:00	x	x	x		x
0512-24	08.07.2022	pm19:20:00	x	x		x	x
0612-27	09.07.2022	am04:29:00	x	x	x		x
0713-03	09.07.2022	pm16:10:00	x	x	x		x
0814-01	10.07.2022	am04:16:00	x	x		x	x
0914-05	10.07.2022	pm18:15:00	x	x	x		x
1017-02	11.07.2022	am04:20:00	x	x	x		x
1118-02	11.07.2022	pm14:40:00	x	x		x	x
1221-02	13.07.2022	pm13:58:00	x	x	x		x
1322-02	15.07.2022	am04:18:00				x	x
1422-04	15.07.2022	pm16:19:00				x	x
1522-07	16.07.2022	am04:59:00	x	x	x		x

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Table A 2: Classification of stations according to pico- and nanophytoplankton (P/NP) >20µm and <20µmmicrophytoplankton (MP) abundance.

SStation	Date	P/NPBiomass classification	Abundance classificationMP classification
0112-03	06.07.2022	Low P/NPHPA>20µm	High MP LPA<20µm
0212-07	07.07.2022	Low P/NPHPA>20µm	High MP LPA<20µm
0312-11	07.07.2022	Low P/NPLPA>20µm	Low MPLPA<20µm
0412-16	08.07.2022	Low P/NPHPA>20µm	High MP LPA<20µm
0512-24	08.07.2022	Low P/NPHPA>20µm	High MP LPA<20µm
0612-27	09.07.2022	High P/NPLPA>20µm	Low MPHPA<20µm
0713-03	09.07.2022	Low P/NPHPA>20µm	High MP LPA<20µm

0814-01	10.07.2022	Low P/NPLPA>20µm	Low MPLPA<20µm
0914-05	10.07.2022	Low P/NPHPA>20µm	High MP LPA<20µm
1017-02	11.07.2022	High P/NPLPA>20µm	Low MPHPA<20µm
1118-02	11.07.2022	High P/NPLPA>20µm	Low MPHPA<20µm
1221-02	13.07.2022	High P/NPHPA>20µm	High MP HPA<20µm
1322-02	15.07.2022	High P/NPna	naHPA<20µm
1422-04	15.07.2022	High P/NPna	naHPA<20µm
1522-07	16.07.2022	High P/NPLPA>20µm	Low MPHPA<20µm

Data availability

The data presented in this study are submitted~~will be submitted~~ to the PANGAEA Data Publisher for Earth & Environmental Science and will be made publicly available after publication of the manuscript (https://doi.org/10.1594/PANGAEA.993574).

Author contributions

JK collected samples during the research cruise, performed surfactant analyses, conducted data analysis, and wrote and prepared the manuscript. AE designed the project, supervised the research, and contributed to manuscript writing and revision. TB assisted with data analysis, contributed to manuscript writing, and participated in manuscript revision. BS supported sample collection and filtration during the cruise and contributed to manuscript proofreading.

Competing interests

The authors declare that they have no conflict of interest.

Disclaimer

Special issue statement

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